

Path Integral Methods for Polarons in Real Materials

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To my mum, Debbie. You never got to see me grow into the person I am today, but as a young boy, you described me as a deep thinker. You encouraged me, with all your heart and through your actions, to never give up. So I dedicate my thesis to you. Although you are no longer with us, your resilience and support have never left me.

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I, Bradley Andrew Alan Martin, hereby declare that the thesis entitled “Path Integral Methods for Polarons in Real Materials” submitted to Imperial College London for the degree of Doctor of Philosophy is my original work and has not been submitted for any other degree or qualification at any other institution.

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— ABSTRACT —

In this thesis, I develop theoretical methods for modelling polaron quasiparticles in semiconductors by extending Feynman’s variational path integral approach [1]. Polarons—quasiparticles formed by electron-phonon interactions—are critical for understanding charge transport in materials with significant electron-phonon coupling. Using Feynman’s variational approximation (FVA) [2] for the Fröhlich polaron [3], I present a non-perturbative framework to model polaron dynamics in materials with complex phonon interactions.

A key contribution is generalising the material action to include multiple phonon modes [4], reflecting realistic phonon spectra in modern materials. This framework extends to the Holstein polaron [5–7], anisotropic effective mass [8], and many-body systems. I generalise the trial path integral action to couple electrons with multiple fictitious spring-mass particles and introduce an extended Feynman-Jensen inequality, incorporating higher-order cumulant corrections for improved self-energy and mobility calculations across various coupling regimes.

Polaron charge-carrier mobility and optical conductivity are computed using the FHIP approximation [9] and extended to temperature- and frequency-dependent models for multimode Fröhlich and Holstein polarons. These results are validated against Diagrammatic Monte Carlo simulations [10].

Numerical results are obtained using `PolaronMobility.jl` [11], an open-source Julia [12] package I co-developed. It enables high-throughput screening of polar semiconductors and is demonstrated on methylammonium lead halide perovskites [4] and rubrene organic crystals [7].

Finally, I conduct high-throughput predictions for polaronic properties of 1,268 materials from the Materials Project [13] and Liège [14] databases, identifying candidates for high-mobility applications based on parameters like effective mass, zero-point renormalisation energy, and room-temperature mobility.

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– LIST OF ACRONYMS –

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
RHS	Right-hand Side
LHS	Left-hand Side
LO	<i>Longitudinal Optical</i>
DC	<i>Direct Current</i>
THz	<i>Terahertz</i>
FHIP	<i>Feynman-Hellwarth-Iddings-Platzman</i>
DSG	<i>Devreese-Sitter-Goovaerts</i>
CGS	<i>Centimetre-Gram-Second</i>
FVA	<i>Feynman Variational Approach</i>
PIMC	<i>Path Integral Monte Carlo</i>
CT-PIMC	<i>Continuous-Time Path Integral Monte Carlo</i>
DiagMC	<i>Diagrammatic Monte Carlo</i>
RES	<i>Relaxed Excited States</i>
FC	<i>Franck-Condon</i>
BTE	<i>Boltzmann Transport Equation</i>
CSPI	<i>Coherent State Path Integral</i>
ZPR	<i>Zero-Point Renormalisation</i>
TDSE	<i>Time Dependent Schrödinger Equation</i>

– LIST OF SYMBOLS –

Greek symbols

$\hbar$	reduced Planck constant
τ	imaginary time coordinate
$\omega_{\bullet}$	phonon frequency
β	reciprocal thermodynamic temperature
δ	Dirac delta
δ_{ij}	Kronecker delta
κ	fictitious particle spring mass
Ω	external field frequency
σ	complex conductivity
Σ	polaron memory function
μ	polaron mobility
μ_0	electron and fictitious particle reduced mass
α	Fröhlich alpha
ρ_S	density function for action S
$\hat{\rho}$	electron density operator
γ	Holstein adiabaticity
Γ	Gamma function
ϵ	dielectric function
ϵ_0	static dielectric constant
ϵ_i	ionic dielectric constant
ϵ_{∞}	optical dielectric constant
ϵ_{vac}	vacuum permittivity
Φ	influence functional phase

Latin symbols

$\mathbf{k}$	electron wavevector
$\mathbf{q}$	phonon wavevector
$\mathbf{r}$	electron position vector
$\mathbf{x}$	phonon position vector
t	real time coordinate
v	polaron variational parameter
w	polaron variational parameter
V_0	3D unit cell volume
V_n	n -dimensional unit cell volume
k_B	Boltzmann constant
T	temperature parameter
m_f	fictitious particle mass
Z	partition function
z	complex impedance
G	trial polaron Green function
D_ω	phonon Green function of frequency ω
M	polaron effective mass
R	polaron effective radius
H	Hamiltonian
L	Lagrangian
S	polaron model action
S_0	polaron trial action
$M_{\mathbf{q}}$	electron-phonon coupling matrix
E	polaron ground-state energy
F	polaron Helmholtz free energy
J	transfer integral
$\mathbf{J}$	external source field
$\mathbf{E}$	electric field
$\mathbf{D}$	electric displacement field
$\mathbf{P}$	polarisation field
$\mathbf{A}$	electric vector potential
c	speed of light
$c_{\mathbf{k}}^\dagger$	fermion creation operator

$c_{\mathbf{k}}$	fermion annihilation operator
$b_{\mathbf{q}}^{\dagger}$	boson creation operator
$b_{\mathbf{q}}$	boson annihilation operator

Polaron Units

ω_0	characteristic angular frequency
m_0	characteristic mass
r_0	characteristic length
e_0	electron charge

CHAPTER 1

INTRODUCTION

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It, therefore, becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

—Paul A. M. Dirac, *Quantum mechanics of many-electron systems*, 1929

In this thesis, I develop methods to predict temperature- and frequency-dependent charge-carrier mobilities for polar semiconductors, thereby offering design clues for and methods to screen new materials computationally. Specifically, this thesis aims to predict semiconductor materials ‘polaronic’ properties and how they impact the underlying electron transport. The key method is Feynman’s path integral approach to quantum physics, which has proven to be a powerful approach to modelling the polaron.

1.1 The Polaron

THE polaron is a quasiparticle formed from the interaction of charge carriers with the polar response of a semiconductor. A polaron forms when an electron moving through a polarisable material induces a surrounding polarisation cloud. This polarisation then backreacts on the electron, effectively trapping and localising it within the distorted lattice, thereby creating a composite quasiparticle consisting of the electron and its self-induced polarisation (see Fig. 1.1). This can equivalently be thought of as a quantum field theory

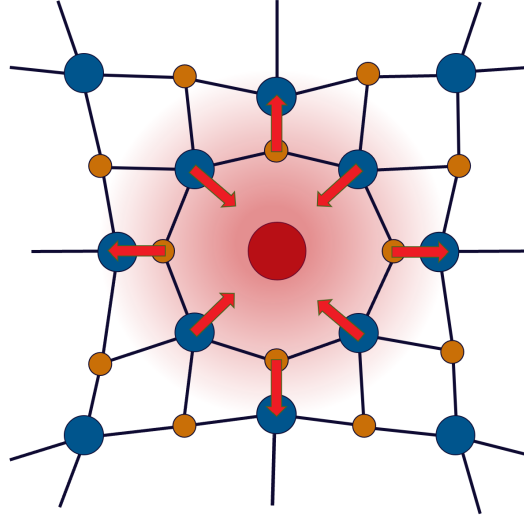


Figure 1.1: An artist view of a polaron. A charge carrier (red) in a polar semiconductor or ionic crystal repels like charges (orange) and attracts opposite charges (blue). This induces a polarisation field, which acts back on the charge-carrier and modifies its properties.

of a single charged fermion interacting with a bosonic field; this is the phonon field for the polaron.

The formation of a polaron can significantly alter the properties of a material [15], and it is essential to understand polarons to predict the mobility of charge carriers accurately. The extent of a polaron can be large (encompassing multiple unit cells), where the polaron often moves more freely around the material, or small (comparable or smaller than a lattice constant), where the polaron becomes localised to individual lattice sites. A simplified model for the large polaron is given by the Fröhlich Hamiltonian [3], and the small polaron by the Holstein Hamiltonian [5, 6].

The key methodology this thesis builds upon is Feynman’s 1955 variational path integral approximation (FVA) [2]. This method translates the Fröhlich polaron Hamiltonian into an action, which is used to derive the partition function for the system as a path integral (see Appendix A for examples of common path integrals). Since the phonon coordinates enter the action quadratically, the phonon path integral is Gaussian. Its closed-form expression results in an effective temporally non-local potential acting on the electron. This model action typically has no known exact solution. This partition function is then approximated by a trial partition function derived from a trial action, requiring that this partition function has a closed-form expression (typically limiting the trial action to be quadratic). Feynman chose this trial action to represent an electron harmonically coupled to a fictitious particle via a spring, his so-called ‘spring-mass model’. Using Jensen’s inequality for convex functions, Feynman derived an inequality for the polaron-free energy. An optimal upper bound is then found by varying the mass and spring constant of the trial model.

1.2 Polaron Response Functions

Further developments were also made using the Feynman-Vernon ‘influence functional’ method [16] to derive the reduced density matrix for a quantum system interacting with some external bath (see Appendix B for examples of common influence functionals). The reduced density matrix can provide dynamic response functions such as optical conductivity and charge-carrier mobility. Building upon the success of the FVA, in 1962 Feynman, Hellwarth, Iddings and Platzmann (FHIP) [17] derived an approximate density matrix for the Fröhlich polaron model from a functional Taylor expansion of the polaron action about the optimal trial action. This was then used to predict polaron mobility in FHIP and later extended to optical conductivity by Devreese, Sitter and Goovaerts (DSG) in 1972 [18].

1.3 Semiconductors

Semiconductors have enormous technical applications ranging from photovoltaic cells and light-emitting diodes to field-effect transistors, computer chips and solid-state lasers. A fundamental phenomenological quantity that influences the performance of a semiconductor is the charge-carrier mobility. The mobility required depends on the application; for example, a photovoltaic cell requires sufficient mobility to facilitate charge separation. As a phenomenological quantity, mobility arises from competitive dynamic processes within a material and can be strongly temperature-dependent. Most mobility theories, like the Boltzmann Transport Equation (BTE) [19], use semi-classical approximations to model mobility, using an effective scattering time such as in Drude-like models or neglecting electron-phonon interactions as in the adiabatic Born-Oppenheimer approximation. Alternatively, the electron-phonon coupling is assumed to be sufficiently weak or strong, so perturbative approaches can be taken. However, some semiconductors, such as lead halide perovskites, possess significant dielectric electron-phonon interactions, forming large polarons. These materials typically exhibit intermediate electron-phonon coupling strengths, which are difficult to model using perturbative approximations. Instead, one can use the path integral formulation of quantum mechanics to derive an inherently quantum mobility theory [2, 17]. Though based on a linear-response theory, this is non-perturbative and can provide a temperature and frequency-dependent mobility model valid to all orders in the electron-phonon coupling strength.

1.4 Thesis Overview

Although historically successful, the FVA and FHIP approaches to modelling polarons have not been extensively applied in the materials community. As such, much of the

underlying theory has not been expanded upon and is only used for simple ‘toy models’. Likewise, these approaches have not been implemented in modern codes. Therefore, I aim to generalise the applicability of these methods to more complicated models that might better represent technologically significant materials and implement them in a user-friendly computational Julia [12] package `PolaronMobility.jl` [11].

In this thesis, I describe my progress over four main chapters:

Chapter 3 — Generalise the material action: In this chapter, I describe extending the effective model Lagrangian to provide greater material-specific detail, including multiple phonon branches, the small Holstein polaron, anisotropic effective masses and general many-body polaron theories formulated using coherent-state path integrals (CSPI) and quantum field theory techniques.

Chapter 4 — Improve the trial action: I describe extending the trial polaron Lagrangian beyond Feynman’s original spring-mass harmonic model (while retaining the analytic solution) to increase the accuracy of the variational approximation and the predicted response functions. This includes extending the variational method to the multimode large Fröhlich and small Holstein polarons. I then generalise the trial action to couple the electron to multiple spring masses and a general bath spectral function with self-consistent equations. Finally, I describe extending to general many-body polarons using a trial self-energy function and expanding the Feynman-Jensen inequality with an infinite series of cumulant corrections whilst retaining the variational bound.

Chapter 5 — Compute the response functions: I first confirm the accuracy of the FHIP method by comparing the predicted temperature- and frequency-mobility with Diagrammatic Monte Carlo (DiagMC) calculations by Mishchenko et al. [10]. Next, I generalise the FHIP method to compute the charge-carrier mobility and optical conductivity for more complicated models. This extends FHIP to the multimode Fröhlich polaron, the Holstein small polaron, the many spring-mass extended trial solution, general many-body polarons and for an optimal self-consistent solution that coincides with the optimal free energy solution.

Chapter 6 — Material classification: In this chapter, I apply these methods to calculate the polaronic properties of materials. Using the multimode extension to the Fröhlich polaron, I evaluate the polaron energy, mass, mobility and optical conductivity of bulk Methylammonium Lead Iodide Perovskites using material data from Brivio et al. [20] and compare the results to the single effective mode method of Hellwarth and Biaggio [21]. I use the small Holstein polaron theory to calculate the polaron energy, mass, mobility and optical conductivity of bulk Rubrene crystals using material-specific parameters calculated by Ordejón et al. [22]. I use the anisotropic effective

mass extension to calculate the Zero-Point Renormalisation (ZPR) and polaron size with weak coupling perturbation results for dozens of II-VI, III-V and oxide semiconductor materials to characterise the validity of the continuum approximation in the Fröhlich model and the use of the perturbation approximation. The data for these materials was taken from Guster et al. [8]. Finally, I describe a high-throughput analysis of 1260 materials from the Materials Project [13] obtained from the Liège Density Functional Theory (DFT) Dataset [14]. I compare my ZPR results with those obtained from perturbation theory [23] and calculate the material polaron mass and mobility.

Chapter 2 outlines the key existing research that precedes this dissertation and provides a holistic re-derivation of the main theories of the Fröhlich [3] and Holstein [5, 6] polarons, Feynman’s variational path integral approximation [2] and the FHIP approximation [17, 18, 21]. Likewise, I show the numerical results of these theories implemented in Julia in the `PolaronMobility.jl` package, some of which go further than in the literature.

Finally, in **Chapter 7**, I conclude this dissertation and discuss how this research could be expanded upon in future.

CHAPTER 2

BACKGROUND

“Feynman’s various presentations are a bit hard to reconcile, as it is not always clear where he has changed his notation or where typographical errors have crept in. I have to confess that I have not reproduced all the derivations and in particular am not entirely certain of what should or need be done about the end points...”

—Lawrence S. Schulman, *Techniques and Applications of Path Integration*, 1981

In this chapter, I outline the key polaron physics from the last 90 years, which I build upon. I first provide a holistic overview of the field’s historical developments. I then present a comprehensive re-derivation of the key theories of the Fröhlich and Holstein polarons, Feynman’s original variational path integral approach to approximating the polaron state, and the Feynman-Hellwarth-Iddings-Platzman (FHIP) influence functional approach to approximating the polaron mobility and optical conductivity. I also re-derive extensions to FHIP including Hellwarth and Biaggio’s effective phonon-mode approach to polaron mobility and Devreese, Sitter and Goovaert’s approach to the optical absorption of polarons.

2.1 Polaron Physics

THIS section begins with a brief conceptual overview of the critical advancements in polaron physics that this thesis builds upon. Whilst polaron physics started with influential work of Landau and Pekar [24, 25], the foundational theoretical formulation of the problem originated with Herbert Fröhlich [3, 26] and Theodore Holstein [5, 6] who formalised rigorous quantum-field Hamiltonians for the large and small polarons respectively. This laid the theoretical groundwork for successive advancements, which

I outline in Table 2.1. I then provide a consistent set of derivations of polaron physics produced over the last 70 years. This covers a comprehensive re-derivation of: the Fröhlich large polaron [3] and Holstein small polaron [5, 6] Hamiltonians; the Feynman variational approach to the polaron model [2], and the extension of Feynman’s approach to finite temperature by Ōsaka [27]; polaron mobility by Feynman, Hellwarth, Iddings and Platzman [17]; polaron optical absorption by Devreese, Sitters and Goovaerts [18]; and effective multimode polarons by Hellwarth and Biaggio [21].

2.1.1 A Brief History

Landau and Pekar, 1933-1948

The self-localisation of an electron in a perfect crystal due to polar deformations was investigated by Landau [24], who was concerned with the effect of lattice defects on materials such as sodium chloride. Later, the word “polaron” was first used by Pekar [28–30] to describe the spontaneous trapping of an electron due to the induced polarisation of a strongly ionic material. Further developments led to a joint paper by Pekar and Landau [25], calculating the effective mass of a large, strongly-coupled, polaron.

The polaron was established as a *quasiparticle* that consists of a charge carrier (such as an electron or hole) ‘dressed’ by a cloud of virtual phonon excitations that follow the charge carrier as it propagates through a polarisable medium. Suppose the polaron’s spatial delocalisation is large compared to the unit cell of a material. The material can be treated as a polarisable continuum, and we have a *large* polaron. However, when the extent of the polaron is of the order of the unit cell, we have a *small* polaron, and we should no longer treat the material as a continuum.

Fröhlich, 1950-1954

The theoretical groundwork for the large polaron theory was formally established by Fröhlich [3]. The Fröhlich Hamiltonian represents a single effective-mass electron linearly coupled to a polarisation field. This continuum polarisation field, generated by longitudinal optical phonons, is represented by a set of quantum harmonic oscillators with no dispersion and oscillating at the same frequency. The strength of the electron-phonon coupling then becomes a dimensionless coupling constant called the “Fröhlich alpha parameter”. This can be determined from the material’s properties (dielectric constants, effective mass and longitudinal optical phonon frequency). The exact solution to the Fröhlich Hamiltonian is unknown despite its simple representation.

Year	Authors	Research development	Refs
1933	Landau	Charge moving in a dielectric crystal	[24]
1946-1948	Landau & Pekar	Landau–Pekar model	[28–30]
1950-1954	Fröhlich	Large polaron Hamiltonian	[3, 26]
1955	Feynman	Variational path integral (athermal)	[2]
1959	Holstein	Small polaron Hamiltonian	[5, 6]
1959	Schultz	FVA polaron effective mass	[31]
1959	Feynman & Vernon	Influence functionals	[16]
1959-1961	Ōsaka	Variational path integral (thermal)	[27, 32]
1962	FHIP	Path integral mobility	[17]
1963	Kadanoff	BTE Fröhlich polaron mobility	[19]
1966-1971	Thornber	Nonlinear polaron mobility	[33–35]
1972	DSG	Path integral optical conductivity	[18]
1980-1984	Adamowski et al.	Optimal FVA functional solution	[36, 37]
1983-1985	De Raedt et al.	Lattice polaron path integral	[38, 39]
1986-1987	Peeters et al.	n -dimensional Fröhlich model	[40, 41]
1998-2000	Prokofev et al.	DiagMC Fröhlich polaron	[42, 43]
1999	Hellwarth et al.	Multimode polaron action	[21]
2001	Titantah et al.	PIMC Fröhlich polaron	[44]
1997-2004	Kornilovitch et al.	CTPIMC lattice polarons	[45–51]
2001	Tempere et al.	Many polaron optical gas	[52]
2009	Tempere et al.	BEC-impurity polarons	[53]
2010	Devreese et al.	Many polaron FVA	[54]
2014-2015	Mishchenko et al.	DiagMC Holstein polaron	[55, 56]
2016	Klimin et al.	All coupling polaron response	[57–59]
2017	Frost	Calculating polaron mobility	[60]
2019	Mishchenko et al.	DiagMC Fröhlich mobility	[10]
2019-2022	Ichmoukhamedov et al.	General memory polaron	[61–63]
2020	Miglio et al.	Generalised Fröhlich model	[64]
2021	Franchini et al.	Polarons in materials	[15]
2021	Guster et al.	Anisotropic band polarons	[8]
2021	Houtput et al.	Anharmonic phonon FVA	[65]
2023	Martin et al.	Explicit multimode FVA polaron	[4]
2023	de Melo et al.	High-throughput polarons	[23]
2024	Martin et al.	Holstein small polaron FVA	[7]
2024	Klimin et al.	Nonparabolic band polarons	[66]

Table 2.1: A (non-exhaustive) compendium of theoretical and computation results for studying polarons.

Feynman, 1955

In his 1955 paper [2], Feynman reformulated the Fröhlich Hamiltonian as a Lagrangian by converting the electron and phonon creation and annihilation operators into their corresponding coordinates and momenta, followed by a Legendre transformation. After performing a Gaussian integration over the momenta, he obtained a Gaussian path integral over the phonon coordinates, which could be evaluated explicitly. The result was an exact *model* action, where the electron is coupled to itself at a previous time through a temporally non-local Coulomb potential.

However, this path integral could not be solved exactly, as the remaining action has a $1/r$ dependence on the electron coordinates from the Coulomb interaction driving the Fröhlich coupling, making the path integral non-Gaussian. To address this, Feynman proposed a *trial* action that approximates the main features of the model action but is quadratic in the electron coordinates, making a solvable Gaussian path integral. Feynman's trial action describes an electron coupled to a fictitious massive particle via a harmonic potential that decays exponentially in time. This additional mass represents the mass renormalisation of the electron as it forms the polaron quasiparticle. By transforming the model and trial actions into imaginary-time, Feynman obtained an expression for the quantum statistical partition function, which is a convex functional, allowing the application of Jensen's inequality. A variational inequality was then used to minimise the difference between the trial and model actions, providing an approximate upper bound on the polaron's ground-state self-energy.

Feynman's variational inequality has two variational parameters. The first, denoted by C , controls the strength of the harmonic coupling, while the second, w , determines the decay rate of the coupling in time. Later in his paper, Feynman replaced C with ν , representing the frequency of the harmonic coupling. Using this approach, Feynman calculated the polaron's ground-state energy and its effective mass for all electron-phonon coupling strengths.

Holstein, 1959

Holstein [5, 6] investigated small polaron formation and transport, focusing on charge carriers in molecular crystals where electron-phonon interactions play a critical role. His work is divided into two parts, with the first [5] addressing the fundamental principles of polaron formation and mobility within tight-binding systems. Holstein uses a quantum mechanical framework to describe the interactions between an electron and the lattice's vibrational modes (phonons). The model has the electron interacting only with localised vibrational modes on the same site (Einstein oscillators) rather than with delocalised, collective modes such as Bloch or Debye phonons. Additionally, Holstein examines the

linear interaction between the electron and phonons in terms of phonon displacement. He further assumes that phonons are confined to individual sites, neglecting inter-site phonon coupling and restricting the lattice distortion to the electron's local environment. Holstein's theory predicts how electrons become localised as small polarons through their interactions with local lattice vibrations, determines the polarons' effective masses and mobilities, and describes how these charge carriers move (their transport properties) in molecular crystals where electron-phonon interactions are confined to individual lattice sites.

Ōsaka, 1959-1961

Ōsaka [27, 32], generalised Feynman's path integral variational approach to finite temperatures and derived Feynman's trial model's full temperature-dependent density matrix. Ōsaka achieved this by identifying a Lagrangian that produces the same equation of motion as Feynman's trial action. On elimination of the phonon field, this Lagrangian reproduces Feynman's trial action with the non-local harmonic self-interaction for the electron. Ōsaka was then able to use this Lagrangian to derive the temperature-dependent density matrix for the polaron state and generalise the variational approach to finite temperatures. At zero temperature, Ōsaka's formulation is identical to Feynman's expression for the polaron self-energy.

Feynman & Vernon, 1959

Feynman and Vernon [16] introduced a powerful method for studying quantum systems interacting with external environments, focusing mainly on open systems and non-equilibrium dynamics. The central concept is the 'influence functional', which encapsulates the effects of an environment (modelled as a collection of harmonic oscillators) on a quantum system by tracing over the environmental degrees of freedom. This process results in an equivalent action for the system alone but with a non-local self-interaction that fully encapsulates the environmental effects on the system and enables the study of how the environment induces dissipation and decoherence in the system. Crucially, the influence functional provides a formal framework for deriving the reduced density matrix of the system, which describes its state after tracing out the environment. This formalism has far-reaching applications in quantum mechanics, particularly for quantum Brownian motion, quantum dissipative systems, and non-equilibrium quantum processes. Feynman and Vernon's work laid the foundation for understanding how environmental coupling influences quantum dynamics, with critical implications for quantum thermodynamics.

Feynman, Hellwarth, Iddings & Platzman, 1962

Feynman, Hellwarth, Iddings, and Platzman [17] (often referred to as “FHIP”) developed an approximate expression for the polaron impedance function using a path-integral approach and the Feynman-Vernon influence functional formalism. This expression accounted for all frequencies of the applied electric field, all temperatures, and all electron-phonon coupling strengths. Unlike a variational approach, the impedance function was derived from a second-order functional expansion around the quadratic trial action previously introduced by Feynman in 1955 [2]. A crucial aspect of the derivation involved calculating the “memory function”, which was obtained from the imaginary part of the dynamic structure factor. The structure factor, in turn, was derived from the electron density-density correlation function and evaluated via path integrals. The memory function encapsulates the polaron’s dynamics and depends on variational parameters that minimise the polaron self-energy. These parameters were assumed to yield the most accurate predictions for polaron dynamics. The authors provided an explicit expression for the imaginary part of the memory function, from which they derived the DC mobility of the polaron and explored its behaviour in the limits of zero, low, and high temperatures.

Devreese, Sitter & Goovaerts, 1972

Starting from the FHIP approach [17], Devreese, Sitter & Goovaerts [18] (commonly referred to as “DSG”) calculated the optical absorption of Fröhlich polarons, for all coupling, temperature, and frequency. They demonstrated that three different kinds of polaron excitations appear in the resulting spectra produced from their expression: scattering states where, for example, one real phonon is excited, relaxed excited states (RES), and Franck-Condon (FC) states. It was found that these spectral features only appear in an expansion of the impedance function obtained from FHIP and not from the corresponding conductivity function, which is reciprocal to the impedance. This was argued as justification for the choice in FHIP to expand the impedance to second-order instead of the conductivity. Additionally, they explicitly provide the real and imaginary parts of the memory function as an infinite series of special functions (in this case Bessel functions), and simplified forms of these series for zero temperature.

Hellwarth & Biaggio, 1999

Hellwarth & Biaggio [21] derived a Lagrangian that described a free electron interacting with a polar lattice with multiple infrared-active optical-phonon modes, in the presence of an applied field. From this Lagrangian, they derived an effective model action comparable to Feynman’s model action, except that it has a summation over terms differing in the phonon frequency and electron-phonon coupling strength corresponding to each phonon

mode. Rather than use this effective action directly, they defined a single effective phonon frequency and electron-phonon coupling (which they provided two different schemes to obtain) and used Ōsaka’s free energy minimisation procedure instead. They used the mobility equation derived in FHIP and their own derived Lorentz-Lorenz relation to produce accurate predictions for the room-temperature electron mobility and reflectivity in $\text{Bi}_{12}\text{SiO}_{20}$.

Mishchenko, Prokof’ev, Sakamoto & Svistunov, 1998-2000

Prokof’ev & Svistunov [42], in addition to Mishchenko & Sakamoto [43], performed a detailed study on the Fröhlich polaron model using a diagrammatic Monte Carlo method (DiagMC). They produced precise numerical data for the polaron self-energy, effective mass, the general structure of the polaron cloud and spectral density of the polaron from intermediate to strong electron-phonon couplings. Their method used a set of Green functions of the polaron, which they simulated using a standard diagrammatic expansion Matsubara technique at zero temperature, and related them to the polaron parameters. These results are considered the ‘gold standard’ for the Fröhlich model and are often used as a theoretical benchmark to compare newer model predictions against.

Mishchenko, Pollet, Prokof’ev, Kumar, Maslov and Nagaosa, 2019

Mishchenko et al. [10] calculated the mobility of a Fröhlich polaron in situations where inelastic scattering rates exceed the thermal energy of quasiparticles, moving the system beyond the quasiparticle regime. They studied several non-perturbative phenomena using diagrammatic Monte Carlo methods, particularly in materials with strong electron-phonon coupling. They found a significant violation of the Mott-Ioffe-Regel (MIR) criterion at intermediate and strong couplings, indicating that traditional kinetic theories are insufficient. They also observed a mobility minimum at temperatures around the optical phonon frequency (Ω) in the strong coupling limit, a result of the complex interplay between thermal excitations and polaron mass renormalisation. Additionally, the expected exponential increase in mobility at low temperatures ($T < \Omega$) is delayed, occurring only at much lower temperatures than predicted.

Furthermore, the typical Drude peak associated with quasiparticle transport is completely smeared at strong couplings, showing that polaron mobility cannot be described by simple quasiparticle models. These findings are crucial for understanding charge transport in materials with strong electron-phonon interactions. They will be used later in this thesis as a result to benchmark Fröhlich polaron mobility results against.

2.1.2 Fröhlich's Large Polaron

Fröhlich [3] studied a system whereby a charged particle in a dielectric medium polarises its surroundings. The resultant polarisation field interacts with the particle, and the particle then possesses self-energy in the field due to the changes it, in turn, causes in the field. A simple example is the motion of an effective-mass electron in an ionic crystal. This is a relevant model for physical materials and also theoretically interesting as it is a simple example of a non-relativistic quantum field theory of a fermion interacting with a bosonic quantum field. For a slow electron, the electronic dispersion relation ϵ_k is approximately quadratic in the momentum $\hbar\mathbf{k}$

$$\epsilon_k = \frac{\hbar^2 k^2}{2m_0}. \quad (2.1)$$

Here m_0 is the effective band mass of the electron and is usually different to the electronic mass m_e , and $\mathbf{k}$ is the wave vector of the electron with momentum $\mathbf{p} = \hbar\mathbf{k}$. Eq. (2.1) is typically only valid near the extrema of the valence and conduction bands, such as for slow electrons and certain materials. This dispersion is described by analogy with a free electron but with a renormalised mass from the Bloch electron plane wave moving through a rigid lattice.

Fröhlich improved upon the Bloch plane wave approximation concept by modelling an electron moving through a non-rigid isotropic polar lattice. Here, the electron experiences an electrostatic potential generated by the displacement of ions from their lattice sites. For small ion displacements compared to the lattice spacing, this potential takes the form of one generated by an electric dipole. Since the lattice is polar, ion displacements that lead to electric polarisations (longitudinal optical modes) interact more strongly with electrons than other types of displacements (transverse optical modes and acoustic modes), which Fröhlich disregards. Likewise, there is only one longitudinal optical mode in two-component ionic solids, and the dispersion is approximately flat. Therefore, Fröhlich considers that all polarisation occurs via one single dispersionless mode.

The electronic wavefunction varies slowly over many lattice spacings for sufficiently low-energy electrons. Therefore, the ionic lattice can be approximated by a continuum such that the electric field, generated by the displacement of ions in the lattice, can be described by a macroscopic continuous polarisation field, $\mathbf{P}(\mathbf{r})$.

Classical field theory

From the usual definition of the electric displacement field $\mathbf{D}(\mathbf{r})$, the polarisation field is related to the total electric field intensity $\mathbf{E}(\mathbf{r})$ by (in CGS units),

$$\mathbf{E}(\mathbf{r}) = \mathbf{D}(\mathbf{r}) - 4\pi\mathbf{P}(\mathbf{r}). \quad (2.2)$$

Therefore, $-4\pi\mathbf{P}(\mathbf{r})$ is the contribution made by the lattice to the total electric field intensity. Since the main force acting on the electron is the polarisation field $\mathbf{P}(\mathbf{r})$ from the ionic displacement, the classical equation of motion of the electron is

$$m_0\ddot{\mathbf{r}}_{el} = 4\pi e\mathbf{P}(\mathbf{r}_{el}). \quad (2.3)$$

For a single free electron with charge e and position $\mathbf{r}_{el}$, the electric displacement is

$$\mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) = -e\nabla_{\mathbf{r}} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_{el}|} \right), \quad (2.4)$$

such that $\nabla_{\mathbf{r}} \times \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) = 0$ and $\nabla_{\mathbf{r}} \cdot \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) = 4\pi e\delta(\mathbf{r} - \mathbf{r}_{el})$. This electric displacement represents the ‘external’ electric fields that act on the electron in the crystal. Since the displacement field is longitudinal ($\nabla_{\mathbf{r}} \times \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) = 0$), the polarisation field generated by the electron will be longitudinal too (assuming that magnetic fields can be neglected). Therefore, if $\mathbf{P}(\mathbf{r})$ is the electric polarisation at the position $\mathbf{r}$, then the rotational part of the field must be zero,

$$\nabla_{\mathbf{r}} \times \mathbf{P}(\mathbf{r}) = 0. \quad (2.5)$$

The electric field generated by the polarisation, $-4\pi\mathbf{P}$, can be expressed by an electric potential $\Phi(\mathbf{r})$ given by Poisson’s equation,

$$-\nabla_{\mathbf{r}}\Phi(\mathbf{r}) = -4\pi\mathbf{P}(\mathbf{r}). \quad (2.6)$$

The energy of the interaction between the electron and the lattice displacements is then

$$\begin{aligned} E_{e-l}(\mathbf{r}_{el}) &= - \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el})\mathbf{P}(\mathbf{r})d^3\mathbf{r}, \\ &= \frac{e}{4\pi} \int \nabla_{\mathbf{r}} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_{el}|} \right) \nabla_{\mathbf{r}}\Phi(\mathbf{r})d^3\mathbf{r}, \\ &= e\Phi(\mathbf{r}_{el}). \end{aligned} \quad (2.7)$$

The longitudinal modes of the lattice that generate the polarisation field are either optical lattice modes (where two adjacent ions move in opposite directions) or acoustic modes (where adjacent ions move in the same direction). Only the optical modes produce dipole moments that add constructively for small lattice displacements, generating a significant resultant polarisation. This is especially true of long-wavelength optical modes (near the gamma-point $\mathbf{q} = 0$), which have the most significant interaction with the electron and are dispersion-less with constant vibrational frequency ω_0 . Fröhlich assumed that only these long-wavelength longitudinal optical modes had any considerable effect on the conduction electron and neglected all other lattice modes. This approximation is very good for two-component materials since only one longitudinal optical branch exists.

The total lattice polarisation has two contributions, one from high-frequency (ultra-violet) oscillations $\mathbf{P}_{uv}(\mathbf{r})$ due to the electronic structure (particularly for materials that possess a band-gap), and one from low-frequency (infrared) oscillations due to ionic displacement $\mathbf{P}_{ir}(\mathbf{r})$

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}_{uv}(\mathbf{r}) + \mathbf{P}_{ir}(\mathbf{r}). \quad (2.8)$$

Under an external field $\mathbf{D}(\mathbf{r})$ (assuming linear response), the equations of motion for these two polarisations are driven harmonic oscillator equations

$$\ddot{\mathbf{P}}_{ir}(\mathbf{r}) + \omega_{ir}^2 \mathbf{P}_{ir}(\mathbf{r}) = \mathbf{D}(\mathbf{r}, \mathbf{r}_{el})/\gamma, \quad (2.9a)$$

$$\ddot{\mathbf{P}}_{uv}(\mathbf{r}) + \omega_{uv}^2 \mathbf{P}_{uv}(\mathbf{r}) = \mathbf{D}(\mathbf{r}, \mathbf{r}_{el})/\delta. \quad (2.9b)$$

Here $\omega_{uv}/2\pi$ and $\omega_{ir}/2\pi$ are the frequencies corresponding to the optical absorption in the high (electronic) and infrared regions, respectively; γ and δ are constants related to the energy associated with the respective displacements. To determine these constants, we go to the zero-frequency “static” case where $\dot{\mathbf{P}} = 0$ and $\mathbf{D} = \epsilon_0 \mathbf{E}$, with ϵ_0 the total zero-frequency dielectric constant. In the zero-frequency limit, the polarisation is

$$4\pi\mathbf{P}(\mathbf{r}) = (\epsilon_0 - 1)\mathbf{E}(\mathbf{r}) = (1 - \epsilon_0^{-1})\mathbf{D}(\mathbf{r}, \mathbf{r}_{el}). \quad (2.10)$$

In the high-frequency limit, the frequency Ω of the external field $\mathbf{D}$ satisfies $\omega_{uv} \gg \Omega \gg \omega_{ir}$ such that the lattice polarisation is not excited. In the high-frequency limit, the polarisation is

$$4\pi\mathbf{P}(\mathbf{r}) = 4\pi\mathbf{P}_{uv}(\mathbf{r}) = (1 - \epsilon_\infty^{-1})\mathbf{D}(\mathbf{r}, \mathbf{r}_{el}), \quad (2.11)$$

where ϵ_∞ is the high-frequency dielectric constant. In the high-frequency limit, the ions can no longer keep up, $\mathbf{P}_{ir} \approx 0$, whereas the electronic oscillators can follow nearly adiabatically. Therefore, the $\ddot{\mathbf{P}}_{uv}$ term would be negligible compared to $\omega_{uv}^2 \mathbf{P}_{uv}$, and so for a field $\mathbf{D}$ of equal strength, $\mathbf{P}_{uv}$ would have roughly the same value in the static limit as in the high-frequency limit. Hence, we can combine the two expressions above to obtain the ionic polarisation

$$\mathbf{P}_{ir}(\mathbf{r}) = \mathbf{P}(\mathbf{r}) - \mathbf{P}_{uv}(\mathbf{r}) = \frac{1}{4\pi} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}), \quad (2.12)$$

where $\mathbf{P}_{uv}$ in either limit will cancel. Now, using the equations of motion in the static limit ($\ddot{\mathbf{P}}_{uv} = \ddot{\mathbf{P}}_{ir} = 0$) and our expressions for $\mathbf{P}_{ir}$ and $\mathbf{P}_{uv}$ we find

$$\frac{1}{\gamma} = \frac{\omega_{ir}^2}{4\pi} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right), \quad (2.13a)$$

$$\frac{1}{\delta} = \frac{\omega_{uv}^2}{4\pi} \left(1 - \frac{1}{\epsilon_\infty} \right). \quad (2.13b)$$

Combined with the equation of motion for the electron, all three equations of motion can be obtained from the overall Lagrangian

$$\begin{aligned} L = & \frac{1}{2} m_0 \dot{\mathbf{r}}_{el}^2 + \frac{1}{2} \gamma \int \left[\dot{\mathbf{P}}_{ir}^2(\mathbf{r}) - \omega_{ir}^2 \mathbf{P}_{ir}^2(\mathbf{r}) \right] d^3\mathbf{r} + \frac{1}{2} \delta \int \left[\dot{\mathbf{P}}_{uv}^2(\mathbf{r}) - \omega_{uv}^2 \mathbf{P}_{uv}^2(\mathbf{r}) \right] d^3\mathbf{r} \\ & + \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) \left[\mathbf{P}_{uv}(\mathbf{r}) + \mathbf{P}_{ir}(\mathbf{r}) \right] d^3\mathbf{r} + E_{zp}, \end{aligned} \quad (2.14)$$

by using the standard method of extremising the corresponding action $\delta S = \int dt \delta L = 0$ with $\mathbf{r}_{el}$, $\mathbf{P}_{uv}(\mathbf{r})$ and $\mathbf{P}_{ir}(\mathbf{r})$ as variables. E_{zp} is an arbitrary constant representing the polarisation field's zero-point energy without the electron's interaction.

The corresponding Hamiltonian can be derived via a Legendre transformation by noting that the conjugate momenta (defined as $\partial L / \partial \dot{X}$ with the generalised coordinate $X \in \{\mathbf{r}_{el}, \mathbf{P}_{uv}(\mathbf{r}), \mathbf{P}_{ir}(\mathbf{r})\}$) are $\mathbf{p}_{el} = m_0 \dot{\mathbf{r}}_{el}$, $\mathbf{\Pi}_{uv}(\mathbf{r}) = \gamma \dot{\mathbf{P}}_{uv}(\mathbf{r})$ and $\mathbf{\Pi}_{ir}(\mathbf{r}) = \delta \dot{\mathbf{P}}_{ir}(\mathbf{r})$. Hence, the Hamiltonian is

$$\begin{aligned} H = & \sum_X \frac{\partial L}{\partial \dot{X}} \dot{X} - L \\ = & \frac{\mathbf{p}_{el}^2}{2m_0} + \frac{1}{2} \int \left[\mathbf{\Pi}_{ir}^2(\mathbf{r}) / \gamma + \gamma \omega_{ir}^2 \mathbf{P}_{ir}^2(\mathbf{r}) \right] d^3\mathbf{r} + \frac{1}{2} \int \left[\mathbf{\Pi}_{uv}^2(\mathbf{r}) / \delta + \delta \omega_{uv}^2 \mathbf{P}_{uv}^2(\mathbf{r}) \right] d^3\mathbf{r} \\ & - \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) \left[\mathbf{P}_{uv}(\mathbf{r}) + \mathbf{P}_{ir}(\mathbf{r}) \right] d^3\mathbf{r} - E_{zp}. \end{aligned} \quad (2.15)$$

The canonically conjugate variables all obey the classical Poisson's Brackets

$$\{p_{el,j}, r_{el,j'}\} = \delta_{j,j'}, \quad (2.16a)$$

$$\{P_j(\mathbf{r}), \Pi_{j'}(\mathbf{r}')\} = \delta_{j,j'} \delta(\mathbf{r} - \mathbf{r}'), \quad (2.16b)$$

where the subscripts j and j' denote the Cartesian components.

Classically, when the electron is at rest, the force acting on the electron must vanish, and so the electric potential, $\Phi(\mathbf{r})$, must be minimum at $\mathbf{r} = \mathbf{r}_{el}$. However, the above Hamiltonian diverges as $\mathbf{r} \rightarrow \mathbf{r}_{el}$. This happens because the lattice has been approximated as a continuum. This can be accounted for by representing the polarisation vectors as

a Fourier series and excluding terms with wavelengths shorter than the lattice constant. With this cut-off, $\Phi(\mathbf{r})$ will now have a minimum at $\mathbf{r} = \mathbf{r}_{el}$ and $\mathbf{P}(\mathbf{r}_{el}) = \mathbf{0}$. Nonetheless, when the electron is moving slowly, $\mathbf{P}(\mathbf{r}_{el}) \neq 0$ due to the time-dependent terms in the equation of motion, but $\mathbf{P}_{uv}(\mathbf{r}_{el}) \ll \mathbf{P}_{ir}(\mathbf{r}_{el})$ because $\omega_{uv}^2 \gg \omega_{ir}^2$. This means that for a slow electron, the displacement of ions in the lattice is primarily due to the infrared polarisation field $\mathbf{P}_{ir}$. Therefore, for a slow electron, the $\mathbf{P}_{uv}$ terms remain mostly constant and can be disregarded from the lattice dynamics. This gives Fröhlich's Hamiltonian for a slow electron in an ionic lattice to be

$$H = \frac{\mathbf{p}_{el}^2}{2m_0} + \frac{1}{2} \int \left[\Pi_{ir}^2(\mathbf{r})/\gamma + \gamma\omega_{ir}^2 \mathbf{P}_{ir}^2(\mathbf{r}) \right] d^3\mathbf{r} - \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) \mathbf{P}_{ir}(\mathbf{r}) d^3\mathbf{r} - E_{zp}. \quad (2.17)$$

Quantising Fröhlich's Hamiltonian

From now on, I will drop the 'ir' index for the infrared polarisation field, and $\mathbf{P}(\mathbf{r})$ will represent the infrared ionic displacement polarisation field, with frequency ω_0 . To prepare this Hamiltonian for quantisation, Fröhlich introduced an auxiliary complex vector field $\mathbf{B}(\mathbf{r})$ that is defined by

$$\mathbf{B}(\mathbf{r}) = \sqrt{\frac{\gamma\omega_0}{2\hbar}} \left[\mathbf{P}(\mathbf{r}) + \frac{i}{\gamma\omega_0} \Pi(\mathbf{r}) \right], \quad (2.18a)$$

$$\mathbf{B}^*(\mathbf{r}) = \sqrt{\frac{\gamma\omega_0}{2\hbar}} \left[\mathbf{P}(\mathbf{r}) - \frac{i}{\gamma\omega_0} \Pi(\mathbf{r}) \right], \quad (2.18b)$$

where $\nabla_{\mathbf{r}} \times \mathbf{B}(\mathbf{r}) = \nabla_{\mathbf{r}} \times \mathbf{B}^\dagger(\mathbf{r}) = 0$. Equivalently, this can be written in terms of the infrared polarisation field,

$$\mathbf{P}(\mathbf{r}) = \sqrt{\frac{\hbar}{2\gamma\omega_0}} [\mathbf{B}^*(\mathbf{r}) + \mathbf{B}(\mathbf{r})], \quad (2.19a)$$

$$\Pi(\mathbf{r}) = i\sqrt{\frac{\gamma\hbar\omega_0}{2}} [\mathbf{B}^*(\mathbf{r}) - \mathbf{B}(\mathbf{r})]. \quad (2.19b)$$

Substituting these into (2.17) gives the Hamiltonian

$$H = \frac{\mathbf{p}_{el}^2}{2m_0} + \hbar\omega_0 \int \mathbf{B}^*(\mathbf{r})\mathbf{B}(\mathbf{r}) d^3\mathbf{r} - \sqrt{\frac{\hbar}{2\gamma\omega_0}} \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) [\mathbf{B}^*(\mathbf{r}) + \mathbf{B}(\mathbf{r})] d^3\mathbf{r} - E_{zp}. \quad (2.20)$$

To quantise this Hamiltonian, $\mathbf{B}(\mathbf{r})$ is given a periodic boundary condition over a cube of volume $V_0 = L^3$ and then expressed as a Fourier series,

$$\mathbf{B}(\mathbf{r}) = \frac{1}{\sqrt{V_0}} \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} b_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (2.21a)$$

$$\mathbf{B}^*(\mathbf{r}) = \frac{1}{\sqrt{V_0}} \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} b_{\mathbf{q}}^* e^{-i\mathbf{q} \cdot \mathbf{r}}. \quad (2.21b)$$

The Fourier coefficients are given by

$$b_{\mathbf{q}} = \frac{1}{\sqrt{V_0}} \frac{\mathbf{q}}{q} \cdot \int d^3\mathbf{r} \mathbf{B}(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}, \quad (2.22a)$$

$$b_{\mathbf{q}} = \frac{1}{\sqrt{V_0}} \frac{\mathbf{q}}{q} \cdot \int d^3\mathbf{r} \mathbf{B}^*(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (2.22b)$$

where the components q_j of the wave-vector $\mathbf{q}$ satisfy

$$q_j = \frac{2\pi}{V_0^{1/3}} n_j, \quad n_j = 0, \pm 1, \pm 2, \dots \quad (2.23)$$

In the limit as the volume goes to infinity $V_0 \rightarrow \infty$ the sum over $\mathbf{q}$ becomes an integral,

$$\sum_{\mathbf{q}} \rightarrow \frac{V_0}{(2\pi)^3} \int d^3\mathbf{q}. \quad (2.24)$$

The fact that $\mathbf{P}(\mathbf{r})$ and $\mathbf{\Pi}(\mathbf{r})$ are real functions imposes the following condition on the Fourier components $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^*$,

$$b_{\mathbf{q}}^* = -b_{-\mathbf{q}}. \quad (2.25)$$

The infrared polarisation field and its momenta conjugate can be written in terms of $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^*$

$$\mathbf{P}(\mathbf{r}) = \sqrt{\frac{\hbar}{2\gamma\omega_0 V_0}} \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} \left[b_{\mathbf{q}}^* e^{-i\mathbf{q} \cdot \mathbf{r}} + b_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \right], \quad (2.26a)$$

$$\mathbf{\Pi}(\mathbf{r}) = i \sqrt{\frac{\gamma\hbar\omega_0}{2V_0}} \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} \left[b_{\mathbf{q}}^* e^{-i\mathbf{q} \cdot \mathbf{r}} - b_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} \right]. \quad (2.26b)$$

To derive the Poisson brackets for $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^*$, note that $\mathbf{P}(\mathbf{r})$ and $\mathbf{\Pi}(\mathbf{r})$ are conjugate variables. This means that $\sqrt{\hbar/2\gamma\omega_0}(b_{\mathbf{q}}^* + b_{\mathbf{q}})$ and $i\sqrt{\hbar\omega_0/2\gamma}(b_{\mathbf{q}}^* - b_{\mathbf{q}})$ are conjugate too. Therefore, from the Poisson brackets for $\mathbf{P}(\mathbf{r})$ and $\mathbf{\Pi}(\mathbf{r})$ (see Eq. (2.16)) we have

$$\left\{ b_{\mathbf{q}}^* + b_{\mathbf{q}}, b_{\mathbf{q}'}^* - b_{\mathbf{q}'} \right\} = \frac{2}{i\hbar} \delta_{\mathbf{q},\mathbf{q}'}, \quad (2.27)$$

and since Poisson brackets involving the same operator but different $\mathbf{q}$ s vanish, the Poisson brackets for $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^*$ are

$$\{b_{\mathbf{q}}, b_{\mathbf{q}'}^*\} = \frac{1}{i\hbar} \delta_{\mathbf{q}, \mathbf{q}'}, \quad (2.28a)$$

$$\{b_{\mathbf{q}}, b_{\mathbf{q}'}\} = \{b_{\mathbf{q}}^*, b_{\mathbf{q}'}^*\} = 0. \quad (2.28b)$$

The interaction energy between the electron and the infrared polarisation field can now be defined in terms of $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^*$,

$$\begin{aligned} e\Phi(\mathbf{r}_{el}) &= - \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) \mathbf{P}(\mathbf{r}) d^3\mathbf{r} \\ &= - \left(\frac{\hbar}{2\gamma\omega_0 V_0} \right)^{\frac{1}{2}} \int \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} \left[b_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}} + b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \right] d^3\mathbf{r}. \end{aligned} \quad (2.29)$$

To proceed, we integrate by parts to give

$$\begin{aligned} e\Phi(\mathbf{r}_{el}) &= 4\pi i \left(\frac{e^2 \hbar}{2\gamma\omega_0 V_0} \right)^{\frac{1}{2}} \int \delta(\mathbf{r} - \mathbf{r}_{el}) \sum_{\mathbf{q}} \frac{1}{q} \left[b_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}} - b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \right] d^3\mathbf{r} \\ &= 4\pi i \left(\frac{e^2 \hbar}{2\gamma\omega_0 V_0} \right)^{\frac{1}{2}} \sum_{\mathbf{q}} \frac{1}{q} \left[b_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}_{el}} - b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_{el}} \right], \end{aligned} \quad (2.30)$$

where we have used that $\nabla_{\mathbf{r}} \cdot \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}) = 4\pi e \delta(\mathbf{r} - \mathbf{r}_{el})$. Hence, for the Hamiltonian (written in symmetrised form), we get

$$\begin{aligned} H &= \frac{\mathbf{p}_{el}^2}{2m_0} + \frac{\hbar\omega_0}{2} \sum_{\mathbf{q}} \left[b_{\mathbf{q}}^* b_{\mathbf{q}} + b_{\mathbf{q}} b_{\mathbf{q}}^* \right] - E_{zp} \\ &\quad + 4\pi i e \left(\frac{\hbar}{2\gamma\omega_0 V_0} \right)^{\frac{1}{2}} \sum_{\mathbf{q}} \frac{1}{q} \left[b_{\mathbf{q}}^* e^{-i\mathbf{q}\cdot\mathbf{r}_{el}} - b_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}_{el}} \right]. \end{aligned} \quad (2.31)$$

The result for $\Phi(\mathbf{r}_{el})$ in Eq. (2.30) only holds if $\mathbf{q} \neq 0$, and the summations must exclude the case for when $\mathbf{q} = 0$. This situation represents an electron in a neutral, rigid lattice and must not be subjected to periodic boundary conditions. Otherwise, the periodic boundary conditions would repeat this charge since each volume V_0 contains a charge e . This cannot happen as it leads to a diverging overlap of the many long-range repulsive Coulomb interactions (a ‘Coulomb’ bomb). To avoid this, typically the opposite charge $-e$ is distributed homogeneously over the volume V_0 , which compensates for the $\mathbf{q} = 0$ component of the electronic charge. So, the $\mathbf{q} = 0$ component does not contribute to the interaction energy. This distributed oppositive charge is known as the homogeneous background charge.

To quantise, the electron momentum $\mathbf{p}$ is replaced with the operator $-i\hbar\hat{\nabla}_{\mathbf{r}}$, $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^*$ by the operators $\hat{b}_{\mathbf{q}}$ and $\hat{b}_{\mathbf{q}}^\dagger$, and the Poisson Brackets by $i\hbar$ times the corresponding commutator

$$[b_{\mathbf{q}}, b_{\mathbf{q}'}^\dagger] = \delta_{\mathbf{q}, \mathbf{q}'}, \quad (2.32a)$$

$$[b_{\mathbf{q}}, b_{\mathbf{q}}^\dagger] = [b_{\mathbf{q}'}, b_{\mathbf{q}'}^\dagger] = 0. \quad (2.32b)$$

The polarisation field can be viewed as a set of harmonic oscillators $\mathbf{q}$, all with the same frequency $\omega_0/2\pi$. The operators $b_{\mathbf{q}}^\dagger$ and $b_{\mathbf{q}}$ then represent the creation and annihilation operators, respectively, of quanta of polarisation with different wave-numbers $\mathbf{q}$ but the same energy $\hbar\omega_0$. These quanta are usually referred to as *phonons*. Thus, $\hat{b}_{\mathbf{q}}^\dagger$ and $\hat{b}_{\mathbf{q}}$ possess ‘raising’ and ‘lowering’ properties when acting on a normalised eigenfunction $|n_{\mathbf{q}}\rangle$,

$$(\hat{b}_{\mathbf{q}}^\dagger)^n |0_{\mathbf{q}}\rangle = (n!)^{\frac{1}{2}} |n_{\mathbf{q}}\rangle \quad (2.33a)$$

$$(\hat{b}_{\mathbf{q}})^n |n_{\mathbf{q}}\rangle = (n!)^{\frac{1}{2}} |0_{\mathbf{q}}\rangle, \quad \hat{b}_{\mathbf{q}} |0_{\mathbf{q}}\rangle = 0. \quad (2.33b)$$

Fröhlich defined a single dimensionless parameter α that quantifies the strength of the electron-phonon interaction described by the last term in the Hamiltonian. This is defined as

The Fröhlich Dimensionless Coupling Constant

$$\alpha = \frac{2\pi e^2}{\hbar\gamma\omega_0^3} \sqrt{\frac{2m_0\omega_0}{\hbar}} = \frac{1}{\sqrt{2}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{e^2}{\hbar\omega_0 r_0}. \quad (2.34)$$

where I define the characteristic length scale $r_0 \equiv \sqrt{\hbar/m_0\omega_0}$. The Fröhlich Hamiltonian then becomes

$$\hat{H} = -\frac{\hat{\nabla}_{\mathbf{r}}^2}{2m_0} + \frac{\hbar\omega_0}{2} \sum_{\mathbf{q}} \left[\hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} + \hat{b}_{\mathbf{q}} \hat{b}_{\mathbf{q}}^\dagger \right] - E_{zp} + \sum_{\mathbf{q}} \left(M_{\mathbf{q}} \hat{b}_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + M_{\mathbf{q}}^* \hat{b}_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} \right), \quad (2.35)$$

with the interaction term (with units of energy)

$$M_{\mathbf{q}} = i \frac{\hbar\omega_0}{q} \left(\frac{2\sqrt{2}\pi r_0 \alpha}{V_0} \right)^{\frac{1}{2}}. \quad (2.36)$$

The zero-point energy E_{zp} of the phonon/polarisation field can be eliminated using the commutation relations where E_{zp} is given by

$$E_{zp} = \sum_{\mathbf{q}} \frac{\hbar\omega_0}{2}. \quad (2.37)$$

This results in

The Fröhlich Hamiltonian

$$\hat{H} = -\frac{\hat{\nabla}_{\mathbf{r}}^2}{2m_0} + \frac{\hbar\omega_0}{2} \sum_{\mathbf{q}} \hat{b}_{\mathbf{q}} \hat{b}_{\mathbf{q}}^{\dagger} + \sum_{\mathbf{q}} \left(M_{\mathbf{q}} \hat{b}_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}} + M_{\mathbf{q}}^* \hat{b}_{\mathbf{q}}^{\dagger} e^{-i\mathbf{q} \cdot \mathbf{r}} \right). \quad (2.38)$$

The first term is the electron's band energy measured relative to the bottom of the conduction band (or from the top of the valence band for holes). The second term gives the polarisation field's energy measured relative to the zero-point energy of the polarisation field. The third term is the electron-phonon interaction energy (written here in a symmetrised form).

2.1.3 Holstein's Small Polaron

Holstein studied the motion of an electron in a one-dimensional molecular crystal. We have a linear chain of N identical molecules. Holstein considered these molecules to be diatomic and on a lattice with fixed orientation and centre of gravity (on the lattice site) but variable internuclear separations. The lattice vibrations correspond to variations in the individual internuclear separations (i.e. intramolecular modes) and are assumed to be uncoupled. If these vibrations are harmonic (i.e. the potential energy of a particular molecule is parabolic as you change the molecular bond length), the Hamiltonian is,

$$H_{\text{chain}} = \frac{1}{2M} \sum_{n=1}^N p_n^2 + \frac{M}{2} \sum_{n=1}^N \omega_0^2 x_n^2, \quad (2.39)$$

where x_n is the deviation of an internuclear separation from its equilibrium position, $p_n \equiv -i\hbar\partial/\partial x_n$ is the corresponding canonical momentum, M is the nuclear mass and ω_0 is the harmonic vibrational frequency.

Holstein considered the motion of a single charge carrier within the tight-binding approximation, where one assumes that the one-electron potential may be written as the sum of molecular potentials,

$$V(\mathbf{r}, x_1, \dots, x_N) = \sum_{n=1}^N U(\mathbf{r} - n\mathbf{a}, x_n), \quad (2.40)$$

where $\mathbf{r}$ is the electron position and $\mathbf{a}$ is the unit lattice vector. The molecular potential U is assumed to be short-range, $U(\mathbf{a}, x_n) \ll U(0, x_n)$.

The ‘‘molecular’’ electron wavefunction $\phi(\mathbf{r} - n\mathbf{a}, x_n)$ are obtained from the Time-Independent Schrödinger Equation (TISE),

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r} - n\mathbf{a}, x_n) \right] \phi(\mathbf{r} - n\mathbf{a}, x_n) = E(x_n) \phi(\mathbf{r} - n\mathbf{a}, x_n). \quad (2.41)$$

with $E(x_n)$ the electron energy of the corresponding molecular site x_n . The total wavefunction is then a linear superposition,

$$\psi(\mathbf{r}, x_1, \dots, x_N) = \sum_{m=1}^N c_m(x_1, \dots, x_N) \phi(\mathbf{r} - m\mathbf{a}, x_m), \quad (2.42)$$

of the molecular electron wavefunctions $\phi(\mathbf{r} - n\mathbf{a}, x_n)$ localised around the n th molecular site. The coefficients $c_n(x_1, \dots, x_N)$ depend on all the internuclear coordinates and ψ

should obey the Time-Dependent Schrödinger Equation (TDSE),

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_{j=1}^N U(\mathbf{r} - j\mathbf{a}, x_j) + \sum_{j=1}^N \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_j^2} + \frac{M}{2} \omega_0^2 x_j^2 \right) \right] \psi. \quad (2.43)$$

Multiplying on the left with $\phi^*(\mathbf{r} - n\mathbf{a}, x_n)$ and integrating over the electron coordinate $\mathbf{r}$ we get,

$$\begin{aligned} & \sum_{m=1}^N T_{nm} \left[i\hbar \frac{\partial}{\partial t} - \sum_{j=1}^N \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_j^2} + \frac{M}{2} \omega_0^2 x_j^2 \right) - E(x_m) \right] c_m(x_1, \dots, x_N) \\ &= \sum_{\substack{m=1 \\ j \neq m}}^N \left[\int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) U(\mathbf{r} - j\mathbf{a}, x_j) \phi(\mathbf{r} - m\mathbf{a}, x_m) \right] c_m(x_1, \dots, x_N) \\ & - \frac{\hbar^2}{2M} \sum_{m=1}^N \int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) \left[2 \frac{\partial \phi(\mathbf{r} - m\mathbf{a}, x_m)}{\partial x_m} \frac{\partial c_m}{\partial x_m} + c_m \frac{\partial^2 \phi(\mathbf{r} - m\mathbf{a}, x_m)}{\partial x_m^2} \right], \end{aligned} \quad (2.44)$$

where,

$$T_{nm} \equiv \int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) \phi(\mathbf{r} - m\mathbf{a}, x_m) = \delta_{nm} + S_{nm}. \quad (2.45)$$

S_{nm} are non-orthogonality integrals, assumed to be non-zero only for nearest neighbours and small compared to unity. Note that in the last line of Eq. (2.44), the $x_1, \dots, x_N$ dependence of c_m has been suppressed for brevity, but is implicit.

Multiply on the left by the inverse of the overlap matrix, T_{ln}^{-1} ,

$$\begin{aligned} & \left[i\hbar \frac{\partial}{\partial t} - \sum_{j=1}^N \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_j^2} + \frac{M}{2} \omega_0^2 x_j^2 \right) - E(x_l) \right] c_l(x_1, \dots, x_N) \\ &= \sum_{\substack{n,m=1 \\ j \neq m}}^N T_{ln}^{-1} \left[\int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) U(\mathbf{r} - j\mathbf{a}, x_j) \phi(\mathbf{r} - m\mathbf{a}, x_m) \right] c_m(x_1, \dots, x_N) \\ & - \frac{\hbar^2}{2M} \sum_{n,m=1}^N T_{ln}^{-1} \int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) \left[2 \frac{\partial \phi(\mathbf{r} - m\mathbf{a}, x_m)}{\partial x_m} \frac{\partial c_m}{\partial x_m} + c_m \frac{\partial^2 \phi(\mathbf{r} - m\mathbf{a}, x_m)}{\partial x_m^2} \right], \end{aligned} \quad (2.46)$$

where we use that $\sum_{n=1}^N T_{ln}^{-1} T_{nm} = \delta_{lm}$. Holstein simplifies this expression by imposing the *tight-binding* approximation. First, he assumes the smallness of overlap integrals (i.e. integrals involving electrons localised at different sites). These integrals are of two types: non-orthogonality integrals (i.e. S_{ln}) and any terms for which $n \neq m$. Expanding $T_{ln}^{-1} \approx \delta_{ln} - S_{ln} + \dots$, any terms that contain products of more than one overlap integral

are discarded. The first line on the RHS of Eq. (2.46) is thus approximated by

$$\begin{aligned}
 & \sum_{\substack{n,m=1 \\ j \neq m}}^N T_{ln}^{-1} \left[\int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) U(\mathbf{r} - j\mathbf{a}, x_j) \phi(\mathbf{r} - m\mathbf{a}, x_m) \right] c_m(x_1, \dots, x_N) \\
 &= \sum_{\substack{m=1 \\ j \neq m}}^N \left[\int d\mathbf{r} \phi^*(\mathbf{r} - l\mathbf{a}, x_l) U(\mathbf{r} - j\mathbf{a}, x_j) \phi(\mathbf{r} - m\mathbf{a}, x_m) \right] c_m(x_1, \dots, x_N) \\
 &\quad - \sum_{\substack{m=1 \\ j \neq m}}^N S_{lm} \left[\int d\mathbf{r} U(\mathbf{r} - j\mathbf{a}, x_j) |\phi(\mathbf{r} - m\mathbf{a}, x_m)|^2 \right] c_m(x_1, \dots, x_N).
 \end{aligned} \tag{2.47}$$

Second, Holstein assumes that due to the local character of the molecular potential U , terms containing products of electron wavefunctions and potentials localised to *different* sites are smaller than terms where two or more are localised to *the same* site. The first line on the RHS of Eq. (2.47) is thus approximated by

$$\begin{aligned}
 & \sum_{\substack{m=1 \\ j \neq m}}^N \left[\int d\mathbf{r} \phi^*(\mathbf{r} - l\mathbf{a}, x_l) U(\mathbf{r} - j\mathbf{a}, x_j) \phi(\mathbf{r} - m\mathbf{a}, x_m) \right] c_m(x_1, \dots, x_N) \\
 &= \sum_{\substack{m=1 \\ m \neq l}}^N \left[\int d\mathbf{r} \phi^*(\mathbf{r} - l\mathbf{a}, x_l) U(\mathbf{r} - l\mathbf{a}, x_l) \phi(\mathbf{r} - m\mathbf{a}, x_m) \right] c_m(x_1, \dots, x_N) \\
 &\quad + \left[\int d\mathbf{r} |\phi(\mathbf{r} - l\mathbf{a}, x_l)|^2 \sum_{\substack{j=1 \\ j \neq l}}^N U(\mathbf{r} - j\mathbf{a}, x_j) \right] c_l(x_1, \dots, x_N),
 \end{aligned} \tag{2.48}$$

where the result is that one of the two summation indices is suppressed. Likewise, the second line on the RHS of Eq. (2.47), which contains the overlap integral S_{ln} , may be dropped.

Any terms in the TDSE involving derivatives of the electronic wavefunctions with respect to the internuclear coordinates represent the effect of the nuclear kinetic energy on the localised electron wavefunctions. Holstein also assumes these terms to be negligible so that they may be discarded. Introducing the notations,

$$W_n(x_1, \dots, x_N) \equiv \sum_{\substack{j=1 \\ j \neq l}}^N \int d\mathbf{r} U(\mathbf{r} - j\mathbf{a}, x_j) |\phi(\mathbf{r} - n\mathbf{a}, x_n)|^2, \tag{2.49}$$

$$J(x_n, x_m) \equiv \int d\mathbf{r} \phi^*(\mathbf{r} - n\mathbf{a}, x_n) U(\mathbf{r} - n\mathbf{a}, x_n) \phi(\mathbf{r} - m\mathbf{a}, x_m), \tag{2.50}$$

and restricting $J(x_n, x_m)$ to nearest neighbours, $x_m = x_{n\pm 1}$, the TDSE reduces to

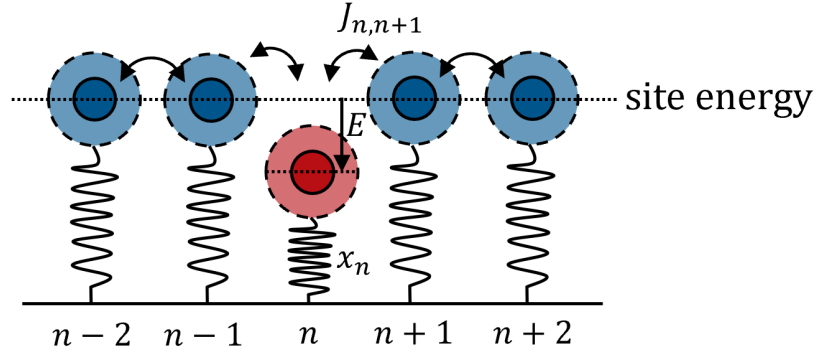


Figure 2.1: Schematic representation of the Holstein molecular crystal model in a one-dimensional lattice. The blue circles represent lattice sites connected to a spring, symbolising local phonon modes. The arrows indicate that the electron can hop between neighbouring sites with amplitude $J_{n,n+1}$. At site n , an electron (red) induces a local lattice distortion with displacement x_n , leading to a shift in the site energy E . This interaction between the electron and the local phonon at site n captures the electron-phonon coupling that can lead to polaron formation.

Holstein-Peierls Molecular Crystal TDSE

$$\left[i\hbar \frac{\partial}{\partial t} - \sum_{j=1}^N \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_j^2} + \frac{M}{2} \omega_0^2 x_j^2 \right) - E(x_n) - W(x_1, \dots, x_N) \right] \times c_n(x_1, \dots, x_N) = \sum_{\pm} J(x_n, x_{n\pm 1}) c_{n\pm 1}(x_1, \dots, x_N). \quad (2.51)$$

where the sum $\sum_{\pm}$ is over the neighbours of site n .

$E(x_n)$ describes the intramolecular “on-site” interaction energy (often just referred to as *the* Holstein electron-phonon coupling) of the electron on site n and the molecule on the same site. This is related to the *inner*-sphere reorganisation energy in Marcus theory [67].

$W_n(x_1, \dots, x_N)$ describes the intermolecular “off-site” interaction energy (often referred to as the ‘Peierls’ electron-phonon coupling) between the electron on site n and the other molecules on sites $m \neq n$. This is related to the *outer*-sphere reorganisation energy in Marcus theory [67].

$J(x_n, x_{n\pm 1})$ are the transfer integrals and describe the energy associated with the overlap of the n -th site electron wavefunction and neighbouring sites’ molecular electronic wavefunctions ϕ . J therefore depends on the internuclear displacements x_n and $x_{n\pm 1}$.

Fig. 2.1 shows a mechanistic interpretation of Holstein’s molecular-crystal model.

Holstein introduced further simplifications to this molecular-crystal model:

1. He neglects the “off-site” intermolecular couplings $W_n(x_1, \dots, x_N) \rightarrow 0$. This means no ‘Peierls’ coupling.

2. He neglects the x -dependence of the transfer integral (equivalent to assuming small distortions between the molecules), which means a constant value between all neighbouring sites $J(x_n, x_{n\pm 1}) \rightarrow -J$.
3. He assumes a linear “on-site” intramolecular coupling, $E(x_n) = -gx_n$.

The TDSE is then,

Holstein Molecular Crystal TDSE

$$\left[i\hbar \frac{\partial}{\partial t} - \sum_{j=1}^N \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_j^2} + \frac{M}{2} \omega_0^2 x_j^2 \right) + gx_n \right] c_n + J(c_{n+1} + c_{n-1}) = 0. \quad (2.52)$$

Note that c_n and $c_{n\pm 1}$ still depend on all the molecular positions $x_1, \dots, x_N$ – I have just suppressed this notation for brevity.

In second quantisation, the Holstein Hamiltonian becomes,

$$\hat{H} = -J \sum_{n=1}^N \hat{c}_n^\dagger (\hat{c}_{n+1} + \hat{c}_{n-1}) + \hbar\omega_0 \sum_{n=1}^N \hat{b}_n^\dagger \hat{b}_n + g \sum_{n=1}^N \hat{c}_n^\dagger \hat{c}_n (\hat{b}_n^\dagger + \hat{b}_n), \quad (2.53)$$

where $\hat{c}_n^\dagger$ and $\hat{c}_n$ are the fermion creation and annihilation operators for an electron/hole on site n , $\hat{b}_n^\dagger$ and $\hat{b}_n$ are the boson creation and annihilation operators for a phonon at site n , J is the constant transfer integral, ω_0 the Einstein-mode phonon frequency, N the number of lattice sites and g the electron-phonon coupling constant.

In the momentum space, the Holstein Hamiltonian is,

The Holstein Hamiltonian

$$\hat{H} = -J \sum_{\mathbf{k}} \hat{c}_{\mathbf{k}}^\dagger \hat{c}_{\mathbf{k}} + \hbar\omega_0 \sum_{\mathbf{q}} \hat{b}_{\mathbf{q}}^\dagger \hat{b}_{\mathbf{q}} + \frac{g}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} \hat{c}_{\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{\mathbf{k}} (\hat{b}_{-\mathbf{q}}^\dagger + \hat{b}_{\mathbf{q}}) \quad (2.54)$$

where the electronic and phononic wave numbers k and q assume N discrete values within the first Brillouin zone $-\frac{\pi}{a} < k, q < \frac{\pi}{a}$, where a is the lattice constant. The electron dispersion $\epsilon_{\mathbf{k}}$ is the typical tight-binding electron dispersion,

$$\epsilon_{\mathbf{k}} = -2J \sum_{i=1}^n \cos(k_i), \quad (2.55)$$

where n is the number of dimensions and k_i indicates the component of the electron wavevector along the i -th dimension. In analogy to the Fröhlich Hamiltonian in Eq. (2.17),

we can express the electron-phonon coupling matrix element as $M_{\mathbf{q}}$ (units of energy),

$$\begin{aligned} M_{\mathbf{q}} &= M_0 = \frac{g_n}{\sqrt{N}}, \\ &= \sqrt{\frac{2Jn\hbar\omega_0\alpha_H}{N}}, \end{aligned} \tag{2.56}$$

where g_n is the Holstein electron-phonon coupling strength in n dimensions and is parameterised by the *unitless* coupling constant α_H .

As J is the main energy scale in this model, we also need to define another unitless parameter $\gamma \equiv \hbar\omega_0/J$, which is the ratio of the phonon energy and electron hopping amplitude and is called the adiabaticity.

The Holstein model can thus be fully described by two parameters, α and γ .

2.2 The Feynman Path Integral & Variational Approach

In 1955 [2], Feynman developed a variational principle to find the lowest energy of a system described by a path integral. This variational principle was applied to the Fröhlich model of the polaron [3] and was the first method to accurately predict the ground-state energy and effective mass of the polaron for all values of the electron-phonon coupling constant.

We start with Fröhlich's Hamiltonian for a slow electron as given in Eq. (2.38) and cast the phonon creation and annihilation operators into their corresponding coordinates $\hat{x}_{\mathbf{q}}$ and momenta $\hat{p}_{\mathbf{q}}$

$$\hat{x}_{\mathbf{q}} = \frac{1}{\sqrt{2}} r_0 \left(\hat{b}_{\mathbf{q}}^\dagger + \hat{b}_{\mathbf{q}} \right), \quad \hat{p}_{\mathbf{q}} = i\hbar \frac{1}{\sqrt{2}} \frac{1}{r_0} \left(\hat{b}_{\mathbf{q}}^\dagger - \hat{b}_{\mathbf{q}} \right), \quad (2.57)$$

or Fourier components

$$\hat{b}_{\mathbf{q}} = \frac{1}{\sqrt{2}} \frac{1}{r_0} \left(\hat{x}_{\mathbf{q}} + i \frac{\hat{p}_{\mathbf{q}}}{m_0 \omega_0} \right), \quad \hat{b}_{\mathbf{q}}^\dagger = \frac{1}{\sqrt{2}} \frac{1}{r_0} \left(\hat{x}_{\mathbf{q}} - i \frac{\hat{p}_{\mathbf{q}}}{m_0 \omega_0} \right), \quad (2.58)$$

which substituted into Eq. (2.38) gives

$$H = \frac{\hat{\mathbf{p}}^2}{2m_0} + \frac{1}{2} \sum_{\mathbf{q}} \left(\hat{p}_{\mathbf{q}}^2 + \omega_0^2 \hat{x}_{\mathbf{q}}^2 \right) + \sum_{\mathbf{q}} M_{\mathbf{q}} \hat{p}_{\mathbf{q}} \hat{x}_{\mathbf{q}}, \quad (2.59)$$

where $\mathbf{p}$ is the conduction band electron (or valence and hole) momentum, $\mathbf{r}$ is electron position, m_0 is the effective band mass, ω_0 is the longitudinal optical phonon frequency, $M_{\mathbf{q}}$ is the electron-phonon coupling matrix element, and $\hat{p}_{\mathbf{q}} = e^{i\mathbf{q} \cdot \hat{\mathbf{r}}}$ is the operator for the q th Fourier component of the electron density.

2.2.1 Ground-State Polaron

If the wavefunction $\psi(\mathbf{r}_i, x_i, t_i)$ corresponding to the polaron system is known at some initial time t_i , then the wavefunction at some later time t_f is given by,

$$\psi(\mathbf{r}_f, x_f, t_f) = \int d^3 \mathbf{r}_i \int dx_i K(\mathbf{r}_f, x_f, t_f; \mathbf{r}_i, x_i, t_i) \psi(\mathbf{r}_i, x_i, t_i), \quad (2.60)$$

where $\mathbf{r} \equiv \mathbf{r}$ and $x \equiv \{x_{\mathbf{q}}\}$ represents the set of all polarisation coordinate oscillators. $K(\mathbf{r}_f, x_f, t_f; \mathbf{r}_i, x_i, t_i)$ is commonly called the time-evolution “kernel” or “propagator” and gives the probability amplitude to go from the state of the system $\{\mathbf{r}_i, x_i\}$ at time t_i to the state of the system $\{\mathbf{r}_f, x_f\}$ at time t_f . We can use the unitary time evolution operator to

define it as

$$\begin{aligned} K(\mathbf{r}_f, x_f, t_f; \mathbf{r}_i, x_i, t_i) &\equiv \langle \psi(\mathbf{r}_f, x_f) | e^{-i\hat{H}(t_f-t_i)/\hbar} | \psi(\mathbf{r}_i, x_i) \rangle \\ &= \sum_n \psi_n(\mathbf{r}_f, x_f) \psi_n^*(\mathbf{r}_i, x_i) e^{-iE_n(t_f-t_i)/\hbar}, \end{aligned} \quad (2.61)$$

where ψ_n are a complete orthonormal set of the Fröhlich Hamiltonian eigenfunctions and E_n are the corresponding energy eigenvalues. The ground-state energy can be obtained by letting $\phi_0(x)$ be any function of the phonon coordinates x that is not orthogonal to the exact ground-state wavefunction $\psi_0(\mathbf{r}, x)$. The inner product of the kernel with $\phi_0(x)$ gives the probability amplitude $G_{0,0}$ for the system in the ground state to return to the ground state,

$$\begin{aligned} G_{0,0}(t_f, t_i) &= \langle \phi_0(x_f) | K(\mathbf{r}_f, x_f, t_f; \mathbf{r}_i, x_i, t_i) | \phi_0(x_i) \rangle \\ &= \iint dx_f dx_i \phi_0^*(x_f) K(\mathbf{r}_f, x_f, t_f; \mathbf{r}_i, x_i, t_i) \phi_0(x_i) \\ &= \sum_n a_{n,0}(\mathbf{r}_f) a_{n,0}^*(\mathbf{r}_i) e^{-iE_n(t_f-t_i)/\hbar}, \end{aligned} \quad (2.62)$$

where,

$$a_{n,0}(\mathbf{r}) = \int dx \phi_0^*(x) \psi_n(\mathbf{r}, x). \quad (2.63)$$

If we evaluate this for the electron to start and end at the same position (which we choose to be 0 for convenience), $\mathbf{r}_f = \mathbf{r}_i = \mathbf{0}$ from imaginary-time 0 to $-i\tau$ we obtain,

$$\begin{aligned} G_{0,0}(t_f = -i\tau, t_i = 0) &= \langle \phi_0(x_f) | K(\mathbf{0}, x_f, -i\tau; \mathbf{0}, x_i, 0) | \phi_0(x_i) \rangle \\ &= \iint dx_f dx_i \phi_0^*(x_f) K(\mathbf{0}, x_f, -i\tau; \mathbf{0}, x_i, 0) \phi_0(x_i) \\ &= \sum_n a_{n,0}(0) a_{n,0}^*(0) e^{-E_n\tau/\hbar}, \end{aligned} \quad (2.64)$$

which in the limit as $\tau \rightarrow \infty$ projects out the ground-state of the system,

$$\lim_{\tau \rightarrow \infty} \sum_n a_{n,0}(0) a_{n,0}^*(0) e^{-E_n\tau/\hbar} \rightarrow a_{0,0}(0) a_{0,0}^*(0) e^{-E_0\tau/\hbar}. \quad (2.65)$$

Therefore we find that ground-state energy E_{gs} ,

$$E_{gs} = \lim_{\tau \rightarrow \infty} \left[-\frac{\hbar}{\tau} \ln G_{0,0}(\tau) \right]. \quad (2.66)$$

If we identify $\tau = \hbar/(k_B T) = \hbar\beta$ (where β is the thermodynamic beta) then the kernel $K(\mathbf{r}_f, x_f, -i\hbar\beta; \mathbf{r}_i, x_i, 0)$ is the same as the statistical density matrix $\rho(\mathbf{r}_f, x_f, \beta; \mathbf{r}_i, x_i, 0)$ [68],

and $G_{0,0}(-i\hbar\beta)$ is the same as the statistical partition function Z where,

$$Z(\beta) = \text{Tr} [\rho] = \iint d\mathbf{r} dx \rho(\mathbf{r}, x, \mathbf{r}, x; \beta), \quad (2.67)$$

and is related to the Helmholtz free energy F by,

$$Z(\beta) = e^{-\beta F} = \text{Tr} \left[e^{-\beta \hat{H}} \right] = \sum_n e^{-\beta E_n}. \quad (2.68)$$

Therefore, we can rewrite the expression for the ground-state energy as,

$$E_{gs} = \lim_{\beta \rightarrow \infty} [F(\beta)] = \lim_{\beta \rightarrow \infty} \left[-\frac{1}{\beta} \ln Z(\beta) \right]. \quad (2.69)$$

Path Integral Expression

The kernel can be expressed explicitly as a path integral (see Appendix A for a textbook ‘time-slice’ derivation of the path integral),

$$K(\mathbf{r}_f, x_f, t_f; \mathbf{r}_i, x_i, t_i) = \int_{\mathbf{r}(t_i)=\mathbf{r}_i}^{\mathbf{r}(t_f)=\mathbf{r}_f} D\mathbf{r}(t) \int_{x_i, t_i}^{x_f, t_f} Dx(t) \exp \left\{ \frac{iS[\mathbf{r}(t), x(t)]}{\hbar} \right\}, \quad (2.70)$$

where the Fröhlich action $S[\mathbf{r}, x]$ is given by,

$$\begin{aligned} S[\mathbf{r}(t), x(t)] &= \frac{m_0}{2} \int_{t_i}^{t_f} dt \dot{\mathbf{r}}^2(t) + \frac{1}{2} \sum_{\mathbf{q}} \int_{t_i}^{t_f} dt \left(\dot{x}_{\mathbf{q}}^2(t) - \omega_0^2 x_{\mathbf{q}}^2(t) \right) \\ &\quad - \sum_{\mathbf{q}} M_{\mathbf{q}} \int_{t_i}^{t_f} dt x_{\mathbf{q}}(t) \rho_{\mathbf{q}}(\mathbf{r}(t)). \end{aligned} \quad (2.71)$$

Since the phonon coordinates $x(t)$ appear quadratically in the action, the path integral over them can be made to be Gaussian and done explicitly to simplify $G_{0,0}$,

$$G_{0,0}(t_f, t_i) = \prod_{\mathbf{q}} \int_{\mathbf{r}(t_i)=\mathbf{0}}^{\mathbf{r}(t_f)=\mathbf{0}} D\mathbf{r}(t) G_{\mathbf{q}}[\mathbf{r}(t)] \exp \left\{ \frac{i}{\hbar} \frac{m_0}{2} \int_{t_i}^{t_f} dt \dot{\mathbf{r}}^2(t) \right\}, \quad (2.72)$$

where,

$$\begin{aligned} G_{\mathbf{q}}[\mathbf{r}(t)] &= \int_{-\infty}^{\infty} dx_{\mathbf{q},f} \int_{-\infty}^{\infty} dx_{\mathbf{q},i} \phi_0^*(x_{\mathbf{q},f}) \phi_0(x_{\mathbf{q},i}) \\ &\times \left[\int_{x_{\mathbf{q}}(t_i)=x_{\mathbf{q},i}}^{x_{\mathbf{q}}(t_f)=x_{\mathbf{q},f}} Dx_{\mathbf{q}}(t) \exp \left\{ \frac{i}{\hbar} \int_{t_i}^{t_f} dt \frac{1}{2} \left(\dot{x}_{\mathbf{q}}^2(t) - \omega_0^2 x_{\mathbf{q}}^2(t) \right) - M_{\mathbf{q}} x_{\mathbf{q}}(t) \rho_{\mathbf{q}}(\mathbf{r}(t)) \right\} \right]. \end{aligned} \quad (2.73)$$

Since in the Fröhlich model, the phonons are purely harmonic (they do not interact with themselves), we can choose $\phi_0(x_{\mathbf{q}})$ to be the ground-state wavefunction of a simple harmonic oscillator,

$$\phi_0(x_{\mathbf{q}}) = \left(\frac{1}{\pi r_0^2} \right)^{1/4} \exp \left\{ -\frac{x_{\mathbf{q}}^2}{2r_0^2} \right\}. \quad (2.74)$$

Now the integrals in $G_{\mathbf{q}}$ can be solved analytically to give,

$$G_{\mathbf{q}}(t_f, t_i) = Z_{\text{ph}} \exp \left\{ -\frac{|M_{\mathbf{q}}|^2}{2} \int_{t_i}^{t_f} \int_{t_i}^{t_f} dt ds \rho_{\mathbf{q}}(t) D_{\omega_{\mathbf{q}}}(t-s) \rho_{\mathbf{q}}^*(s) \right\}, \quad (2.75)$$

where we have written $\rho_{\mathbf{q}}(\mathbf{r}(t)) \equiv \rho_{\mathbf{q}}(t)$ for brevity. Generally,

Bare Phonon Green Function

$$\begin{aligned} D_{\omega_{\mathbf{q}}}(t-s) &= \langle x_{\mathbf{q}}(t) x_{-\mathbf{q}}(s) \rangle_0 \\ &= n_{\omega_{\mathbf{q}}} e^{i\omega_{\mathbf{q}}|t-s|} + (n_{\omega_{\mathbf{q}}} + 1) e^{-i\omega_{\mathbf{q}}|t-s|}, \end{aligned} \quad (2.76)$$

is the equilibrium bare (non-interacting) phonon Green function and $n_{\omega_{\mathbf{q}}} = (e^{\hbar\beta\omega_{\mathbf{q}}} - 1)^{-1}$ is the Bose-Einstein distribution. For Einstein (dispersionless) modes ω_0 and low temperatures $D_{\omega_0}(t) \rightarrow e^{-i\omega_0|t|}$. The determinant of the bare phonon Green function can be evaluated from the inverse phonon Green function $D_{\omega_{\mathbf{q}}}^{-1} = \frac{\partial}{\partial \tau} + \omega_{\mathbf{q}}$ to obtain the phonon partition function,

$$\begin{aligned} Z_{\text{ph}} &= \text{Tr} e^{-\beta \hat{H}} \\ &\equiv \prod_{\mathbf{q}} \det \left(D_{\omega_{\mathbf{q}}}^{-1} \right)^{-1} = \det \left(\frac{\partial}{\partial \tau} + \omega_{\mathbf{q}} \right) \\ &= \prod_{\mathbf{q}, \omega_n} (-i\omega_n + \omega_{\mathbf{q}})^{-1} = \prod_{\mathbf{q}} \prod_{n=1}^{\infty} \left[\left(\frac{2n\pi}{\hbar\beta} \right)^2 + \omega_{\mathbf{q}}^2 \right]^{-1} \\ &= \prod_{\mathbf{q}} \frac{1}{2 \sinh(\hbar\omega_{\mathbf{q}}\beta/2)}, \end{aligned} \quad (2.77)$$

where we have expanded the inverse Green function operator into Matsubara modes $\omega_n \equiv 2n\pi/\hbar\beta$ ($n \in \mathbf{Z}$). Feynman then obtained the total polaron kernel defined entirely in

terms of the electron coordinate,

$$G_{0,0}(t_f, t_i) = \int_{\mathbf{r}(t_i)=\mathbf{0}}^{\mathbf{r}(t_f)=\mathbf{0}} D\mathbf{r}(t) \times \exp \left\{ \frac{i}{\hbar} \left[\frac{m_0}{2} \int_{t_i}^{t_f} dt \dot{\mathbf{r}}^2 - \frac{1}{2} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \int_{t_i}^{t_f} \int_{t_i}^{t_f} dt ds \rho_{\mathbf{q}}(t) D_{\omega_0}(t-s) \rho_{\mathbf{q}}^*(s) \right] \right\}, \quad (2.78)$$

where the summation over the phonon wavevector $\mathbf{q}$ can be evaluated to give,

$$\begin{aligned} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \rho_{\mathbf{q}}(t) \rho_{\mathbf{q}}^*(s) &= |M_0|^2 V_0 \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \frac{e^{i\mathbf{q} \cdot (\mathbf{r}(t) - \mathbf{r}(s))}}{q^2} \\ &= |M_0|^2 \frac{V_0}{4\pi} \frac{1}{|\mathbf{r}(t) - \mathbf{r}(s)|}, \end{aligned} \quad (2.79)$$

where $M_0 \equiv M_{\mathbf{q}=\mathbf{0}} = i\hbar\omega_0\sqrt{2\sqrt{2}\pi r_0\alpha/V_0}$. Substituting the result of this summation and setting $t_i = 0$ and $t_f = T$ gives the final form of $G_{0,0}$ to be

$$G_{0,0}(T) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(T)=\mathbf{0}} D\mathbf{r}(t) \exp \left\{ \frac{i}{\hbar} S_{\text{eff}}[\mathbf{r}(t)] \right\}, \quad (2.80)$$

where the new effective action S_{eff} is given by

$$S_{\text{eff}}[\mathbf{r}(t)] = \frac{m_0}{2} \int_0^T dt \dot{\mathbf{r}}(t)^2 - \frac{\alpha\hbar r_0 \omega_0^2}{2\sqrt{2}} \int_0^T \int_0^T dt ds \frac{D_{\omega_0}(t-s)}{|\mathbf{r}(t) - \mathbf{r}(s)|}. \quad (2.81)$$

This new effective *model* action represents an electron coupled by a non-local time-retarded Coulomb potential to itself from an earlier time. If we do a Wick rotation into imaginary-time ($T \rightarrow -\hbar\beta$, $t \rightarrow -i\tau$ and $s \rightarrow -i\sigma$), we obtain the density matrix as a path integral,

$$\rho(\mathbf{r}_f, \hbar\beta; \mathbf{r}_i, 0) = \int_{\mathbf{r}(0)=\mathbf{r}_i}^{\mathbf{r}(\hbar\beta)=\mathbf{r}_f} D\mathbf{r}(\tau) \exp \left\{ -\frac{S[\mathbf{r}(\tau)]}{\hbar} \right\}, \quad (2.82)$$

with the model action in imaginary-time,

Feynman's Polaron *Model* Action

$$S = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \left(\frac{d\mathbf{r}(\tau)}{d\tau} \right)^2 - \frac{\alpha\hbar r_0 \omega_0^2}{2\sqrt{2}} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma \frac{e^{-\omega_0|\tau-\sigma|}}{|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|}, \quad (2.83)$$

where low temperature $\beta \gg 1$ is assumed so that $D_{\omega_0}(\tau - \sigma) \approx e^{-\omega_0|\tau-\sigma|}$. Therefore, we

can find the exact ground-state energy of the polaron using

$$E_{gs} = \lim_{\beta \rightarrow \infty} \left\{ \frac{1}{\beta} \ln \int_{\mathbf{r}(0)=0}^{\mathbf{r}(\hbar\beta)=0} D\mathbf{r}(\tau) e^{-S[\mathbf{r}(\tau)]/\hbar} \right\}. \quad (2.84)$$

The power of this result is that the many-body problem involving an infinite number of phonons interacting with a single conduction electron has been reduced to a one-body problem with one integral over a temporally non-local effective potential. Due to the Coulomb nature of this potential, the model action is not functionally-integrable. However, Feynman devised a variational approach to approximate it.

2.2.2 Feynman-Jensen Variational Principle

The model action cannot be solved exactly as a path integral since it is not quadratic in the electron coordinates. However, Feynman was able to obtain a variational upper-bound approximation of the ground-state energy of the polaron. Feynman noticed that he could use Jensen's inequality: for a set of real values f , the average of $\exp(f)$ exceeds the exponential of the average,

$$\langle \exp(f) \rangle \geq \exp(\langle f \rangle). \quad (2.85)$$

Therefore, if one can find another functionally-integrable trial action S_0 that closely approximates the model action S for the paths $\mathbf{r}(\tau)$ that most significantly contribute to the path integral, then Jensen's inequality can give a lower-bound on the partition function:

The Feynman-Jensen Variational Principle

$$\begin{aligned} Z(\beta) &= \int_{\mathbf{r}(0)=0}^{\mathbf{r}(\hbar\beta)=0} D\mathbf{r}(\tau) e^{-S[\mathbf{r}(\tau)]/\hbar} \\ &= \int_{\mathbf{r}(0)=0}^{\mathbf{r}(\hbar\beta)=0} D\mathbf{r}(\tau) e^{-(S[\mathbf{r}(\tau)]-S_0[\mathbf{r}(\tau)])/ \hbar} e^{-S_0[\mathbf{r}(\tau)]/\hbar} \\ &= \langle \exp([S - S_0]/\hbar) \rangle_{S_0} \cdot Z_{S_0}(\beta) \\ &\geq \exp(\langle S - S_0 \rangle_{S_0} / \hbar) \cdot Z_{S_0}(\beta). \end{aligned} \quad (2.86)$$

The average taken with positive weight S_0 is given by

$$\langle S - S_0 \rangle_{S_0} = [Z_{S_0}(\beta)]^{-1} \int_{\mathbf{r}(0)=0}^{\mathbf{r}(\hbar\beta)=0} D\mathbf{r}(\tau) (S - S_0) e^{-S_0[\mathbf{r}]/\hbar}, \quad (2.87)$$

where,

$$Z_{S_0}(\beta) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(\hbar\beta)=0} D\mathbf{r}(\tau) e^{-S_0[\mathbf{r}(\tau)]/\hbar}, \quad (2.88)$$

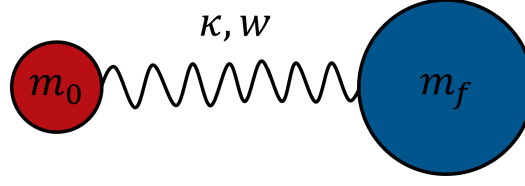


Figure 2.2: A schematic for Feynman's spring-mass model of an electron of mass m_0 coupled via a spring with frequency w and spring constant κ to a fictitious particle of mass m_f .

is the partition function for the system described by the trial action S_0 . Therefore, using the relation between the partition function and the ground-state energy, we obtain

$$\begin{aligned} E_{gs} &= \lim_{\beta \rightarrow \infty} \left[-\frac{1}{\beta} \ln Z(\beta) \right], \\ &\leq \lim_{\beta \rightarrow \infty} \left[-\frac{1}{\beta} \ln Z_{S_0}(\beta) - \frac{1}{\hbar\beta} \langle S - S_0 \rangle_{S_0} \right], \\ &\leq E_{gs}^0 - \lim_{\beta \rightarrow \infty} \left[\frac{1}{\hbar\beta} \langle S - S_0 \rangle_{S_0} \right], \end{aligned} \quad (2.89)$$

where E_{gs}^0 is the ground-state energy of the trial system.

2.2.3 Feynman's Quasi-Particle Trial Model

The next step is determining which trial action, S_0 , to use. Feynman proposed several trial actions.

His first suggestion corresponds to the free electron, $S_0 = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2(\tau)$, which gives the weak-coupling first-order perturbation method result by Fröhlich [3], $E_{gs} \leq -\hbar\omega_0\alpha$. His second choice was an electron in a local potential, $S_0 = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2(\tau) + \int_0^{\hbar\beta} d\tau V(\mathbf{r}(\tau))$. If this local-potential is Coulombic, $V(\mathbf{r}(\tau)) = Q/|\mathbf{r}(\tau)|$, with a variational charge-like parameter Q , one obtains Landau's variational result for strong-coupling [25], $E_{gs} \leq -0.098\hbar\omega_0\alpha^2$. Instead, if the local-potential is harmonic, $V(\mathbf{r}(\tau)) = \frac{1}{2}\kappa\mathbf{r}^2(\tau)$, with a variational spring-constant parameter κ , then the upper-bound is improved to $E_{gs} \leq -0.106\hbar\omega_0\alpha^2$. However, Fröhlich and Feynman concluded that binding the electron to a position using a local potential would only give worse results at low couplings than for a free electron [2].

To obtain a method that works over the entire range of α , Feynman proposed coupling the electron to some fictitious particle with finite mass so that the electron is not bound to a position and is free to move. Motivated by the harmonic local potential outperforming the Coulombic local potential and the comparative ease in corresponding derivation, Feynman chose to couple the electron and fictitious particle with a harmonic spring. The Hamiltonian

for this harmonic spring-mass system is [68]

$$H_F = \frac{\mathbf{p}_{\text{el}}^2}{2m_0} + \frac{\mathbf{p}^2}{2m_f} + \frac{\kappa}{2}(\mathbf{r} - \mathbf{x})^2, \quad (2.90)$$

where $\mathbf{p}_{\text{el}}$ and $\mathbf{p}$ are the momentum of the electron and fictitious particle, m_0 and m_f are their masses, $\mathbf{r}$ and $\mathbf{x}$ their positions, and κ is the spring-constant. The Feynman polaron quasi-particle thus has a direct mechanistic interpretation as depicted in Fig. 2.2.

The corresponding Lagrangian is obtained from the Legendre transformation and is given by

Feynman's Spring-Mass Lagrangian

$$L = \frac{m_0}{2} \dot{\mathbf{r}}(t)^2 + \frac{m_f}{2} \dot{\mathbf{x}}(t)^2 - \frac{\kappa}{2} (\mathbf{r}(t) - \mathbf{x}(t))^2. \quad (2.91)$$

Following the same procedure as we did for deriving Feynman's effective Fröhlich action in Eq. (2.83), we find that the effective trial action corresponds to the replacement

$$-\frac{\alpha \hbar r_0 \omega_0}{2\sqrt{2}} \frac{D_{\omega_0}(\tau - \sigma)}{|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|} \longrightarrow \frac{\kappa w}{8} D_w(\tau - \sigma) [\mathbf{r}(\tau) - \mathbf{r}(\sigma)]^2, \quad (2.92)$$

where κ and w are now variational parameters and $D_w(\tau)$ is the same phonon Green function (Eq. (2.2.1)) in imaginary-time, but with the replacement $\omega_0 \rightarrow w$.

The trial action is then,

Feynman's Polaron Trial Action

$$S_0 = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \left(\frac{d\mathbf{r}(\tau)}{d\tau} \right)^2 + \frac{\kappa w}{8} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma D_w(\tau - \sigma) [\mathbf{r}(\tau) - \mathbf{r}(\sigma)]^2. \quad (2.93)$$

2.2.4 The Variational Ground State Energy

As we will see later in this subsection, the expectations $\langle S \rangle_{S_0}$ and $\langle S_0 \rangle_{S_0}$ result in a double integral over the imaginary-time variables τ and σ over some function $f(|\tau - \sigma|)$, where the limits of integration are from 0 to $\hbar\beta$. The double integral covers redundant regions since the integrand depends only on the absolute difference $|\tau - \sigma|$. Specifically, when $\tau \geq \sigma$, the integrand is the same as when $\sigma \geq \tau$ due to the absolute value. This allows us to reduce the integration domain to a triangular region while multiplying the result by a

factor of 2,

$$\begin{aligned} \frac{1}{\hbar\beta} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\sigma f(|\tau - \sigma|) &= \frac{2}{\hbar\beta} \int_0^{\hbar\beta} d\tau (\hbar\beta - \tau) f(|\tau|) \\ &\sim 2 \int_0^{\hbar\beta} d\tau f(\tau) \quad (\text{as } \beta \rightarrow \infty). \end{aligned} \quad (2.94)$$

The double integral reduces to a single integral over τ , and the factor $(\hbar\beta - \tau)$ appears as a result of the remaining integration over σ , which runs from τ to $\hbar\beta$. The factor of 2 compensates for the reduction in the integration domain.

Therefore, we may write the expectations values $\langle S \rangle_{S_0}$ and $\langle S_0 \rangle_{S_0}$ in Eq. (2.89) as

$$\lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S \rangle_{S_0} = -\frac{\alpha \hbar r_0 \omega_0^2}{\sqrt{2}} \int_0^\infty d\tau D_{\omega_0}(\tau) \left\langle |\mathbf{r}(\tau) - \mathbf{r}(0)|^{-1} \right\rangle_{S_0}, \quad (2.95a)$$

$$\lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S_0 \rangle_{S_0} = \frac{\kappa w}{4} \int_0^\infty d\tau D_w(\tau) \left\langle [\mathbf{r}(\tau) - \mathbf{r}(0)]^2 \right\rangle_{S_0}. \quad (2.95b)$$

To solve $\langle S \rangle_{S_0}$ and $\langle S_0 \rangle_{S_0}$ we concentrate on the $|\mathbf{r}(\tau) - \mathbf{r}(0)|^{-1}$ term in $\langle S \rangle_{S_0}$ and express it by a Fourier transform,

$$\begin{aligned} |\mathbf{r}(\tau) - \mathbf{r}(0)|^{-1} &= 4\pi \int \frac{d^3 \mathbf{q}}{(2\pi)^3} \frac{1}{q^2} e^{i\mathbf{q} \cdot [\mathbf{r}(\tau) - \mathbf{r}(0)]} \\ &\equiv \int \frac{d^3 \mathbf{q}}{2\pi^2} \frac{1}{q^2} \exp \left(\int_0^\infty dt \mathbf{J}_{\mathbf{q},\tau}(t) \cdot \mathbf{r}(t) \right), \end{aligned} \quad (2.96)$$

where we have defined an ‘external force’ (a ‘source’ term) function $\mathbf{J}_{\mathbf{q},\tau}(t) = i\mathbf{q} [\delta(t - \tau) - \delta(t)]$.

Substituting this into $\langle S \rangle_{S_0}$ gives

$$\lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S \rangle_{S_0} = -\frac{\alpha \hbar r_0 \omega_0^2}{\sqrt{2}} \int_0^\infty d\tau D_{\omega_0}(\tau) \int \frac{d^3 \mathbf{q}}{2\pi^2} \frac{1}{q^2} Z[\mathbf{J}_{\mathbf{q},\tau}(t)] \quad (2.97)$$

where,

$$Z[\mathbf{J}_{\mathbf{q},\tau}(t)] \equiv \left\langle \exp \left(\int_0^\infty dt \mathbf{J}_{\mathbf{q},\tau}(t) \cdot \mathbf{r}(t) \right) \right\rangle_{S_0}, \quad (2.98)$$

is the generating functional. In statistical mechanics, a generating functional encodes the statistical properties of a system by incorporating an external source, allowing for the systematic computation of correlation functions and other observables through functional differentiation. It is a powerful tool to derive quantities like moments and cumulants in systems with many degrees of freedom.

For example, we can use the generating functional to calculate $\langle S_0 \rangle_{S_0}$ too by differentiating $Z[\mathbf{J}_{\mathbf{q},\tau}(t)]$ twice with respect to $\mathbf{q}$ and then setting $\mathbf{q} = \mathbf{0}$,

$$\lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S_0 \rangle_{S_0} = \frac{\kappa w}{4} \int_0^\infty d\tau D_w(\tau) \left(-\nabla_{\mathbf{q}}^2 Z[\mathbf{J}_{\mathbf{q},\tau}(t)] \Big|_{\mathbf{q}=\mathbf{0}} \right). \quad (2.99)$$

We need the ground-state energy E_{gs}^0 associated with the trial system. We can avoid directly evaluating the path integral Z_{S_0} by noting that the partition function and ground state energy are functions of the spring-constant, κ ,

$$\lim_{\beta \rightarrow \infty} Z_{S_0}(\beta, \kappa) = e^{-\beta E_{gs}^0(\kappa)} = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(\hbar\beta)=\mathbf{0}} D\mathbf{r}(\tau) \exp\left(-\frac{S_0[\mathbf{r}(\tau)]}{\hbar}\right). \quad (2.100)$$

So, we can use the “coupling constant trick” where we differentiate both sides with respect to κ ,

$$\frac{\partial E_{gs}^0}{\partial \kappa} = \frac{1}{\kappa} \lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S_0 \rangle_{S_0} \quad (2.101)$$

and then integrate both sides to give,

$$E_{gs}^0 = \int_0^\kappa dk' \frac{1}{k'} \lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S_0(k') \rangle_{S_0}. \quad (2.102)$$

The constant of integration is zero because $E_{gs}^0 = 0$ when $\kappa = 0$ (i.e. the free particle).

Therefore, solving for the upper-bound to the ground-state energy has been reduced to solving $Z[\mathbf{J}_{\mathbf{q},\tau}(t)]$, which, written explicitly, is,

$$Z[\mathbf{J}_{\mathbf{q},\tau}(t)] = \frac{\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(\hbar\beta)=\mathbf{0}} D\mathbf{r}(\tau) \exp\left(-\frac{S_0}{\hbar} + \int_0^\infty dt \mathbf{J}_{\mathbf{q},\tau}(t) \cdot \mathbf{r}(t)\right)}{\int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(\hbar\beta)=\mathbf{0}} D\mathbf{r}(\tau) \exp\left(-\frac{S_0}{\hbar}\right)}. \quad (2.103)$$

We can solve the path integral in the numerator by the usual method of changing the path-integration variable to $\mathbf{r}'(\tau) \equiv \mathbf{r}(\tau) - \bar{\mathbf{r}}(\tau)$ where $\bar{\mathbf{r}}(\tau)$ is the path that extremises the trial action S_0 and with the boundary conditions $\bar{\mathbf{r}}(0) = \bar{\mathbf{r}}(\hbar\beta) = 0$. Thus, $\bar{\mathbf{r}}(\tau)$ contributes most to the path integral and is the classical path, whereas $\mathbf{r}'(\tau)$ are the ‘quantum fluctuations’ about the classical path. The path integral now only contains $\bar{\mathbf{r}}(\tau)$ quadratically, which then separates off as a normalisation factor that excludes the force term $\mathbf{J}_{\mathbf{q},\tau}(t)$ and is equal to the denominator (i.e. the trial partition function $Z_{S_0}(\beta)$), so it cancels. This methodology is further explained in Appendix A and demonstrated on simple systems like the free particle and harmonic oscillator.

Now, $\bar{\mathbf{r}}(\tau)$ solves the classical equation of motion that is obtained by extremising the trial action S_0 and gives the following integral-differential equation of motion,

$$\frac{d^2 \bar{\mathbf{r}}(t)}{dt^2} = \frac{\kappa w}{2} \int_0^\infty ds D_w(t-s) [\bar{\mathbf{r}}(t) - \bar{\mathbf{r}}(s)] - J_{\mathbf{q},\tau}(t), \quad (2.104)$$

which can be used to simplify $Z[J_{\mathbf{q},\tau}(t)]$ by eliminating the classical action term $S_0[\bar{\mathbf{r}}]$ to leave,

$$Z[J_{\mathbf{q},\tau}(t)] = \exp \left(\frac{1}{2} \int_0^\infty dt J_{\mathbf{q},\tau}(t) \cdot \bar{\mathbf{r}}(t) \right). \quad (2.105)$$

Now, all that is left is to solve the equation of motion to find the classical path $\bar{\mathbf{r}}(t)$. This can be done by first defining,

$$\mathbf{x}(t) \equiv \frac{w}{2} \int_0^\infty ds D_w(t-s) \bar{\mathbf{r}}(s). \quad (2.106)$$

Since $d|t-s|/dt = \text{sgn}(t-s)$ and $d \text{sgn}(t-s)/dt = 2\delta(t-s)$, we have,

$$\frac{d^2 \mathbf{x}(t)}{dt^2} = w^2 [\mathbf{x}(t) - \bar{\mathbf{r}}(t)], \quad (2.107)$$

and

$$\frac{d^2 \bar{\mathbf{r}}(t)}{dt^2} = \kappa [\bar{\mathbf{r}}(t) - \mathbf{x}(t)] - J_{\mathbf{q},\tau}(t), \quad (2.108)$$

where in the second equation and in the limit $\beta \rightarrow \infty$ we obtain the term,

$$\int_0^\infty ds D_w(t-s) = \int_0^\infty ds e^{-w|t-s|} = \frac{2}{w} - \frac{e^{-wt}}{w}, \quad t \in [0, \infty) \quad (2.109)$$

and we neglect the second transient term since it makes a negligible contribution. These differential equations can be separated and solved to give the classical path as,

$$\bar{\mathbf{r}}(t) = \int_0^\infty ds g(t-s) J_{\mathbf{q},\tau}(t), \quad (2.110)$$

where,

$$\begin{aligned} g(t-s) &= \frac{1}{2\pi} \oint dz \frac{z^2 + w^2}{z^2 (z^2 + v^2)} \left(e^{-z|t-s|} - 1 \right) \\ &= i \left[\frac{1}{2} \text{Res}(z=0) + \text{Res}(z=iv) \right] \\ &= -\frac{1}{2v^2} \left[\frac{v^2 - w^2}{v} \left(1 - e^{-v|t-s|} \right) + w^2 |t-s| \right], \end{aligned} \quad (2.111)$$

where Res is the residue, and $v^2 \equiv w^2 + \kappa = (1 + M/m_0)w^2$.

Substituting the solution for $\bar{\mathbf{r}}(t)$ into $Z[J_{\mathbf{q},\tau}(t)]$ then gives,

$$Z[J_{\mathbf{q},\tau}(t)] = \exp \left(\frac{1}{2} \int_0^{\hbar\beta} dt \int_0^{\hbar\beta} ds J_{\mathbf{q},\tau}(t) \cdot g(t-s) \cdot J_{\mathbf{q},\tau}(s) \right). \quad (2.112)$$

For $\mathbf{J}_{\mathbf{q},\tau}(t) = i\mathbf{q} [\delta(t-\tau) - \delta(t)]$ this reduces to

$$Z[J_{\mathbf{q},\tau}(t)] = \exp \left(r_0^2 \mathbf{q}^2 g(\tau - \sigma) \right). \quad (2.113)$$

We can use substitute this solution for $Z[J_{\mathbf{q},\tau}(t)]$ into Eq. (2.97) to determine $\langle S \rangle_{S_0}$,

$$\lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S \rangle_{S_0} = -\frac{\alpha \hbar \omega_0^2}{\sqrt{\pi}} \int_0^\infty d\tau \frac{e^{-\tau \omega_0}}{\sqrt{G(\tau)}}, \quad (2.114)$$

where,

$$G(\tau) = -2g(\tau) = \frac{w^2}{v^2} \tau + \frac{v^2 - w^2}{v^3} (1 - e^{-v\tau}), \quad (2.115)$$

and also into Eqs. (2.99) & (2.102) to determine $\langle S_0 \rangle_{S_0}$ and E_{gs}^0 ,

$$\lim_{\beta \rightarrow \infty} \frac{1}{\beta} \langle S_0 \rangle_{S_0} = -\frac{3\hbar\kappa}{4v} = -\frac{3}{4}\hbar \frac{v^2 - w^2}{v}, \quad (2.116)$$

$$E_{gs}^0 = \frac{3}{2}\hbar(v - w). \quad (2.117)$$

Finally, inserting these solutions for $\langle S \rangle_{S_0}$, $\langle S_0 \rangle_{S_0}$ and E_{gs}^0 into the variational principle (Eq. (2.89)) gives us the ground-state energy of the polaron,

Variational Polaron Ground-State Energy

$$E_{gs} \leq \frac{3\hbar}{4v} (v - w)^2 - \alpha \hbar \omega_0^2 \sqrt{\frac{1}{\pi}} \int_0^\infty d\tau \frac{e^{-\tau \omega_0}}{\sqrt{G(\tau)}}. \quad (2.118)$$

Here, v and w are to be varied to find the lowest approximate upper bound to the exact ground-state E_{gs} .

In terms of these variational parameters, the quasiparticle spring constant is $\kappa = v^2 - w^2$, and the fictitious mass is $m_f = (v^2 - w^2)/w^2$.

2.2.5 Weak- and strong- coupling limits

The original work of Feynman [2] provides several asymptotic estimates of this w parameter. The standard approximations often reproduced in textbooks are $w = 3$ for small α coupling and $w = 1$ for large α coupling.

Precise work requires a numerical solution, but these limits inform us that the internal polaron mode, as a function of electron-phonon coupling, starts as a harmonic of $3\omega_0$ and continuously red-shifts to the phonon fundamental frequency ω_0 .

For extremal values of the coupling α , w smoothly approaches limits of 1 and 3.

In the weak-coupling (small α) limit, the energy minimum occurs when v is near w . Therefore, Feynman set $v = (1 + \varepsilon)w$ where ε is small and expanded the energy expression (RHS of Eq. (2.118)) with respect to ε . Feynman then minimised the energy first with respect to ε , and then w . He found that in the weak-coupling limit, the energy is least when,

$$\begin{aligned} \frac{w}{\omega_0} &= 3, \quad \frac{v}{\omega_0} = 3 \left[1 + \frac{2\alpha}{3w} \left(1 - \frac{2}{w} \left[\sqrt{w-1} - 1 \right] \right) \right], \\ \frac{E_{gs}}{\hbar\omega_0} &\leq -\alpha - \left(\frac{\alpha}{9} \right)^2 - \mathcal{O}(\alpha^4) \approx -\alpha - 0.0123\alpha^2 - \mathcal{O}(\alpha^4). \end{aligned} \quad (2.119)$$

The result agrees well with the perturbative result [69] E_{gs}^w ,

$$\frac{E_{gs}^w}{\hbar\omega_0} = -\alpha - 0.0159196220\alpha^2 - 0.000806070048\alpha^3 - \mathcal{O}(\alpha^4). \quad (2.120)$$

In the strong-coupling (large α) limit, v is large, and w approaches one, so $w/v \ll 1$. Therefore, Feynman expanded the energy expression with respect to w/v and then minimised the energy with respect to v and w and found that in the strong-coupling limit the energy is least when,

$$\begin{aligned} \frac{w}{\omega_0} &= 1, \quad \frac{v}{\omega_0} = \frac{4\alpha^2}{9\pi} - 4 \left(\log 2 + \frac{1}{2}\gamma \right) + 1, \\ \frac{E_{gs}}{\hbar\omega_0} &\leq -\frac{\alpha^2}{2\pi} - \frac{3}{2}(2\log 2 + \gamma) - \frac{3}{4} + \mathcal{O}\left(\frac{1}{\alpha^2}\right) \approx -0.1061\alpha - 2.8294 + \mathcal{O}\left(\frac{1}{\alpha^2}\right), \end{aligned} \quad (2.121)$$

where $\gamma = 0.5772 \dots$ is the Euler-Mascheroni constant.

This is reasonable when compared to the result of the exact strong-coupling expansion [70] E_{gs}^s ,

$$\frac{E_{gs}^s}{\hbar\omega_0} = -0.108513\alpha^2 - 2.836 - \mathcal{O}\left(\frac{1}{\alpha^2}\right) \quad (2.122)$$

obtained from perturbation theory.

2.2.6 Feynman's polaron effective mass

Feynman found the effective polaron mass at zero temperature [2] by assuming that the electron moves with a small velocity $\mathbf{v}$ from an initial coordinate $\mathbf{r}(0) = \mathbf{0}$ to a final

coordinate $\mathbf{r}(\hbar\beta) = \mathbf{v}\hbar\beta$ in imaginary-time $\hbar\beta$. Feynman then sought the total energy of the polaron and equated it to the form $E_0 + \frac{1}{2}Mv^2$ by expanding the expression of the total energy to quadratic order in the velocity $\mathbf{v}$. From the kinetic energy term, Feynman defines the polaron effective mass,

The Polaron Effective Mass

$$M = m_0 \left[1 + \frac{\alpha\omega_0^3}{3\sqrt{\pi}} \int_0^\infty d\tau \frac{\tau^2 e^{-\tau\omega_0}}{[G(\tau)]^{3/2}} \right]. \quad (2.123)$$

Here, the variational parameter values minimise the polaron ground-state energy when $\mathbf{v} = 0$ in Eq. (2.118). From the values in Eq. (2.119) Feynman obtained the weak-coupling expression,

$$M = m_0 \left[1 + \frac{\alpha}{6} + 2.469136 \left(\frac{\alpha}{10} \right)^2 + 3.566719 \left(\frac{\alpha}{10} \right)^3 + \dots \right], \quad (2.124)$$

and from the values in Eq. (2.121) the strong-coupling expression,

$$\begin{aligned} M &\approx m_0 \left[11.85579 - \frac{4}{3\pi}(1 + \ln 4)\alpha^2 + \frac{16}{81\pi^2}\alpha^4 \dots \right], \\ &\approx m_0 \left[11.85579 - 1.012775\alpha^2 + 0.020141\alpha^4 + \dots \right]. \end{aligned} \quad (2.125)$$

For comparison, the exact weak-coupling mass is [71],

$$M_w = m_0 \left[1 + \frac{\alpha}{6} + 2.362763 \left(\frac{\alpha}{10} \right)^2 + O(\alpha^4) \right], \quad (2.126)$$

and the exact strong-coupling result is [70],

$$M_s = m_0 \left[0.0227019\alpha^4 + O(\alpha^2) \right]. \quad (2.127)$$

Alternatively, in 1959 [31] Schultz defined the ‘zeroth-order’ effective mass in his early computational evaluation,

The ‘Zeroth-Order’ Polaron Effective Mass

$$M = m_0 + m_f = m_0 \left(\frac{v}{w} \right)^2, \quad (2.128)$$

which is obtained by approximating the model action S with the trial S_0 ; no higher-order expansion terms are included.

At finite temperatures, the effective polaron mass (as described by Peeters et al. [72]) is proportional to the imaginary part of the complex impedance function $Z(\Omega, \beta)$ provided by FHIP [17] (Eqs. (35), (36) & (41)) in the zero frequency limit $\Omega \rightarrow 0$,

$$M(\beta) = em_0 \lim_{\Omega \rightarrow 0} \left\{ \frac{\text{Im}Z(\Omega, \beta)}{\Omega} \right\}. \quad (2.129)$$

2.2.7 Schultz's polaron effective size

Schultz [31] estimated the polaron size by calculating the root mean square distance between the electron and the fictitious particle. The reduced mass of their relative motion is

$$\mu_0 = \frac{m_f m_0}{m_f - m_0}. \quad (2.130)$$

Schultz then used the ground-state harmonic oscillator wavefunction for the relative coordinate $\Delta r = \mathbf{r} - \mathbf{x}$ between the electron and the fictitious mass,

$$\phi_0(\Delta r) = \left(\frac{\mu_0 v}{\pi m_0 \omega_0 r_0^2} \right)^{3/4} \exp \left(-\frac{\mu_0 v \Delta r^2}{2 m_0 \omega_0 r_0^2} \right), \quad (2.131)$$

to define a polaron radius as the root mean square distance between the electron and the fictitious mass,

$$R \equiv \langle \Delta r^2 \rangle^{\frac{1}{2}} = \frac{r_0}{2} \left(\frac{3 m_0 \omega_0}{\mu_0 v} \right)^{\frac{1}{2}} = \frac{r_0}{2} \left(\frac{3 \omega_0 v}{(v^2 - w^2)} \right)^{\frac{1}{2}}. \quad (2.132)$$

The same result for the polaron radius is obtained from the density matrix for the trial action S_0 without any higher-order corrections from the model action S .

In the weak-coupling limit, with v and w given in Eq. (2.119), this expression for the polaron radius reduces to,

$$\frac{R}{r_0} \sim \frac{3}{4} \sqrt{\frac{6}{\alpha}}, \quad (2.133)$$

and in the strong-coupling limit (Eq. (2.121)) the radius becomes,

$$\frac{R}{r_0} \sim \frac{3\sqrt{\pi}}{2\alpha}. \quad (2.134)$$

2.2.8 Generalisation to n dimensions

The form of the Fröhlich Hamiltonian in n dimensions was obtained by Peeters et al. [40] and is the same as in 3D, except that all the vectors will be n -dimensional and the Fröhlich electron-phonon coupling matrix $M_{\mathbf{q}}$ is different, as it is proportional to the Fourier

transform of the n -dimensional generalisation of the Coulomb potential,

$$|M_{\mathbf{q}}|^2 = \frac{1}{V_n} \frac{|M_n|^2}{q^{n-1}}, \quad (2.135)$$

where V_n is the n -dimensional unit-cell volume of the crystal and the coefficient M_n is

$$M_n = i\hbar\omega_0 \left(\alpha r_0 \Gamma \left(\frac{n-1}{2} \right) (2\sqrt{\pi})^{n-1} \right)^{\frac{1}{2}}, \quad (2.136)$$

with α the usual Fröhlich dimensionless electron-phonon coupling and $\Gamma(x)$ the Gamma function. This definition shows that the electron-phonon matrix diverges in 1D as $\lim_{x \rightarrow 0} \Gamma(x) \rightarrow \infty$. Due to the new scaling for the phonon wave-vector, $\mathbf{q}$, any summation or integrals over $\mathbf{q}$ will be of the general form (assuming a dispersionless phonon frequency $\omega_{\mathbf{q}} = \omega_0$),

$$\sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \bullet_q \rightarrow |M_n|^2 \int \frac{d^n \mathbf{q}}{(2\pi)^n} \frac{1}{q^{n-1}} \bullet_q, \quad (2.137)$$

where $\bullet_q$ are any other $|\mathbf{q}| = q$ -dependent terms in the integrand. Note that the volume terms have been cancelled. To solve equations of this type, we transform the integral to spherical coordinates,

$$|M_n|^2 \int \frac{d^n \mathbf{q}}{(2\pi)^n} \frac{1}{q^{n-1}} \bullet_q = \frac{|M_n|^2}{(2\pi)^n} \int_S dS \int_0^\infty dq q^{3-n} \bullet_q, \quad (2.138)$$

where $\int_S dS$ denotes the integral over the surface $\mathcal{S}$ of an n -dimensional ball; an $(n-1)$ -sphere. Assuming the integrand contains no angle-dependent terms (i.e. the integrand only depends on $|\mathbf{q}| = q$), this integral is

$$\begin{aligned} \frac{|M_n|^2}{(2\pi)^n} \int_S dS \int_0^\infty dq q^{3-n} \bullet_q &= |M_n|^2 \frac{S_{n-1}}{(2\pi)^n} \int_0^\infty dq q^{3-n} \bullet_q \\ &= \frac{2|M_n|^2}{\Gamma\left(\frac{n}{2}\right) (2\sqrt{\pi})^n} \int_0^\infty dq q^{3-n} \bullet_q, \end{aligned} \quad (2.139)$$

where $S_{n-1} = 2\pi^{n/2}/\Gamma(\frac{n}{2})$ is the surface area of the unit $(n-1)$ -sphere of radius 1.

In the Feynman variational approach, these q -space integrals typically have $\bullet_q = q^{2m} e^{-q^2 G}$ where m is zero or some positive integer and G is the trial polaron Green function in Eq. (2.115).

Therefore, all q -space integrals in the FVA to the n -dimensional Fröhlich model are typically of the form,

$$\begin{aligned} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^{2m} e^{-q^2 G} &\rightarrow |M_n|^2 \frac{S_{n-1}}{(2\pi)^n} \int_0^\infty dq q^{3+2m-n} e^{-q^2 G} \\ &= \frac{1}{2} |M_n|^2 \frac{S_{n-1}}{(2\pi)^n} \Gamma\left(2+m-\frac{n}{2}\right) G^{\frac{n}{2}-m-2} \\ &= \frac{|M_n|^2}{(2\sqrt{\pi})^n} \frac{\Gamma(2+m-n/2)}{\Gamma(n/2)} G^{\frac{n}{2}-m-2}. \end{aligned} \quad (2.140)$$

In summary, these q -space integrals, in the Feynman variational approach to the n -dimensional Fröhlich model, are

General q -space Integrals for the FVA to the Fröhlich Model

$$\sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 (qr_0)^{2m} e^{-q^2 r_0^2 G} \rightarrow \frac{\hbar^2 \omega_0^2 \alpha r_0^{n-3}}{2\sqrt{\pi}} \frac{\Gamma(2+m-n/2) \Gamma(n/2-1/2)}{\Gamma(n/2)} G^{\frac{n}{2}-m-2}, \quad (2.141)$$

with G the polaron trial Green function, n the number of dimensions and m zero or some positive integer. For example, in the variational equation for the polaron energy (Eq. (2.118)) $m = 0$, for the effective mass calculation (Eq. (2.123)) and later during the polaron mobility calculation (see Eq. (2.204)) $m = 2$, reflecting the q -dependence of these different polaron quantities.

From this n -dimensional formalism, one can derive scaling relations between n -dimensions and the standard 3D theory for the Fröhlich polaron energy E_n , effective mass M_n , memory function Σ_n (see Eq. (2.203)) and mobility μ_n (see Eq. (2.212)) [41],

Polaron Scaling Relations

$$E_n(\alpha) = \frac{n}{3} E_3(A_n \alpha), \quad (2.142a)$$

$$M_n(\alpha) = M_3(A_n \alpha), \quad (2.142b)$$

$$\Sigma_n(\alpha) = \Sigma_3(A_n \alpha), \quad (2.142c)$$

$$\mu_n(\alpha) = \mu_3(A_n \alpha), \quad (2.142d)$$

where A_n is,

$$A_n = \frac{3\sqrt{\pi}}{2n} \frac{\Gamma(n/2-1/2)}{\Gamma(n/2)}. \quad (2.143)$$

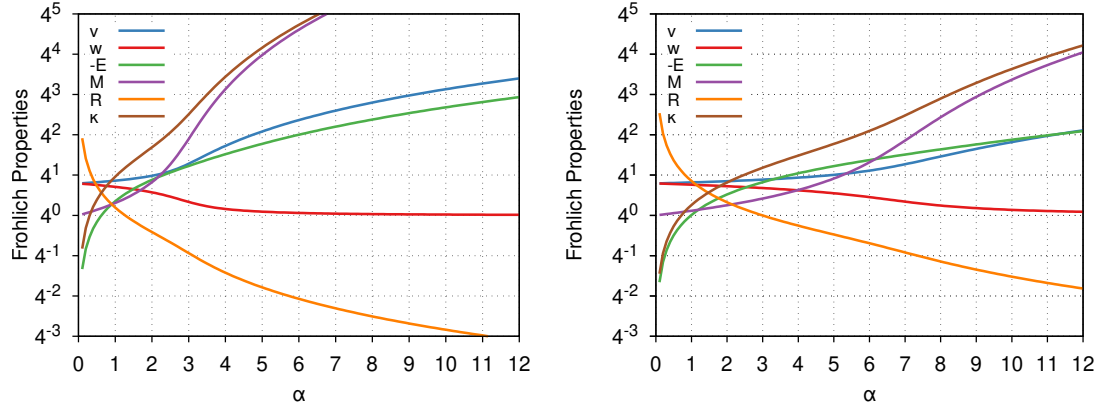


Figure 2.3: Electron-phonon coupling dependence of the Feynman athermal polaron theory in 2D (left) and 3D (right) in polaron units. Green: the negative of the variationally optimal ground-state energy E (units of $\hbar\omega_0$). Purple: the polaron effective mass M (units of m_0). Blue: the v (units of ω_0) variational parameter. Red: the w (units of ω_0) variational parameter. Orange: the polaron size R (units of r_0). Brown: the polaron spring-constant κ (units of $m_0\omega_0^2$).

2.2.9 Athermal FVA Numerical Results

Using our codes [11], we find the variational solution to Eq. (2.118) for the 2D and 3D Fröhlich model. Fig. 2.3 shows the values of the polaron ground-state energy $-E$ (units $\hbar\omega_0$) (Eq. (2.118)), effective mass M (units m_0) (Eq. (2.130)), radius R (units r_0) (Eq. (2.132)), spring-constant $\kappa = v^2 - w^2$ (units $m_0\omega_0^2$) and the corresponding variational v (units ω_0) and w (units ω_0) parameters, for the 2D (left) and 3D (right) Fröhlich model for α ranging from 0 to 12. These polaron properties are all presented in their ‘polaron units’ form ($\bullet_0$) for easier comparison to Feynman’s original paper. The magnitude of the ground state energy starts at zero for zero coupling before a linear increase at weak coupling and then increases quadratically at large coupling. The effective mass starts roughly equal to the conduction electron band-mass $M = m_0$ at small α and then grows exponentially larger at stronger couplings. The v and w variational parameters start as approximately equal with $v \approx w = 3\omega_0$ at weak couplings but diverge at strong couplings as w asymptotically approaches $w = \omega_0$, and v increases quadratically in α at a similar rate to the ground-state energy. Aside from the overall dimension-dependent scaling constant on the ground-state energy, the main difference between the 2D and 3D Fröhlich models is the value of α for which the polaron transitions from weak to strong coupling. In 3D, this occurs around $\alpha \approx 6$, whereas in 2D, it is $\alpha \approx 6/(3\pi/4) \approx 2.55$ as determined by the scaling relations in Eq. (2.142).

2.2.10 Finite Temperature Polaron

In 1959 [27], Ōsaka extended Feynman’s athermal path integral polaron model to finite temperature. This means that the variational principle for the ground-state energy of the

polaron is replaced by the variation of the *free energy*. Ōsaka begins with the density matrix of the polaron system with the model action of the polaron at a finite temperature given by

$$S = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2(\tau) - \frac{\alpha \hbar r_0 \omega_0^2}{2\sqrt{2}} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma \frac{D_{\omega_0}(\tau - \sigma)}{|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|}. \quad (2.144)$$

Ōsaka then chose the trial action to be

$$S_0 = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2(\tau) + \frac{\kappa w}{8} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma D_w(\tau - \sigma) |\mathbf{r}(\tau) - \mathbf{r}(\sigma)|^2, \quad (2.145)$$

where $D_w(\tau)$ is the phonon Green function (Eq. (2.2.1)) with frequency w . The model and trial density matrices are then,

$$\rho_S(\mathbf{r}_f, \mathbf{r}_i; \hbar\beta) = \int_{\mathbf{r}(0)=\mathbf{r}_i}^{\mathbf{r}(\hbar\beta)=\mathbf{r}_f} D\mathbf{r}(\tau) \exp\left(-\frac{S[\mathbf{r}(\tau)]}{\hbar}\right), \quad (2.146a)$$

$$\rho_{S_0}(\mathbf{r}_f, \mathbf{r}_i; \hbar\beta) = \int_{\mathbf{r}(0)=\mathbf{r}_i}^{\mathbf{r}(\hbar\beta)=\mathbf{r}_f} D\mathbf{r}(\tau) \exp\left(-\frac{S_0[\mathbf{r}(\tau)]}{\hbar}\right). \quad (2.146b)$$

The variational principle for finite temperature is

$$\rho_S(\mathbf{r}_f, \mathbf{r}_i; \hbar\beta) \geq \rho_{S_0}(\mathbf{r}_f, \mathbf{r}_i; \hbar\beta) \exp\left(\frac{\langle S - S_0 \rangle_{S_0}}{\hbar}\right), \quad (2.147)$$

where,

$$\langle S - S_0 \rangle_{S_0} = \frac{\int_{\mathbf{r}(0)=\mathbf{r}_i}^{\mathbf{r}(\hbar\beta)=\mathbf{r}_f} D\mathbf{r}(\tau) (S[\mathbf{r}(\tau)] - S_0[\mathbf{r}(\tau)]) \exp\left(-\frac{S_0[\mathbf{r}(\tau)]}{\hbar}\right)}{\rho_{S_0}(\mathbf{r}_f, \mathbf{r}_i; \hbar\beta)}. \quad (2.148)$$

The RHS of the variational equation then has to be calculated and minimised with respect to the variational parameters κ and w . The equation of motion obtained from the trial action S_0 is

$$\begin{aligned} m_0 \ddot{\mathbf{r}}(\tau) &= \frac{\kappa w}{2} \int_0^{\hbar\beta} d\sigma D_w(\tau - \sigma) [\mathbf{r}(\tau) - \mathbf{r}(\sigma)] \\ &= \kappa \mathbf{r}(\tau) - \frac{\kappa w}{2} \int_0^{\hbar\beta} d\sigma D_w(\tau - \sigma) \mathbf{r}(\sigma), \end{aligned} \quad (2.149)$$

which we can use with the boundary conditions $\mathbf{r}(\hbar\beta) = \mathbf{r}_f$ and $\mathbf{r}(0) = \mathbf{r}_i$ to give the trial density matrix,

$$\rho_{S_0}(\mathbf{r}_i, \mathbf{r}_f; \hbar\beta) = Z_{\text{ph}} \exp\left\{-\frac{m_0}{2\hbar} (\mathbf{r}(\hbar\beta) \cdot \dot{\mathbf{r}}(\hbar\beta) - \mathbf{r}(0) \cdot \dot{\mathbf{r}}(0))\right\}, \quad (2.150)$$

where $Z_{\text{ph}} = \left(2 \sinh \left(\frac{\hbar\beta w}{2}\right)\right)^{-3}$ is the free phonon partition function.

As the trial density matrix is quadratic in the harmonic oscillator coordinates, it is determined entirely by the classical path.

Now, directly solving for $\mathbf{r}(\tau)$ from the equation of motion is difficult, so instead Ōsaka considered a system with a different Lagrangian L' ,

$$L' = \frac{1}{2} \left(m_0 \dot{\mathbf{r}}^2 + M \dot{\mathbf{x}}^2 - \kappa (\mathbf{r} - \mathbf{x})^2 \right), \quad (2.151)$$

of a particle of mass m_0 coupled by a harmonic spring with a force constant κ to a particle of mass M . After integrating over the $\mathbf{R}$ coordinate, the density matrix ρ' of the Lagrangian L' is given by

$$\begin{aligned} \rho'(\mathbf{r}_i, \mathbf{r}_f; \hbar\beta) = Z_{\text{ph}} \int_{\mathbf{r}(0)=\mathbf{r}_i}^{\mathbf{r}(\hbar\beta)=\mathbf{r}_f} \exp \left[-\frac{1}{2\hbar} \int_0^{\hbar\beta} d\tau \left(m_0 \dot{\mathbf{r}}^2 + M w^2 \mathbf{r}^2 \right) \right. \\ \left. + \frac{\kappa w}{8\hbar} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma D_w(\tau - \sigma) \mathbf{r}(\tau) \mathbf{r}(\sigma) \right] D\mathbf{r}(\tau), \end{aligned} \quad (2.152)$$

where $w = \sqrt{\kappa/M}$. This new action has the same equation of motion as Feynman's choice of trial action S_0 (Eq. (2.93)),

$$m_0 \ddot{\mathbf{r}}(\tau) = \kappa \mathbf{r}(\tau) - \frac{\kappa w}{2} \int_0^{\hbar\beta} d\sigma D_w(\tau - \sigma) \mathbf{r}(\sigma), \quad (2.153)$$

which, under the classical path approximation, gives the density matrix

$$\rho'(\mathbf{r}_i, \mathbf{r}_f; \hbar\beta) = Z_{\text{ph}} \exp \left\{ -\frac{m_0}{2\hbar} \left(\mathbf{r}(\hbar\beta) \cdot \dot{\mathbf{r}}(\hbar\beta) - \mathbf{r}(0) \cdot \dot{\mathbf{r}}(0) \right) \right\}. \quad (2.154)$$

This means that the density matrix ρ' is the same as ρ , with the same equation of motion. Therefore, Ōsaka used the solution to the equation of motion in Eq. (2.153) to calculate the trial density matrix ρ_{S_0} where the trial action S_0 corresponds to the Lagrangian L' .

The key to calculating $\langle S - S_0 \rangle_{\mathbf{r}_i, \mathbf{r}_f}$ is to evaluate the generating functional $Z[J_{\mathbf{q}, \tau}(t)]$ in Eq. (2.103) using the same method Feynman used, except that Ōsaka replaced the trial action S_0 with that of L' and instead evaluated the path integral in the generating functional $Z[J_{\mathbf{q}, \tau}(t)]$ using the Lagrangian

$$L = \frac{m_0}{2} \dot{\mathbf{r}}^2 + \frac{m_f}{2} \dot{\mathbf{x}}^2 - \frac{\kappa}{2} (\mathbf{r} - \mathbf{x})^2 + \mathbf{J}_{\mathbf{q}, \tau, \sigma}(t) \cdot \mathbf{r}, \quad (2.155)$$

where $\mathbf{J}_{\mathbf{q},\tau,\sigma}(t) = i\mathbf{q} [\delta(t - \tau) - \delta(t - \sigma)]$ as before. This Lagrangian is evaluated by first doing a change of variables

$$\mathbf{x}' = \mathbf{r} - \mathbf{x}, \quad \mathbf{r}' = \frac{m_f}{m_0}\mathbf{x} + \frac{m_0}{m_f + m_0}\mathbf{r}, \quad (2.156)$$

to give

$$L = \frac{m_f + m_0}{2}\dot{\mathbf{r}}'^2 + \mu_0\dot{\mathbf{x}}'^2 - \frac{\kappa}{2}\mathbf{x}'^2 + \mu_0 \mathbf{J}_{\mathbf{q},\tau,\sigma}(t) \cdot \mathbf{x}' + m_0 \mathbf{J}_{\mathbf{q},\tau,\sigma}(t) \cdot \mathbf{r}'. \quad (2.157)$$

This gives equations of motion for $\mathbf{x}'$ and $\mathbf{r}'$,

$$\ddot{\mathbf{x}}' = v\mathbf{x}' - \frac{1}{m_0}\mathbf{J}_{\mathbf{q},\tau,\sigma}(t), \quad \ddot{\mathbf{r}}' = -\frac{1}{m_f + m_0}\mathbf{J}_{\mathbf{q},\tau,\sigma}(t), \quad (2.158)$$

where $v = \sqrt{\kappa/\mu_0}$ ($\mu_0 = m_fm_0/(m_f + m_0)$ is the reduced mass of the electron and fictitious mass) as defined by Feynman. Ōsaka showed that the solution for $\mathbf{x}'$ under the boundary conditions $\mathbf{x}'(0) = \mathbf{x}'_i$ and $\mathbf{x}'(\hbar\beta) = \mathbf{x}'_f$ is

$$\begin{aligned} \mathbf{x}'(t) = & \frac{\mathbf{x}'_i \sinh(v[\hbar\beta - t]) + \mathbf{x}'_f \sinh(vt)}{v \sinh(v\hbar\beta)} + i\mathbf{q} \sinh(vt) \frac{\sinh(v[\hbar\beta - \tau]) - \sinh(v[\hbar\beta - \sigma])}{v \sinh(v\hbar\beta)} \\ & - \frac{i\mathbf{q}}{v} \begin{cases} \sinh(v[t - \tau]) - \sinh(v[t - \sigma]) & t > \tau \\ -\sinh(v[t - \sigma]) & \sigma < t < \tau \\ 0 & t < \sigma, \end{cases} \end{aligned} \quad (2.159)$$

if $\tau > \sigma$, otherwise the conditional is,

$$\begin{cases} \sinh(v[t - \tau]) - \sinh(v[t - \sigma]) & t > \sigma \\ \sinh(v[t - \sigma]) & \sigma < t < \tau \\ 0 & t < \tau. \end{cases} \quad (2.160)$$

Under the boundary conditions $\mathbf{r}'(0) = \mathbf{r}'_i$ and $\mathbf{r}'(\hbar\beta) = \mathbf{r}'_f$ the solution for $\mathbf{r}'$ is

$$\mathbf{r}'(t) = \mathbf{r}'_i + \frac{v^2(\mathbf{r}'_f - \mathbf{r}'_i) - i\mathbf{q}w^2(\tau - \sigma)}{\hbar\beta v^2} - i\mathbf{q} \frac{w^2}{v^2} \left[\left(\begin{cases} t - \tau & t > \tau \\ 0 & t < \tau \end{cases} \right) - \left(\begin{cases} t - \sigma & t > \sigma \\ 0 & t < \sigma \end{cases} \right) \right]. \quad (2.161)$$

Using the equations of motion, Ōsaka obtains the generating functional,

$$\begin{aligned}
 Z[J_{\mathbf{q},\tau}(t)] = \exp & \left(-\frac{\mu_0}{2\hbar} [\mathbf{x}'(\hbar\beta) \cdot \dot{\mathbf{x}}'(\hbar\beta) - \mathbf{x}'(0) \cdot \dot{\mathbf{x}}'(0)] \right. \\
 & - \frac{m_f + m_0}{2\hbar} [\mathbf{r}(\hbar\beta) \cdot \dot{\mathbf{r}}(\hbar\beta) - \mathbf{r}(0) \cdot \dot{\mathbf{r}}(0)] \\
 & + \frac{\mu_0}{2\hbar} \int_0^{\hbar\beta} dt \mathbf{J}_{\mathbf{q},\tau,\sigma}(t) \cdot \mathbf{x}'(t) \\
 & \left. + \frac{m_0}{2\hbar} \int_0^{\hbar\beta} dt \mathbf{J}_{\mathbf{q},\tau,\sigma}(t) \cdot \mathbf{r}'(t) \right). \quad (2.162)
 \end{aligned}$$

Ōsaka connects this to the original action S by identifying $\mathbf{r}'_{i,f}$ and $\mathbf{x}'_{i,f}$ to $\mathbf{r}_{i,f}$ and $\mathbf{x}_{i,f}$ respectively using the relations in Eq. (2.156) and then integrating over $\mathbf{x}_i$ under the boundary condition $\mathbf{x}_i = \mathbf{x}_f$. Using this, the fact that $\lim_{\mathbf{q} \rightarrow 0} Z[J_{\mathbf{q},\tau}(t)] = Z_{S_0}$ and that the kinetic energy terms in $\langle S - S_0 \rangle$ cancel, Ōsaka obtained $\langle S \rangle_{S_0}$ as

Finite Temperature Model Action Expectation

$$\begin{aligned}
 \langle S \rangle_{S_0} &= \frac{\alpha \hbar r_0 \omega_0^2}{2\sqrt{2}} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma D_{\omega_0}(\tau - \sigma) \int \frac{d^3 \mathbf{q}}{2\pi^2} \frac{1}{q^2} e^{-\frac{r_0^2 q^2}{2} G(\tau)} \\
 &= \frac{\alpha \hbar r_0 \omega_0^2}{\sqrt{pi}} \int_0^{\hbar\beta} d\tau (\hbar\beta - \tau) \frac{D_{\omega_0}(\tau)}{\sqrt{G(\tau)}}. \quad (2.163)
 \end{aligned}$$

Here $G(\tau)$ is now the finite temperature generalisation of (2.115) given by

Finite Temperature Polaron Green Function

$$G(\tau) = \frac{w^2}{v^2} \tau \left(1 - \frac{\tau}{\hbar\beta} \right) - \frac{v^2 - w^2}{v^3} (D_v(\tau) - D_v(0)). \quad (2.164)$$

As $\langle S \rangle_{S_0}$ is independent of the boundary conditions, it can be obtained as before from the power series of $\mathbf{q}$ of $Z[J_{\mathbf{q},\tau}(t)]$ to give,

Finite Temperature Trial Action Expectation

$$\begin{aligned}\langle S_0 \rangle &= \frac{3\kappa w \beta}{4} \int_0^{\hbar\beta} d\tau (\hbar\beta - \tau) D_w(\tau) G(\tau) \\ &= \frac{3\kappa\beta}{4v} \left(\frac{2}{v\hbar\beta} - \coth\left(\frac{v\hbar\beta}{2}\right) \right).\end{aligned}\quad (2.165)$$

Ösaka then obtained the partition function from the diagonal part of the density matrix,

$$Z(\beta) = \rho_S(\mathbf{r}, \mathbf{r}; \hbar\beta) \geq \rho_{S_0}(\mathbf{r}, \mathbf{r}; \hbar\beta) \exp\left(\frac{\langle S - S_0 \rangle_{S_0}}{\hbar}\right) = Z_{S_0}(\beta) \exp\left(\frac{\langle S - S_0 \rangle_{S_0}}{\hbar}\right), \quad (2.166)$$

to give the variational principle,

$$F(\beta) \leq F_{S_0}(\beta) + \frac{1}{\hbar\beta} \langle S - S_0 \rangle_{S_0}. \quad (2.167)$$

Now, in a similar way to Feynman, Ösaka obtained the trial free energy $F_{S_0}(\beta)$ using,

$$\frac{\partial \log Z_{S_0}}{\partial \kappa} = \frac{\langle S_0 \rangle_{S_0}}{\hbar \kappa}, \quad (2.168)$$

and the fact that when $\kappa = 0$, $Z_{S_0} = V_0(m_0/2\pi\hbar^2\beta)^{3/2}$. By integrating $\partial \log Z_{S_0}/\partial \kappa$ with respect to κ , Ösaka obtained,

$$\begin{aligned}F_{S_0}(\beta) &= -\frac{1}{\beta} \log Z_{S_0}(\beta) = -\frac{1}{\beta} \log \left(\frac{V_0}{r_0^3} \right) + \frac{3}{2\beta} \log(2\pi\hbar\omega_0\beta) - \frac{1}{\hbar\beta} \int_0^\kappa d\kappa' \frac{\langle S_0(\kappa') \rangle'}{\kappa} \\ &= -\log \left(\frac{V_0}{r_0^3} \right) + \frac{3}{2\beta} \log(2\pi\hbar\omega_0\beta) + \frac{3\hbar}{2} \int_w^v du \left(\coth\left(\frac{\hbar\beta u}{2}\right) - \frac{2}{\hbar\beta u} \right),\end{aligned}\quad (2.169)$$

which gives,

Free Energy of the Trial Model

$$F_{S_0}(\beta) = -\frac{1}{\beta} \log \left(\frac{V_0}{r_0^3} \right) + \frac{3}{2\beta} \log(2\pi\hbar\omega_0\beta) + \frac{3}{\beta} \log \left(\frac{w \sinh(\hbar\beta v/2)}{v \sinh(\hbar\beta w/2)} \right). \quad (2.170)$$

If one finds the variational parameters v and w that give the lowest upper-bound to the free energy, then the average energy of the polaron state is given by,

$$E = -\frac{\partial}{\partial \beta} \left(F_{S_0} + \frac{\langle S - S_0 \rangle_{S_0}}{\hbar} \right). \quad (2.171)$$

These results generalise Feynman's variational parameter for the polaron at zero temperature to finite temperatures parameterised by the thermodynamic beta parameter $\beta = 1/(k_B T)$. In this zero temperature limit, $\beta \rightarrow \infty$, Ōsaka's result reduces to Feynman's in Eq. (2.118).

2.2.11 Thermal FVA Numerical Results

In Figs. (2.4) and (2.5) are line and contour plots that show the temperature and coupling dependence of the 2D (left column) and 3D (right column) Fröhlich model. These figures show: (top row) the polaron free energy $F(\hbar\omega_0)$; (second row) the polaron effective mass $M(m_0)$; (third row) values of the $v(\omega_0)$ variational parameter; and (bottom row) values of the $w(\omega_0)$ variational parameter.

For the free energy, I split the figure into three sections: a positive logarithmic region; a linear region with $-1 \leq F/\hbar\omega_0 \leq 1$; and a negative logarithmic region using $\log(-F/\hbar\omega_0) \rightarrow -\log(F/\hbar\omega_0)$ (this is similar to the 'symmetrical logarithmic' function from MATLAB). Interestingly, this reveals a region with a slightly positive total polaron free energy. This suggests that polarons do not form at these temperatures at weak coupling. This region vanishes at zero temperature $T = 0$ and above temperatures $T > 6\hbar\omega_0/k_B$, and above $\alpha > 1$ in 2D and $\alpha > 2$ in 3D. As phonons typically have frequencies of order $\omega_{ph} \sim 1$ THz, this upper-temperature limit is roughly on the order of $T \sim 288$ K. In the intermediate regime ($1 \leq \alpha < 6$), the free energy forms a maximum around $T \sim \hbar\omega_0/k_B \sim 48$ K, which shifts to lower temperatures at zero coupling.

The effective mass is $M \sim m_0$ at very low couplings ($\alpha < 1$). At weak and intermediate couplings ($\alpha < 6$), the polaron effective mass shows a maximum around $T \sim 0.25\hbar\omega_0/k_B$. Towards strong coupling ($\alpha > 6$), the effective mass is roughly constant for temperatures $T < \hbar\omega_0/k_B$ and then exponentially decreases towards the band mass as the temperature increases above the Debye temperature.

At weak and intermediate couplings ($\alpha < 6$), the variational parameters v and w show a minimum around $T \sim 0.25\hbar\omega_0/k_B$ coinciding with the effective mass maximum. Both parameters show an exponential increase for temperatures above the Debye temperature $T > \hbar\omega_0/k_B$ towards larger couplings. Their relative difference is zero, as indicated by the effective mass approaching the band mass.

For each quantity, the difference between the 2D and 3D Fröhlich model is determined entirely by the scaling relations in Eq. (2.142). Note that I did not directly use these relations in calculating the 2D results; nonetheless, the scaling relation is evident in Fig. 2.5 by the multiplicative scaling of the α -axis with $\alpha_{2D} \sim \frac{3\pi}{4}\alpha_{3D}$.

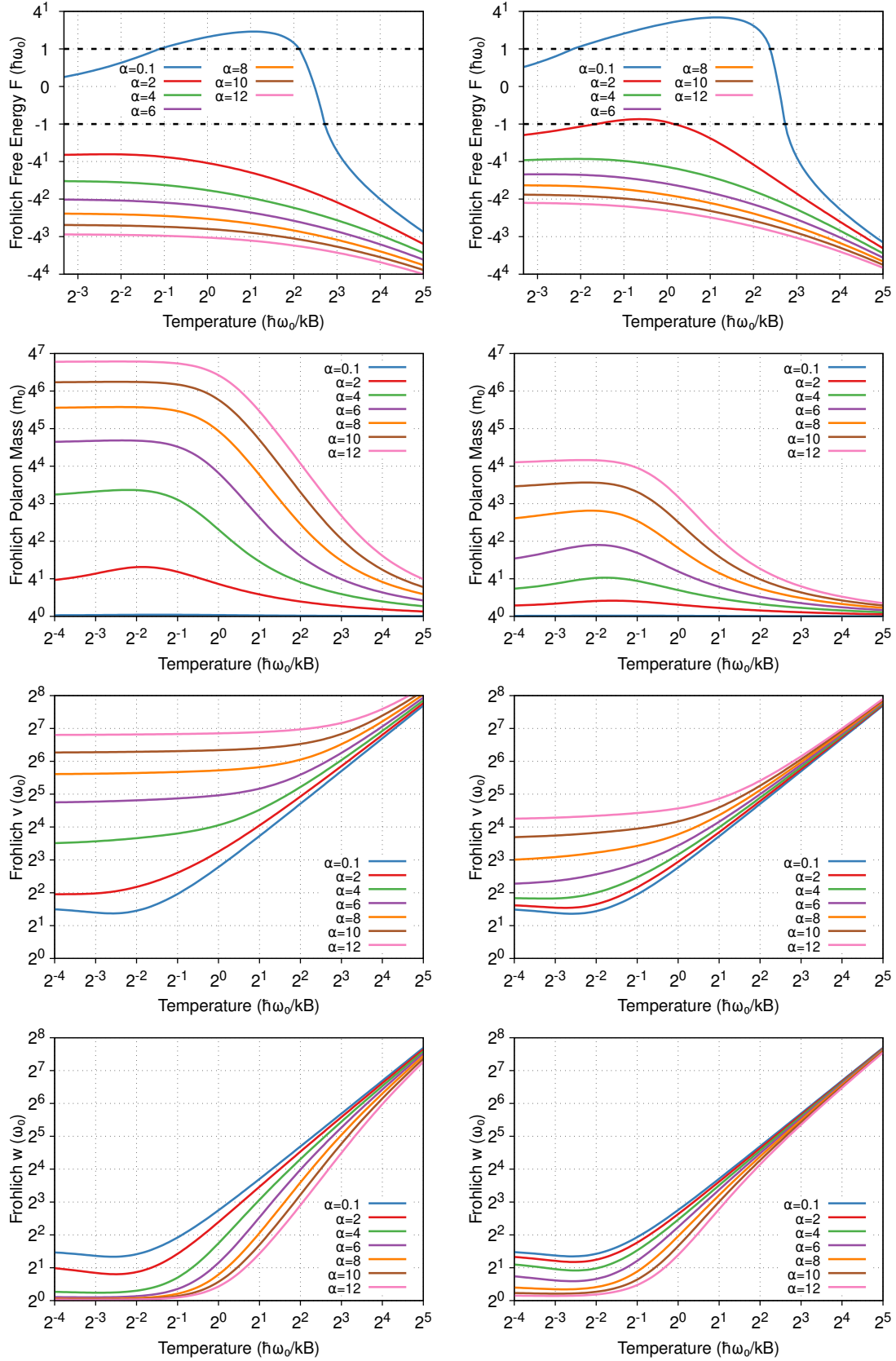


Figure 2.4: The temperature (T in units of $\hbar\omega_0/k_B$)- and electron-phonon α coupling-dependence of the physical properties of Ōsaka's polaron in 2D (left) and 3D (right). Top: the free energy. Second row: the Feynman effective mass. Third row: the v variational parameter. Bottom: the w variational parameter. In the top row, I plot the 'symmetrical logarithm' of the free energy with a linear region $-1 \leq F/\hbar\omega_0 \leq 1$ indicated by the black dotted lines.

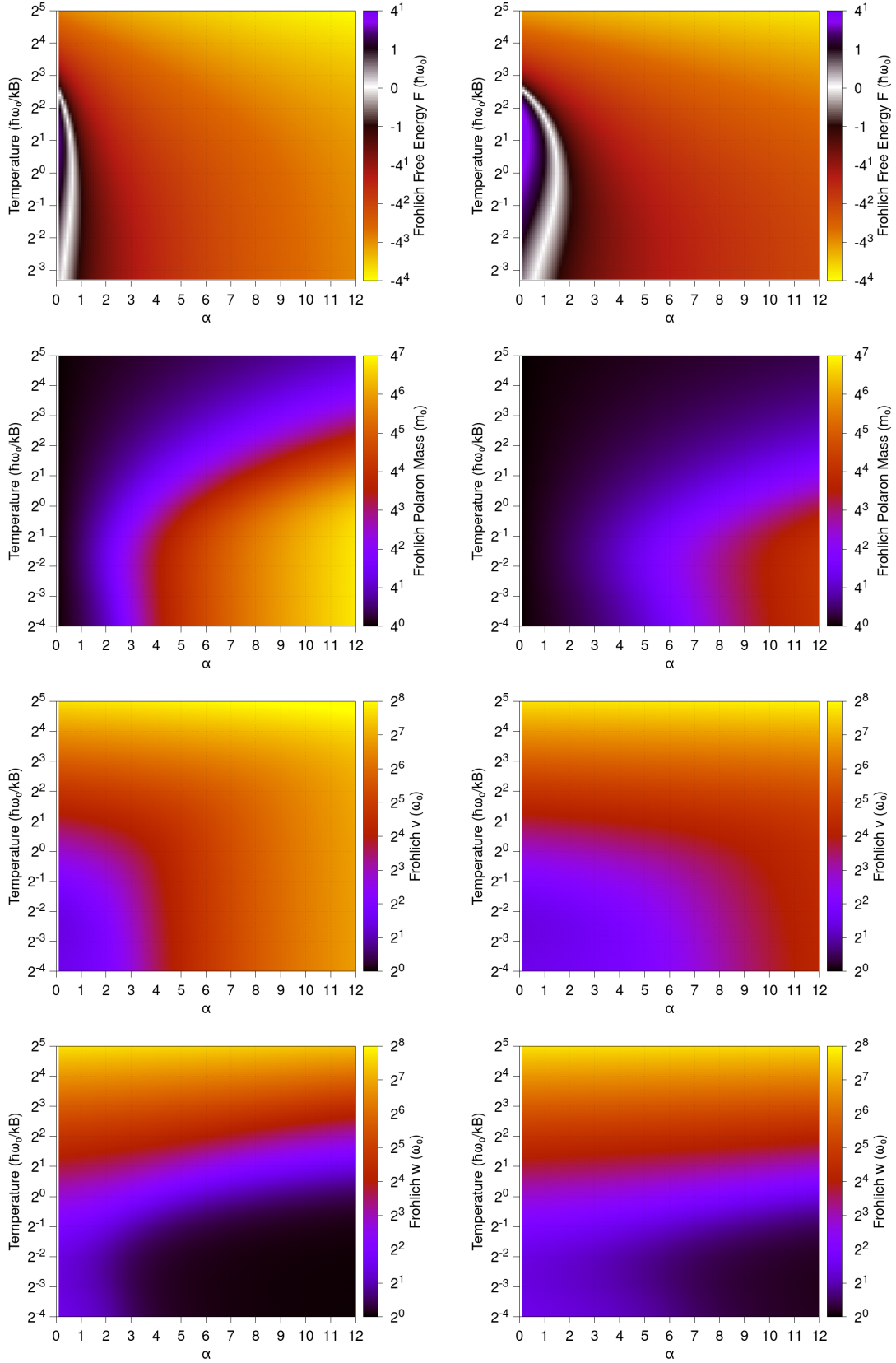


Figure 2.5: The temperature (T in units of $\hbar\omega_0/k_B$)- and electron-phonon α coupling-dependence of the physical properties of Osaka's polaron in 2D (left) and 3D (right). Top: the free energy. Second row: the Feynman effective mass. Third row: the ν variational parameter. Bottom: the w variational parameter. In the top row, I plot the 'symmetrical logarithm' of the free energy with a linear region $-1 \leq F/\hbar\omega_0 \leq 1$ indicated by the black-white palette.

2.3 Influence Functionals & Response Functions

2.3.1 Polaron DC Mobility

FHIP [17] derived an expression for the response of the Feynman polaron to weak, spatially uniform, time-varying electric fields. The current induced by the motion of an electron under the influence of a weak alternating electric field $\mathbf{E} = \mathbf{E}_0 \exp(i\Omega t)$ is generally

$$\mathbf{j}(\Omega) = \frac{\mathbf{E}(\Omega)}{z(\Omega)}, \quad (2.172)$$

where $z(\Omega)$ is the complex impedance function. Here we assume that the material is isotropic so that $\mathbf{j} = \langle \dot{\mathbf{r}} \rangle$, where $\langle \mathbf{r} \rangle = \mathbf{E}/(i\Omega z(\Omega))$ is the expectation of the electron displacement in the $\hat{\mathbf{r}}$ direction.

In the time domain, this is

$$\langle \mathbf{r}(t) \rangle = -i \int_{-\infty}^{\infty} dt' G(t-t') \mathbf{E}(t'), \quad (2.173)$$

where $G(t)$ is the Green function corresponding to the *linear* electron displacement at a time t due to a delta function pulsed electric field at a time zero, $t = 0$. The Fourier transform of $G(t)$ is

$$\int_{-\infty}^{\infty} dt G(t) e^{-i\Omega t} = G(\Omega) = \frac{1}{\Omega z(\Omega)}, \quad (2.174)$$

where $G(t) = 0$ for $t < 0$.

Under the influence of the external electric field $\mathbf{E}(t)$, the Fröhlich Hamiltonian gains a linear force term $-\mathbf{E} \cdot \mathbf{r}$. If ρ is the density matrix of the system, then the expected electron position at a time t is

$$\langle \mathbf{r}(t) \rangle = \text{Tr} \{ \mathbf{r} \rho(t) \}. \quad (2.175)$$

The density matrix at any later time t can be obtained from the Liouville-von Neumann equation,

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]. \quad (2.176)$$

Therefore, by integrating this equation we can express the density matrix as

$$\rho(t) = \exp \left\{ -\frac{i}{\hbar} \int_0^t [H(s) - \mathbf{r}(s) \cdot \mathbf{E}(s)] ds \right\} \rho(0) \exp \left\{ +\frac{i}{\hbar} \int_0^t [H'(s) - \mathbf{r}'(s) \cdot \mathbf{E}'(s)] ds \right\}. \quad (2.177)$$

From now on, we will assume that the system is initially in thermal equilibrium $\rho(t = 0) = \exp(-\beta H) \propto \exp(-\hbar\beta \sum_{\mathbf{q}} \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}})$ such that the phonon oscillators are initially in thermal equilibrium at temperature $(k_B\beta)^{-1}$.

Due to the electron-phonon coupling, the entire polaron system will quickly return to thermal equilibrium after the electron is perturbed since the energy of the electron ($\sim 1/\text{volume}$) is tiny relative to the heat bath of the system of phonon oscillators. As an aside, since $\mathbf{E}$ is not an operator and the system is in thermodynamic equilibrium, then $\mathbf{E}'(s) = \mathbf{E}(s)$. Still, FHIP treats $\mathbf{E}$ and $\mathbf{E}'$ separately to encompass the more general cases, such as in a non-linear response system.

We can write $\text{Tr } \rho(t)$ as the path integral generating functional,

$$\begin{aligned} \text{Tr } \rho(t) &= Z[\mathbf{E}, \mathbf{E}'] \\ &= \int D\mathbf{r}(t) D\mathbf{r}'(t) \exp \left(\frac{i}{\hbar} \Phi[\mathbf{r}(t), \mathbf{r}'(t)] - \frac{i}{\hbar} \int_{-\infty}^{\infty} dt [\mathbf{E}(t) \cdot \mathbf{r}(t) - \mathbf{E}'(t) \cdot \mathbf{r}'(t)] \right), \end{aligned} \quad (2.178)$$

where $\Phi[\mathbf{r}(t), \mathbf{r}'(t)]$ is the influence functional phase for the model action,

FHIP Model Influence Functional Phase

$$\begin{aligned} \Phi &= \frac{iV_0}{\hbar} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \int \frac{d^3 \mathbf{q}}{(2\pi)^3} |M_{\mathbf{q}}|^2 \left\{ \left(e^{i\mathbf{q} \cdot \mathbf{r}(t)} - e^{i\mathbf{q} \cdot \mathbf{r}'(t)} \right) \right. \\ &\quad \times \left. \left(D_{\omega_{\mathbf{q}}}(t - t') e^{-i\mathbf{q} \cdot \mathbf{r}'(t')} - D_{\omega_{\mathbf{q}}}^*(t - t') e^{-i\mathbf{q} \cdot \mathbf{r}(t')} \right) \right\}. \end{aligned} \quad (2.179)$$

For Fröhlich's Hamiltonian we set $\omega_{\mathbf{q}} = \omega_0$ and the interaction term $M_{\mathbf{q}}$ is given by Eq. (2.36).

Since we are taking the trace, the double path integral $D\mathbf{r}(t) D\mathbf{r}'(t)$ is only over closed paths satisfying the boundary condition $\mathbf{r}(t) - \mathbf{r}'(t) = 0$ at times $t \rightarrow \pm\infty$. Since the electric field is weak, we can expand $\langle \mathbf{r}(t) \rangle$ to first-order and find the linear response Green function for $\mathbf{r}(t)$, which can be obtained from the first functional derivative of the partition function with respect to $\mathbf{E}(t) - \mathbf{E}'(t)$ as $t \rightarrow \infty$ when the steady state is reached. This gives,

$$G(t - t') = -\frac{\hbar^2}{2} \frac{1}{Z} \frac{\delta^2 Z[\mathbf{E}, \mathbf{E}']}{\delta \mathbf{E}(t, t') \delta \mathbf{E}'(t, t')} \Big|_{\mathbf{E}=\mathbf{E}'=0}, \quad (2.180)$$

where $Z = Z[0, 0]$ is the partition function that acts as the normalisation constant. In FHIP, they set the electric field to a sum of two delta functions,

$$\mathbf{E}(s) = [\epsilon \delta(s - t') + \eta \delta(s - t)] \hat{\mathbf{E}}, \quad (2.181a)$$

$$\mathbf{E}'(s) = [\epsilon \delta(s - t') - \eta \delta(s - t)] \hat{\mathbf{E}}, \quad (2.181b)$$

where $\hat{\mathbf{E}}$ is the unit vector of the electric field. This gives,

$$G(t - t') = \frac{\hbar^2}{2Z} \frac{\partial^2 Z(\epsilon, \eta)}{\partial \eta \partial \epsilon} \Big|_{\eta=\epsilon=0}. \quad (2.182)$$

Thus, the problem of finding the Green function $G(t - t')$ is reduced to that of finding the dependence of the generating function path integral $Z[\mathbf{E}, \mathbf{E}']$ on the forcing functions $\mathbf{E}(t)$ and $\mathbf{E}'(t)$. The path integral in $Z[\mathbf{E}, \mathbf{E}']$ depends on the functional $\Phi[\mathbf{r}(t), \mathbf{r}'(t)]$ which contains terms similar to the model action S (athermal expression in Eq. (2.83) or thermal expression in Eq. (2.163)). However, note that this is now the real-time version of the model action (obtained from a Wick rotation).

Approximating the polaron complex impedance

The path integral $Z[\mathbf{E}, \mathbf{E}']$ cannot be evaluated exactly. However, it can be approximated using the trial influence functional $\Phi_{S_0}[\mathbf{r}(t), \mathbf{r}'(t)]$,

Trial Influence Functional Phase

$$\Phi_{S_0} = i \frac{\kappa w}{8} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \left\{ \left([\mathbf{r}(t)]^2 - [\mathbf{r}'(t)]^2 \right) \times \left(D_w(t - t') [\mathbf{r}(t')]^2 - D_w^*(t - t') [\mathbf{r}'(t')]^2 \right) \right\}. \quad (2.183)$$

This contains terms similar to the trial action S_0 (such as the athermal trial action in Eq. (2.93) and thermal trial action in Eq. (2.165), but Wick-rotated from the imaginary-time variable to the real-time variable) in which the attractive Coulomb-like potential is replaced by the simpler attractive parabolic potential centred at the mean position of the electron in the past (weighted by an exponential decay with time where w is the decay frequency and κ is the spring-constant coupling strength). In FHIP, it is assumed that the Wick-rotation of the trial partition function Z_{S_0} (the athermal partition function given by Eq. (2.100) and the thermal partition function by Eq. (2.170)), which offers the best approximation to the partition function of the actual model system via either Feynman's (athermal) or Ōsaka's (thermal) variational principle, can describe the dynamical behaviour of the polaron.

Therefore, in FHIP, they approximate the model generating functional $Z[\mathbf{E}, \mathbf{E}']$ with the zeroth and first terms from the expansion of the path integral around the trial action,

$$\begin{aligned} Z[\mathbf{E}, \mathbf{E}'] &\approx \int D\mathbf{r}(t) D\mathbf{r}'(t) e^{\frac{i}{\hbar}(\Phi_{S_0} + \int dt [\mathbf{E} \cdot \mathbf{r} - \mathbf{E}' \cdot \mathbf{r}'])} \\ &+ i \int D\mathbf{r}(t) D\mathbf{r}'(t) e^{\frac{i}{\hbar}(\Phi_{S_0} + \int dt [\mathbf{E} \cdot \mathbf{r} - \mathbf{E}' \cdot \mathbf{r}'])} (\Phi - \Phi_{S_0}) \\ &\equiv Z_{S_0}[\mathbf{E}, \mathbf{E}'] + Z_1[\mathbf{E}, \mathbf{E}']. \end{aligned} \quad (2.184)$$

Calculating the zeroth term of the complex impedance

The zeroth term $Z_{S_0}[\mathbf{E}, \mathbf{E}']$ is the classical response and is the same as the alternative model presented by Ōsaka of two masses coupled by a harmonic spring under the influence of a

linear force $\mathbf{J}$ (Eq. (2.155)), where $\mathbf{J} = \mathbf{E}$. This term is then reanalysed as the sum of two normal mode harmonic oscillators so that $Z_{S_0}[\mathbf{E}, \mathbf{E}']$ is written as the product of two factors, one for each harmonic oscillator. The first oscillator has a mass $m_1 = M + m_0 = m_0 v^2 / w^2$ and frequency $\omega_1 = 0$ coupled by $\mathbf{J}_1(t) = \mathbf{E}(t)$, and the second oscillator has mass $m_2 = M m_0 / (M + m_0)$, frequency $\omega_2 = v \omega_0$ and coupling $\mathbf{J}_2(t) = -M m_0 / (M + m_0) \mathbf{E}(t) = \mathbf{E}(t)(v^2 - w^2)/v^2$ where we have used that $\kappa = v^2 - w^2$.

$Z_{S_0}[\mathbf{E}, \mathbf{E}']$ is then given by,

$$Z_{S_0}[\mathbf{E}, \mathbf{E}'] = \exp \left\{ \frac{i}{4\pi} \int_{-\infty}^{+\infty} d\Omega \left(\mathbf{E}(-\Omega) - \mathbf{E}'(\Omega) \right) \cdot \left[\left(\mathbf{E}(\Omega) + \mathbf{E}'(\Omega) \right) Y_0(\Omega) + i \left(\mathbf{E}(\Omega) - \mathbf{E}'(\Omega) \right) A_0(\Omega) \right] \right\}, \quad (2.185)$$

where,

$$Y_0(\Omega) = \lim_{\varepsilon \rightarrow 0^+} \left\{ i \frac{\Omega^2 - w^2}{(\Omega - i\varepsilon)^2} \left[(\Omega - i\varepsilon)^2 - v^2 \right] \right\}, \quad (2.186)$$

and,

$$A_0(\Omega) = \frac{\pi}{2} \lim_{\varepsilon \rightarrow 0^+} \left\{ \frac{2w^2}{v^2 \beta \varepsilon^2} \left[\delta(\Omega + \varepsilon) - \delta(\Omega - \varepsilon) \right] + \frac{v^2 - w^2}{v^3} \left[1 + \frac{2}{e^{\beta v} - 1} \right] \left[\delta(\Omega + v) + \delta(\Omega - v) \right] \right\}, \quad (2.187)$$

where $\mathbf{E}(\Omega)$ is the Fourier transform of $\mathbf{E}(t)$. To obtain the classical Green function $G_0(t - t')$, in FHIP they substitute,

$$\mathbf{E}(\Omega) = \left(\epsilon e^{-i\Omega t'} + \eta e^{i\Omega t} \right) \hat{\mathbf{E}}, \quad (2.188a)$$

$$\mathbf{E}'(\Omega) = \left(\epsilon e^{-i\Omega t'} - \eta e^{i\Omega t} \right) \hat{\mathbf{E}}, \quad (2.188b)$$

into $Z_{S_0}[\mathbf{E}, \mathbf{E}']$ and find the term of order $\epsilon \eta$. The zeroth order approximation to $G(t - t')$ is then,

$$G_0(t - t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega G_0(\Omega) e^{i\Omega(t-t')}, \quad (2.189)$$

which is the classical response of the system.

Calculating the first correction term of the complex impedance

To include the first order of quantum corrections to the classical response of the electron, FHIP uses the $Z_1[\mathbf{E}, \mathbf{E}']$ path integral to obtain the first order approximation $G_1(t - t')$ to $G(t - t')$. To evaluate $Z_1[\mathbf{E}, \mathbf{E}']$ they first look at the $\Phi \exp(i\Phi_{S_0}/\hbar)$. Substituting the equation for Φ into $\Phi \exp(i\Phi_{S_0}/\hbar)$, the resulting expression contains terms $\mathcal{T}$ that have

the form,

$$\mathcal{T} = \int D\mathbf{r}(t) D\mathbf{r}'(t) e^{\frac{i}{\hbar} \Phi_{S_0}} \left\{ \frac{iV_0}{\hbar} \int \frac{d^3\mathbf{q}}{(2\pi)^3} |M_{\mathbf{q}}|^2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' D_{\omega_{\mathbf{q}}}(t-t') e^{i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(t')]} \right\}. \quad (2.190)$$

The two other terms in $\Phi \exp(i\Phi_{S_0}/\hbar)$ come from the correlations between electron paths in the density matrix $\rho(\mathbf{r}, \mathbf{r}', t)$ (i.e. off-diagonal terms) and are similar to $\mathcal{T}$, but with different replacements of $\mathbf{r}$ with $\mathbf{r}'$. To evaluate $\mathcal{T}$ one has to evaluate the path integral,

$$\begin{aligned} \mathcal{R}(\mathbf{q}, t, t') &= \int_{\mathbf{r}=\mathbf{r}'} D\mathbf{r}(t) D\mathbf{r}'(t) \exp \left\{ i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(t')] + \frac{i}{\hbar} \Phi_{S_0} \right\} \\ &= Z_{S_0} \left\langle e^{i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(t')]} \right\rangle_{\Phi_{S_0}}, \end{aligned} \quad (2.191)$$

where $Z_{S_0} \equiv Z_{S_0}[0, 0]$. This gives $\mathcal{T}$ to be,

$$\mathcal{T} = Z_{S_0} V_0 \int \frac{d^3\mathbf{q}}{(2\pi)^3} |M_{\mathbf{q}}|^2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' D_{\omega_{\mathbf{q}}}(t-t') \left\langle e^{i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(t')]} \right\rangle_{\Phi_{S_0}}. \quad (2.192)$$

The solution to $\mathcal{R}(\mathbf{q}, t, t')$ is the same form as $Z_{S_0}[\mathbf{E}, \mathbf{E}']$ in Eq. (2.185) except for the non-primed components,

$$\mathbf{E}(\Omega) = \left(\epsilon e^{-i\Omega t'} + \eta e^{-i\Omega t} \right) \hat{\mathbf{E}} + \mathbf{q} \left(e^{-i\Omega t} - e^{-i\Omega t'} \right), \quad (2.193a)$$

$$\mathbf{E}(\Omega) = \left(\epsilon e^{-i\Omega t'} - \eta e^{-i\Omega t} \right) \hat{\mathbf{E}}, \quad (2.193b)$$

where $\mathbf{q}$ is the phonon wavevector. This gives,

$$\begin{aligned} \mathcal{R}(\mathbf{q}, t, t') &= Z_{S_0} \exp \left\{ \frac{iq^2}{4\pi} \int_{-\infty}^{\infty} d\Omega \left| e^{i\Omega t} - e^{i\Omega t'} \right|^2 (Y_0 + iA_0) \right. \\ &\quad + \frac{i\mathbf{q} \cdot \hat{\mathbf{r}}}{2\pi} \int_{-\infty}^{\infty} d\Omega \left(e^{i\Omega t} - e^{i\Omega t'} \right) \left(\epsilon Y_0 e^{-i\Omega t'} + i\eta A_0 e^{-i\Omega t} \right) \\ &\quad \left. + \frac{i\mathbf{q} \cdot \hat{\mathbf{r}}}{2\pi} \int_{-\infty}^{\infty} d\Omega \left(e^{-i\Omega t} - e^{-i\Omega t'} \right) \eta e^{i\Omega t} (Y_0 + iA_0) \right\}, \end{aligned} \quad (2.194)$$

where,

$$Z_{S_0} = \exp \left[\frac{i}{\pi} \int_{-\infty}^{\infty} d\Omega \eta e^{i\Omega t} \left(\epsilon Y_0 e^{-i\Omega t'} + i\eta A_0 e^{-i\Omega t} \right) \right], \quad (2.195)$$

for $\mathbf{q} = 0$. Similarly, for the primed components,

$$\mathbf{E}'(\Omega) = \left(\epsilon e^{-i\Omega t'} + \eta e^{-i\Omega t} \right) \hat{\mathbf{E}} - \mathbf{q} e^{-i\Omega t}, \quad (2.196a)$$

$$\mathbf{E}'(\Omega) = \left(\epsilon e^{-i\Omega t'} - \eta e^{-i\Omega t} \right) \hat{\mathbf{E}} - \mathbf{q} e^{-i\Omega t'}. \quad (2.196b)$$

To obtain $G_1(t - t')$ we need to find the first-order derivative of $\mathcal{R}(\mathbf{q}, t, t')$ with respect to ϵ and η and then set $\epsilon = \eta = 0$ and calling the result $2r(q, t, t')$. The result is (including a $1/3$ for averaging over the isotropic dimensions of $\mathbf{q}$),

$$\begin{aligned}
 r(q, t, t') = & \left\{ \frac{i}{2\pi} \int_{-\infty}^{\infty} d\Omega Y_0(\Omega) e^{i\Omega(t-t')} \right. \\
 & - \frac{q^2}{24\pi^2} \int_{-\infty}^{\infty} d\Omega \left(e^{i\Omega t} - e^{i\Omega t'} \right) Y_0(\Omega) e^{-i\Omega t'} \\
 & \times \int_{-\infty}^{\infty} d\Omega' \left[\left(e^{i\Omega' t} - e^{i\Omega' t'} \right) iA_0(\Omega') e^{-i\Omega' t} \right. \\
 & \left. \left. + \left(e^{i\Omega' t} - e^{-i\Omega' t'} \right) e^{i\Omega' t} \left(Y_0(\Omega') + iA_0(\Omega') \right) \right] \right\} \\
 & \times \exp \left\{ \frac{iq^2}{4\pi} \int_{-\infty}^{\infty} d\Omega \left| e^{i\Omega t} - e^{i\Omega t'} \right|^2 \left(Y_0(\Omega) + iA_0(\Omega) \right) \right\}.
 \end{aligned} \tag{2.197}$$

The first term is the classical response $G_0(t - t')$, and the later terms correspond to the trial path integral with no applied electric field $\epsilon = \eta = 0$. Hence, in total $r(q, t, t')$ is the $\mathbf{q}$ -dependent term in $\langle S_0 - S'_0 \rangle_{S'_0, S_0}$, where the classical response G_0 has cancelled with the normalisation and does not contribute to the quantum corrections to the response, G_1 . We can do a change of variables $u \equiv t - t'$ and perform the integral on t' in Eq. (2.197) to give,

$$\begin{aligned}
 r(q, u) = & -\frac{q^2}{12\pi^2} \int_{-\infty}^{\infty} d\Omega \left(1 - \cos(\Omega u) \right) Y_0(\Omega) \left(Y_0(\Omega) + 2iA_0(\Omega) \right) e^{i\Omega u} \\
 & \times \exp \left\{ \frac{iq^2}{2\pi} \int_{-\infty}^{\infty} d\Omega' \left(1 - \cos(\Omega' u) \right) \left(Y_0(\Omega') + iA_0(\Omega') \right) \right\},
 \end{aligned} \tag{2.198}$$

where $Y_0(-\Omega) = Y_0^*(\Omega)$ and $A_0(-\Omega) = A_0(\Omega)$. $r(q, u)$ contributes to $G_1(u)$ and since it is already of the form of a Fourier transform, we can find the contribution $r(q, \Omega)$ to $G_1(\Omega)$ by omitting the Fourier integral on Ω and the factor $e^{i\Omega u}$ to give,

$$\begin{aligned}
 r(q, \Omega) = & -\frac{q^2}{6\pi} \left(1 - \cos(\Omega u) \right) Y_0(\Omega) \left(Y_0(\Omega) + 2iA_0(\Omega) \right) \\
 & \times \exp \left\{ \frac{iq^2}{2\pi} \int_{-\infty}^{\infty} d\Omega' \left(1 - \cos(\Omega' u) \right) \left(Y_0(\Omega') + iA_0(\Omega') \right) \right\}.
 \end{aligned} \tag{2.199}$$

To obtain $\langle S - S_0 \rangle_{S'_0, S_0}$ we multiply $r(q, u)$ by $D_{\omega_q}(u)$ and integrate on u . Feynman evaluated this integral by splitting the range of u from 0 to ∞ and from $-\infty$ to 0, where in the latter, he put $u \rightarrow -u$ to make all integrals on u positive. The integral in the exponent

is $-q^2/2$ times $G(u)$,

$$\begin{aligned} G(u) &= -\frac{i}{\pi} \int_{-\infty}^{\infty} d\Omega (1 - \cos(\Omega u)) [Y_0(\Omega) + iA_0(\Omega)] \\ &= \frac{i}{\pi} \left(\tilde{Y}_0(u) + \tilde{Y}_0(-u) \right) + 2 \left(\tilde{A}_0(0) - \tilde{A}_0(u) \right) \\ &= 2 \frac{v^2 - w^2}{v^3} \frac{\sin(vu/2) \sin(v[u - i\hbar\omega_0\beta])}{\sinh(v\hbar\omega_0\beta/2)} - i \frac{w^2}{v^2} u \left(1 - \frac{u}{i\hbar\omega_0\beta} \right), \end{aligned} \quad (2.200)$$

where $u > 0$. $\tilde{Y}_0(u)$ and $\tilde{A}_0(u)$ are the inverse Fourier transforms of $Y_0(\Omega)$ and $A_0(\Omega)$ where we note that $\tilde{Y}_0(u) = 0$ for $u < 0$. Therefore, overall for $\mathcal{T}$ we obtain a contribution,

$$\frac{-2q^2}{3\pi} Y_0(\Omega) [Y_0(\Omega) + 2iA_0(\Omega)] \int_0^{\infty} du (1 - \cos(\Omega u)) D_{\omega_q}(u) e^{-\frac{1}{2}q^2 G(u)}, \quad (2.201)$$

which contributes to G_1 . A similar calculation is also done to obtain the $\mathcal{T}$ terms that come from the primed $\mathbf{r}'$ components in $\Phi \exp(i\Phi_{S_0}/\hbar)$. Once all are obtained, they are summed together, and the $\mathbf{q}$ integral gives the first contribution to $G_1(\Omega)$ as,

$$G_1^{(1)}(\Omega) = -i\Omega Y_0^2(\Omega) \Sigma(\Omega), \quad (2.202)$$

where,

FHIP Memory Function

$$\Sigma(\Omega) = \frac{1}{\Omega} \int_0^{\infty} dt (1 - e^{i\Omega t}) \text{Im} S(t), \quad (2.203)$$

with,

$$S(t) = \frac{2}{3} V_0 \int \frac{d^3 \mathbf{q}}{(2\pi)^3} |M_{\mathbf{q}}|^2 q^2 D_{\omega_q}(t) e^{-r_0^2 q^2 G(t)/2}, \quad (2.204)$$

which for the Fröhlich Hamiltonian gives,

FHIP Fröhlich Dynamical Structure Factor

$$S(t) = \frac{2\alpha}{3\sqrt{\pi}} D_{\omega_0}(t) [G(t)]^{-3/2}. \quad (2.205)$$

Next, the second term is obtained analogously from Φ_{S_0} . It can be evaluated by differentiating $\mathcal{R}$ (and thus on $r(q, u)$) twice concerning $\mathbf{q}$ and then setting $\mathbf{q} = 0$ in the expression. This results in an integral on u ,

$$G_1^{(2)}(\Omega) = -i4Y_0^2(\Omega) \int_0^{\infty} du (1 - e^{i\Omega u}) S_0(u) = -iY_0^2(\Omega) \frac{(v^2 - w^2)\Omega^2}{\Omega^2 - w^2}, \quad (2.206)$$

where,

$$S_0(u) = \frac{(v^2 - w^2)w}{4} \text{Im} \left(e^{i w u} + 2n(\beta w) \cos(wu) \right) = \frac{(v^2 - w^2)w}{4} \sin(wu). \quad (2.207)$$

This gives the final result for the first-order change in G as,

$$G_1(\Omega) = G_1^{(1)}(\Omega) + G_1^{(2)}(\Omega) = -iY_0^2(\Omega) \left[\Omega \Sigma(\Omega) + (v^2 - w^2) \frac{\Omega^2}{\Omega^2 - w^2} \right]. \quad (2.208)$$

Hence, FHIP find an approximate form for $G(\Omega)$ composed out of the zeroth and first-order terms of the Green function,

$$G(\Omega) = G_0(\Omega) + G_1(\Omega), \quad (2.209)$$

from which they find the impedance to first-order in $G_1(\Omega)$,

$$\begin{aligned} \Omega z(\Omega) &= \frac{1}{G(\Omega)} \approx \frac{1}{G_0(\Omega) + G_1(\Omega)} \\ &\approx \frac{1}{G_0(\Omega)} - \frac{1}{G_0^2(\Omega)} G_1(\Omega). \end{aligned} \quad (2.210)$$

FHIP argue that this expanded form is more accurate than $z \sim (G_0 + G_1)^{-1}$ by considering a simple example of a free particle perturbed by a harmonic oscillator. The structure of the actual $G(\Omega)$ in this example includes a resonance at the oscillator frequency which is not present in $z \sim (G_0 + G_1)^{-1}$. This resonance is present if one expands $z(\Omega)$. Therefore, FHIP use this expanded form, which is written explicitly as

FHIP Complex Impedance Function

$$z(\Omega) \approx i (\Omega - \Sigma(\Omega)). \quad (2.211)$$

The first term (Ω) on the right-hand side is a free-particle term, while $\Sigma(\Omega)$ contains the corrections from the electron-phonon interactions. All of the dependence on the trial influence functional Φ_{S_0} is contained within $G(t)$, which appears in the exponential term in $S(t)$ (Eq. (2.205)). This exponential term describes the non-linear scattering of the electron due to its interaction with the phonon field oscillators. If the phonon oscillators are linearly coupled to the electron's coordinate, then Eq. (2.211) is exact regardless of the choice of Φ_{S_0} . Otherwise, beyond a linear electron-phonon coupling approximation, Eq. (2.211) includes these higher-order interactions approximately by finding their effect for a trial influence functional Φ_{S_0} that seeks to imitate the actual influence functional Φ . In FHIP, they expect Eq. (2.211) to be an excellent approximation to the actual impedance of the polaron.

Thornber investigated an extension beyond linear response [34], where they evaluate the steady-state response of the electron in a finite electric field of arbitrary strength.

Calculating the polaron mobility

To obtain a general expression for the dissipation, or equivalently the mobility, of the polaron in FHIP, they recognise that the dc mobility μ_{dc} for the polaron is,

FHIP DC Mobility

$$\mu_{dc}^{-1} = \lim_{\Omega \rightarrow 0} \text{Im}\Sigma(\Omega). \quad (2.212)$$

In FHIP, they rewrite $\text{Im}\Sigma(\Omega)$ into a more convenient form for calculation (which may have been true at the time due to their computational capabilities but is no longer necessarily true) by using contour integration. They recognise that since $S(u)$ is analytic between $u = \text{real}$ and $u = \text{real} + i\beta$, the contour of integration can be changed from along the real axis to one which goes first from 0 to $i\beta/2$ up the imaginary axis and then from $i\beta/2$ to $i\beta/2 + \infty$ parallel to the real axis. In the case of Fröhlich's Hamiltonian they obtain for $\text{Im}\Sigma(\Omega)$,

$$\text{Im}\Sigma(\Omega) = -\frac{2\alpha}{3\sqrt{\pi}} \frac{\beta^{3/2} \sinh(\Omega\beta/2)}{\Omega \sinh(\beta/2)} \left(\frac{v}{w}\right)^3 \int_0^\infty \frac{\cos(\Omega x) \cos(x) dx}{[x^2 + a^2 - b \cos(vx)]^{3/2}}, \quad (2.213)$$

where $a^2 \equiv \beta^2/4 + R\beta \coth(\beta v/2)$, $b \equiv R\beta/\sinh(\beta v/2)$ and $R \equiv (v^2 - w^2)/(w^2 v)$.

$\text{Im}\Sigma(\Omega)$ has maxima when Ω is equal to a frequency where absorption can happen to go to an excited polaron state, and the widths of these maxima correspond to the state lifetimes for phonon emission. In FHIP, they compute $\text{Im}\Sigma(\Omega)$ by expanding Eq. (2.213) in an infinite power series of modified Bessel functions of the second kind, K , where only the first few terms are required for convergence in most cases.

In Appendix D, I have reproduced the contour integration for $\text{Im}\Sigma(\Omega)$ and also provided the contour integration for $\text{Re}\Sigma(\Omega)$ as well.

2.3.2 FHIP Polaron Mobility Numerical Results

Fig. 2.6 shows line (top) and contour (bottom) plots of the DC mobility derived in FHIP for the 2D (left) and 3D (right) Fröhlich model, calculated using Eqs. (2.204), (2.203) and (2.212). First, I note the numerical errors caused by strong coupling and low temperatures. These arise due to limited numerical machine precision in capturing low values of the memory function $\Sigma(\Omega)$, which results in noise in the mobility calculation since the memory function and mobility have a reciprocal relationship. Rather than plateauing to a finite

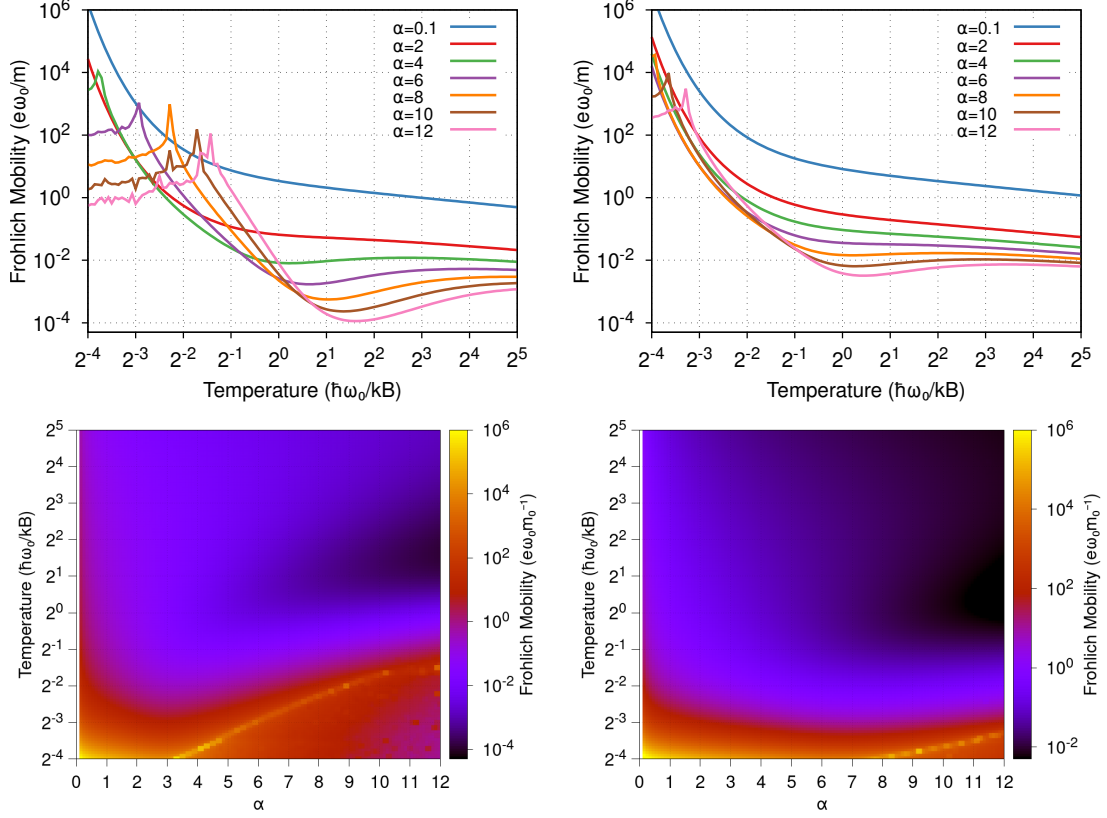


Figure 2.6: The temperature (T in units of the phonon frequency ($\hbar\omega_0/k_B$))- and electron-phonon α coupling-dependence of the polaron DC mobility (μ in units of $e\omega_0m_0^{-1}$) for the Fröhlich model in 2D (left) and 3D (right).

value, the FHIP mobility in this region should exponentially increase to infinity as the temperature approaches zero.

Nonetheless, we see an interesting non-monotonic behaviour in the mobility for sufficiently large couplings with a minimum around the Debye temperature $T = T_D = \hbar\omega_0/k_B$, which is of the order $T_D \sim 48$ K for LO phonon modes. The transition typically indicates a change in regime from band-like transport below the Debye temperature to thermally-activated ‘lattice-hopping’ transport above this temperature. However, as Mishchenko et al. [10] noted, the Fröhlich polaron is defined in a continuum, where the notion of lattice-hopping is inconsistent. Instead, this minimum arises from a competition between decreasing phonon excitations below $T < T_D$ and significant effective mass renormalisation above $T > T_D$. For sufficiently large temperatures, the thermally excited phonons eventually succeed in stripping the polaron of its phonon cloud. Then, the mobility follows the $\mu \sim T^{-1/2}$ power law predicted by the Boltzmann Transport Equation (BTE).

2.3.3 The FHIP initial product state and low-temperature mobility

One source of controversy around the FHIP polaron mobility lies in its low-temperature expression compared to that derived from other approaches, such as the Boltzmann Transport Equation (BTE) [19]. In FHIP [17], they assume a factorised initial product state, which results in an incorrect low-temperature weak-coupling approximation for the DC-mobility with a spurious ‘ 2β ’ appearing in the denominator of the mobility,

FHIP Low Temperature DC Mobility

$$\mu_{\text{FHIP}} = \left(\frac{w}{v}\right)^3 \frac{3e}{2m_0\omega_0} \frac{\exp(\hbar\omega_0\beta)}{2\alpha\hbar\omega_0\beta} \exp\left(\frac{v^2 - w^2}{w^2 v \omega_0^{-1}}\right). \quad (2.214)$$

This observation is important for understanding the ‘ $3/2\beta$ ’ discrepancy between the low-temperature FHIP DC-mobility and Kadanoff’s DC-mobility [19] derived from the BTE,

$$\mu_{\text{K}} = \left(\frac{w}{v}\right)^3 \frac{e}{2m_0\omega_0} \frac{\exp(\hbar\omega_0\beta)}{\alpha} \exp\left(\frac{v^2 - w^2}{w^2 v \omega_0^{-1}}\right). \quad (2.215)$$

Some have argued that this discrepancy is due to taking the incorrect order of the limits $\Omega \rightarrow 0$ and $\alpha \rightarrow 0$ in calculating the impedance [73]. An alternative form of the low-temperature dc-mobility was derived by Los [74–76] and Sels [77]. Their mobility results differ by a factor of 3 from Kadonoff and by a factor of 2β from FHIP,

$$\mu_{\text{L}} = \left(\frac{w}{v}\right)^3 \frac{3e}{2m_0\omega_0} \frac{\exp(\hbar\omega_0\beta)}{\alpha} \exp\left(\frac{v^2 - w^2}{w^2 v \omega_0^{-1}}\right). \quad (2.216)$$

Sels and Brosens [77] show that the difference with Kadonoff is because the relaxation time approximation (neglecting the non-vanishing in-scattering term) used by Kadonoff violates particle number conservation, whereas FHIP does not. However, as mentioned above, the FHIP approximation relies on a nonphysical initial state for Feynman’s polaron model. Further, Los [75, 76] shows that not using a factorised initial state of the electron-phonon system results in corrections (although small) due to proper inclusion of initial correlations between the electron and the phonons.

Correcting the FHIP method may involve using a non-factorised initial state for the polaron density matrix. This would alter the influence functional to include an additional dependence on the imaginary-time paths of the electron. The reduced density matrix would then have an additional integration over these *imaginary*-time paths to produce a triple path integral. This involves generalising the real-time variable to a complex time variable over the so-called Keldish contour used in modern formulations of the influence functional

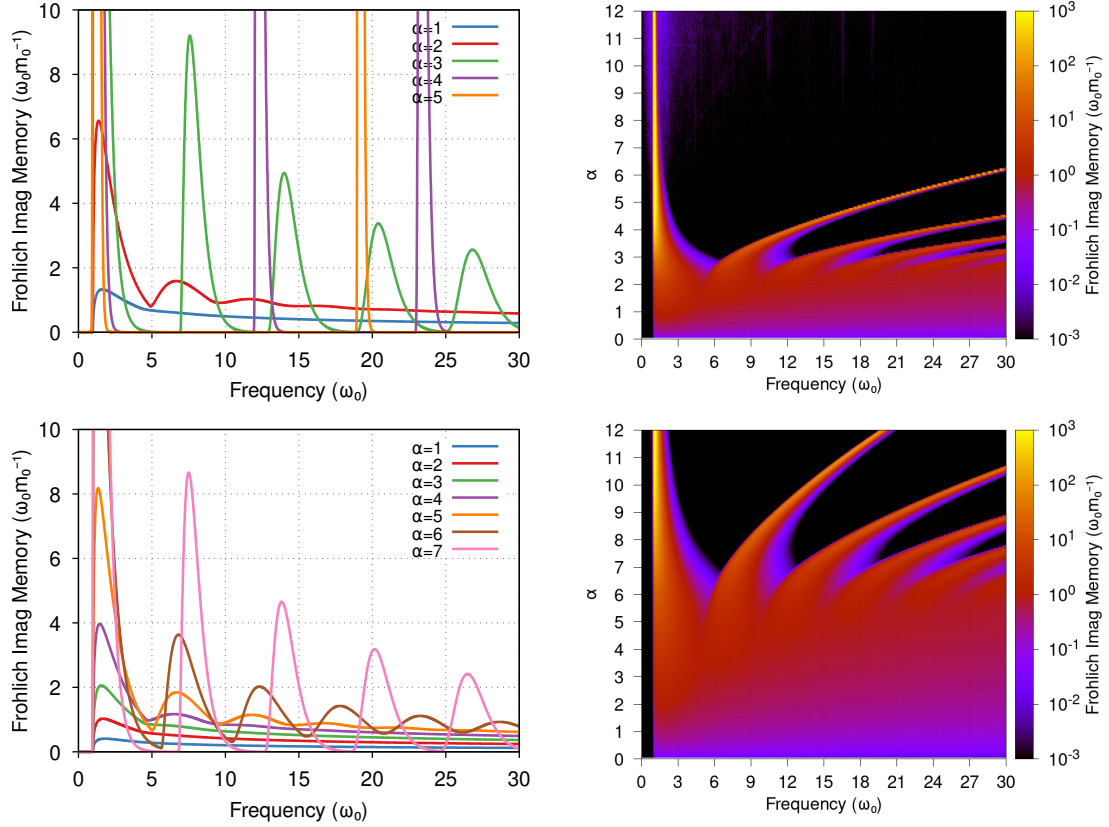


Figure 2.7: The electron-phonon α coupling- and frequency-dependence (Ω in units of ω_0) of the 2D (top) and 3D (bottom) Fröhlich polaron imaginary memory function $\text{Im } \Sigma(\Omega)$ (units of $\omega_0 m_0^{-1}$).

method. The initial state would then be the reduced equilibrium density matrix for the *entire* model system, as defined by Ōsaka, rather than just the equilibrium density matrix for the phonon system used in FHIP.

Ultimately, I do not use the low-temperature form of the FHIP mobility (Eq. (2.3.3)) in this work. Instead, I perform a direct numerical integration of the integral in the memory function Σ in Eq. (2.203). Whilst the FHIP mobility has incorrect low-temperature behaviour, as my application of the FHIP polaron theory will primarily be to determine the room-temperature mobility, this is safely in the temperature range in most materials for which the FHIP mobility is correct.

2.3.4 FHIP Memory Function Numerical Results

Athermal Memory Function

In Fig. 2.7, we show the frequency and electron-phonon coupling (α) dependence of the Fröhlich polaron's imaginary memory function $\text{Im}\Sigma(\Omega)$ in both 2D (top) and 3D (bottom) systems. The imaginary part of the memory function provides insight into energy dissipation and phonon scattering processes associated with the polaron's dynamics.

In both the 2D and 3D cases, the memory function exhibits a few low-frequency peaks at low coupling ($\alpha = 1$), corresponding to resonant scattering between the polaron and phonon modes. These peaks indicate the presence of excited phonon states, where the polaron dissipates energy by interacting with the lattice. As the electron-phonon coupling strength increases ($\alpha \geq 3$), additional peaks emerge at higher frequencies, reflecting multi-phonon scattering processes. These higher-order peaks indicate that the polaron's interaction with multiple phonon modes contributes to greater energy dissipation.

The heatmaps (right panels) show how the memory function evolves with increasing α . The sharp peaks in both 2D and 3D systems broaden into bands at higher α , indicating stronger phonon scattering and more significant energy dissipation. The 3D system shows smoother and more distributed resonances than the 2D system, where the memory function exhibits sharper transitions between different phonon modes. This suggests that 3D systems offer more spatial freedom for the polaron, resulting in more gradual energy dissipation.

The memory function shows a sharp peak at a low frequency, representing single-phonon dissipation processes. As α increases, multi-phonon processes dominate, leading to several higher-frequency peaks. These peaks can be interpreted as transitions between different energy levels of the polaron, where the electron absorbs or emits multiple phonons simultaneously. The peaks are spaced according to $\Omega = \omega_0 + n \cdot \nu$, where ω_0 is the phonon frequency and ν is Feynman variational parameter. These observations are consistent with previous analyses of polaron dynamics by FHIP [17] and DSG [18].

Thermal Memory Function

Figs. 2.8 and 2.9 illustrate the temperature (T) and frequency (Ω) dependence of the imaginary component of the Fröhlich polaron memory function $\text{Im}\Sigma(\Omega)$, across different values of the electron-phonon coupling constant $\alpha = 1, 2, 3, 4, 5, 6$.

At weak coupling ($\alpha = 1$, top-left panels), the memory function exhibits a small, broad peak centred around low frequencies ($\Omega \approx 2 - 4\omega_0$), indicating limited dissipation and weak one-phonon interactions. As temperature increases, the dissipation shifts slightly to higher frequencies, but the overall magnitude remains small. This suggests that energy loss mechanisms are relatively inefficient in the weak-coupling regime.

As the coupling strength increases ($\alpha = 2$ to 3), we observe the development of more pronounced peaks in the memory function, corresponding to stronger dissipation processes as the polaron couples more intensely with the phonon bath. These peaks blueshift toward higher frequencies as temperature increases, reflecting the thermal activation of phonon modes and the enhanced scattering at elevated temperatures. The stronger coupling enhances the energy transfer between the polaron and phonon modes, leading to greater energy loss at specific frequencies.

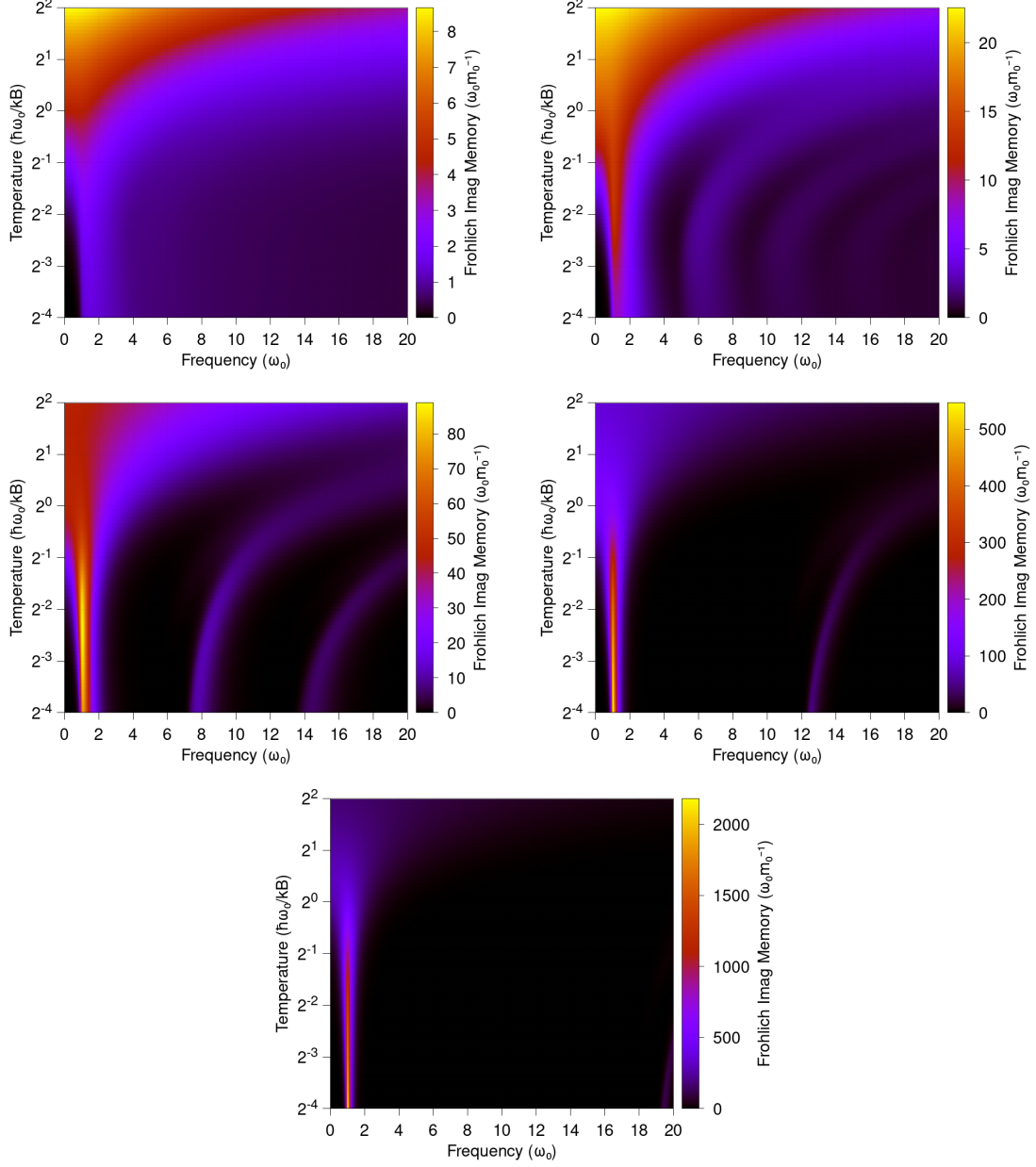


Figure 2.8: The temperature (T in units of $\hbar\omega_0/k_B$)- and frequency-dependence (Ω in units ω_0) of the imaginary component of the 2D Fröhlich polaron memory function $\text{Im } \Sigma(\Omega)$ (units of $\omega_0\omega_0^{-1}$) for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (middle-left), 4 (middle-right) and 5 (bottom).

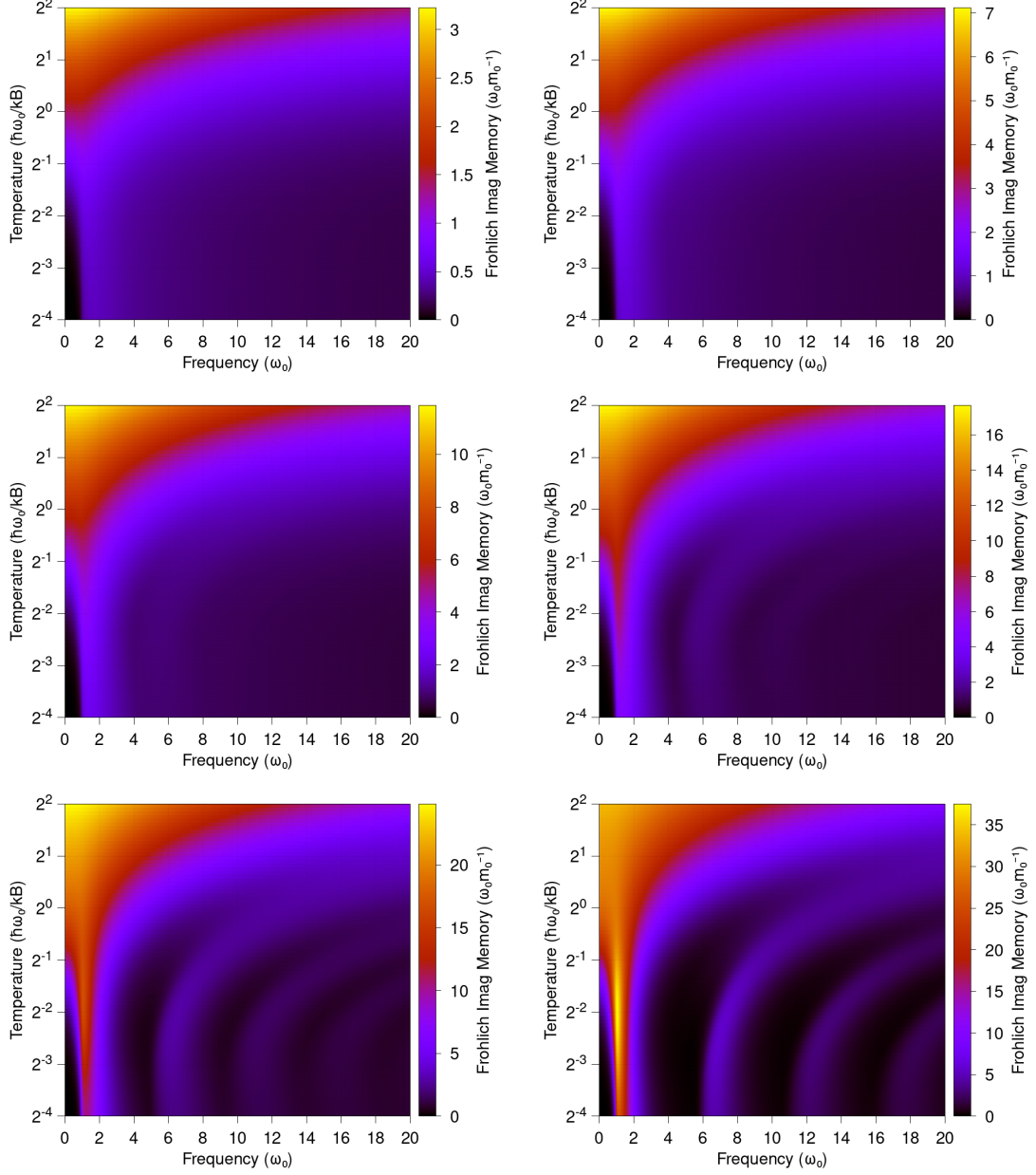


Figure 2.9: The temperature (T in units of $\hbar\omega_0/k_B$)- and frequency-dependence (Ω in units ω_0) of the imaginary component of the 3D Fröhlich polaron memory function $\text{Im } \Sigma(\Omega)$ (units of $\omega_0\omega_0^{-1}$) for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (middle-left), 4 (middle-right), 5 (bottom-left) and 6 (bottom-right).

In the strong-coupling regime ($\alpha = 4, 5, 6$), the memory function displays multiple well-defined peaks, particularly at higher frequencies ($\Omega \approx 8 - 12\omega_0$). These peaks indicate multi-phonon scattering processes, where multiple phonon modes contribute to the dissipation of polaron energy. These peaks broaden significantly at high temperatures, signalling increased thermal effects on the dissipation mechanism. Sharp, high-frequency peaks highlight the Franck-Condon transitions, where the polaron loses energy through a series of phonon emissions at different frequencies during the electronic transition.

2.3.5 Optical Conductivity

Devreese, Sitter and Gooverts [18] (otherwise referred to as “DSG”) expand upon the work done in FHIP by evaluating the optical absorption coefficient (i.e. the optical conductivity) of the polaron. To obtain this coefficient, they compare the expansion of the conductivity $\sigma(\Omega) = 1/z(\Omega)$ to the expansion of the impedance (used by FHIP) $z(\Omega)$ and find further justification for the accuracy of the impedance function expansion. This, in turn, provides a more accurate expression for the frequency-dependent complex mobility $\mu(\Omega)$. To achieve this, they find an expression for the real component of the impedance function $\text{Re}\Sigma(\Omega)$. They then evaluate both $\text{Re}\Sigma(\Omega)$ and $\text{Im}\Sigma(\Omega)$ at zero temperature ($\beta = \infty$) by deriving involved analytical expressions.

DSG state the relation between the optical absorption coefficient $\Gamma(\Omega)$ and the impedance $z(\Omega)$ of polarons as,

Optical Absorption

$$\Gamma(\Omega) = \frac{1}{c\epsilon_0 n} \text{Re} \left\{ \frac{1}{z(\Omega)} \right\}, \quad (2.217)$$

where ϵ_0 is the dielectric constant of the vacuum, n is the index of refraction of the medium, and c is the speed of light. DSG find that for the expansion of $z(\Omega)$ at zero temperature, the optical absorption coefficient requires both the real $\text{Re}z(\Omega)$ and imaginary $\text{Im}z(\Omega)$ components of the impedance (or of $\Sigma(\Omega)$). They obtain the expression,

$$\Gamma_z(\Omega) = \frac{1}{c\epsilon_0 n} \lim_{\beta \rightarrow \infty} \frac{\text{Im}\Sigma(\Omega)}{\Omega^2 - 2\Omega\text{Re}\Sigma(\Omega) + |\Sigma(\Omega)|^2}, \quad (2.218)$$

where the subscript denotes that this optical absorption was obtained from the expansion of the impedance. If the expansion of the conductivity $1/z(\Omega)$ is used instead then they obtain,

$$\Gamma_\sigma(\Omega) = \frac{\text{Im}\Sigma(\Omega)}{\Omega^2} \left(\frac{\Omega^2 - w^2}{\Omega^2 - v^2} \right)^2. \quad (2.219)$$

DSG rigorously takes the zero temperature limit $\beta \rightarrow \infty$ by taking the limit directly in the expression for $\Sigma(\Omega)$ in Eq. (2.203). The real and imaginary components at zero temperature ($\beta = \infty$) are,

$$\text{Re}\Sigma(\Omega) = \text{Im} \int_0^\infty du \frac{[1 - \cos(\Omega u)] e^{iu}}{\Omega [R(1 - e^{ivu}) - iu]^{3/2}}, \quad (2.220a)$$

$$\text{Im}\Sigma(\Omega) = \text{Im} \int_0^\infty du \frac{\sin(\Omega u) e^{iu}}{\Omega [R(1 - e^{ivu}) - iu]^{3/2}}, \quad (2.220b)$$

where $R = (v^2 - w^2)/(w^2v)$. By using a binomial expansion of the denominator of the integrand, we get,

$$\text{Re}\Sigma(\Omega) = \frac{2\alpha}{3\Omega} \frac{v^3}{w^3} \sum_{n=0}^\infty C_{-3/2}^n (-1)^n R^n \times \text{Im} \int_0^\infty du \frac{[1 - \cos(\Omega u)] e^{i(1+nv)u}}{[R - iu]^{3/2+n}}, \quad (2.221a)$$

$$\text{Im}\Sigma(\Omega) = \frac{2\alpha}{3\Omega} \frac{v^3}{w^3} \sum_{n=0}^\infty C_{-3/2}^n (-1)^n R^n \times \text{Im} \int_0^\infty du \frac{\sin(\Omega u) e^{i(1+nv)u}}{[R - iu]^{3/2+n}}, \quad (2.221b)$$

where C_r^n are the binomial coefficients. For $\text{Im}\Sigma(\Omega)$ at $\beta = \infty$ DSG find the expansion,

$$\begin{aligned} \text{Im}\Sigma(\Omega) = & \frac{2\alpha}{3\Omega} \frac{v^3}{w^3} \sum_{n=0}^\infty C_{-3/2}^n (-1)^n \frac{(2R)^n}{(2n+1)!!} \\ & \times |\Omega - 1 - nv|^{n+1/2} e^{-|\Omega-1-nv|R} \frac{1 + \text{sgn}(\Omega - 1 - nv)}{2}, \end{aligned} \quad (2.222)$$

where $(2n+1)!! = (2n+1) \dots 5 \cdot 3 \cdot 1$ indicates the double factorial. In FHIP, they stated the first two terms of this expansion. FHIP find that following the same procedure for $\text{Re}\Sigma(\Omega)$ is far more complicated and has poor convergence properties. Therefore, DSG transform the integrals in Eq. (2.221b) to integrals with rapidly convergent integrands to give the result,

$$\begin{aligned} \text{Re}\Sigma(\Omega) = & -\frac{2\alpha}{3\Omega} \frac{v^3}{w^3} \sum_{n=0}^\infty \frac{1}{\Gamma(n+3/2)} \int_0^\infty dx \left[\left(n + \frac{1}{2}\right) x^{n-1/2} e^{-Rx} - R x^{n+1/2} e^{-Rx} \right] \\ & \times \ln \left| \frac{(1 + nv + x)^2}{\Omega^2 - (1 + nv + x)^2} \right|^{\frac{1}{2}}. \end{aligned} \quad (2.223)$$

From these expansions of $\text{Re}\Sigma(\Omega)$ and $\text{Im}\Sigma(\Omega)$ DSG evaluate the optical absorption coefficient.

In Appendix D, I have derived the expansions of $\text{Re}\Sigma(\Omega)$ and $\text{Im}\Sigma(\Omega)$ for finite temperatures in terms of hypergeometric functions.

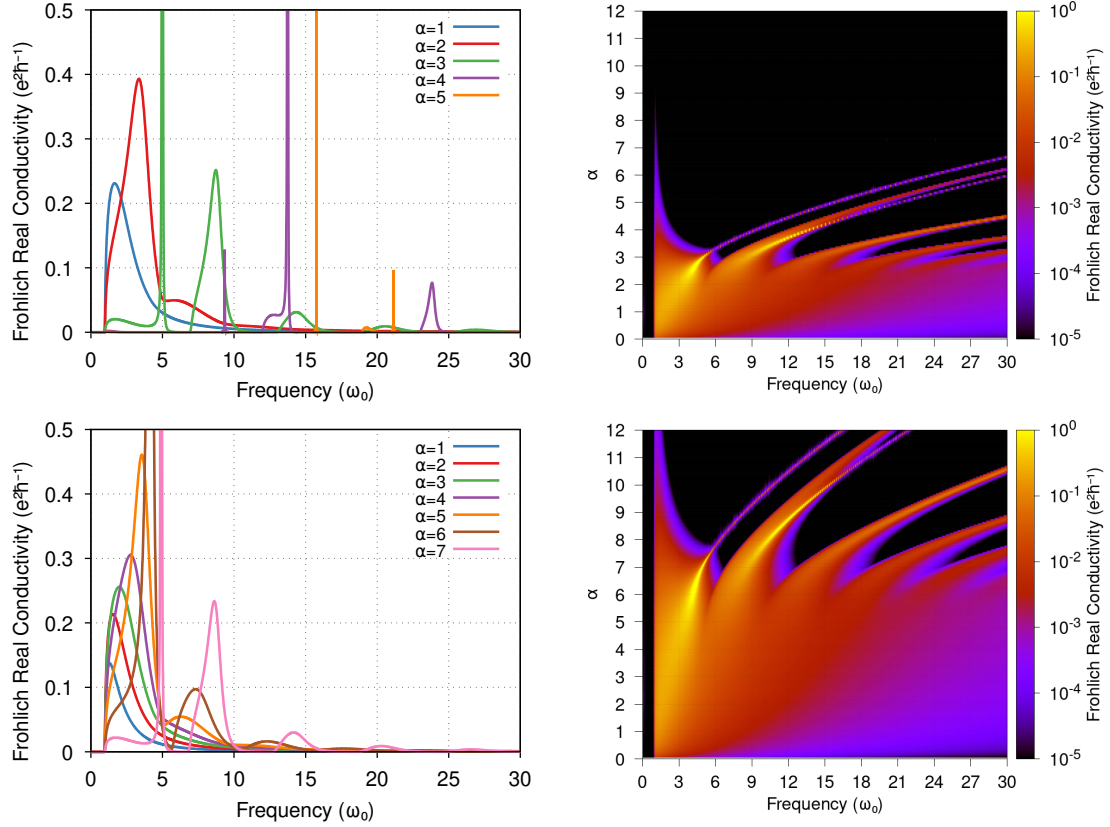


Figure 2.10: The electron-phonon α coupling- and frequency-dependence (Ω in units of ω_0) of the 2D (top) and 3D (bottom) Fröhlich polaron real conductivity $\text{Re } \sigma(\Omega)$ (units of $e^2\hbar^{-1}$).

2.3.6 DSG Optical Conductivity Numerical Results

Athermal Optical Conductivity

In Fig 2.10, we show the frequency and electron-phonon coupling (α) dependence of the Fröhlich polaron optical conductivity $\sigma(\Omega)$ (in units of $e^2/\hbar$) for 2D (top row) and 3D (bottom row) systems. The left column shows real conductivity as a function of frequency for different coupling strengths $\alpha = 1, 2, 3, 4, 5, 6, 7$, while the right column displays heatmaps of the conductivity over a broader range of frequencies and coupling strengths. These were produced using our codes [11].

As discussed in DSG [18], the spectra exhibit distinct peaks in both 2D and 3D cases corresponding to optical absorption processes mediated by electron-phonon interactions. These peaks can be interpreted as the ‘one-phonon’ peak starting at the phonon frequency $\Omega = \omega_0$ followed by ‘Franck-Condon (FC) peaks’, which arise from transitions between vibrational states of the polaron at frequencies $\Omega = \omega_0 + n \cdot \nu$ where n is an integer and ν the Feynman variational parameter. As the electron is excited by a photon, it moves to an excited vibrational state, and the FC principle explains the vertical transitions between

vibrational levels. In the case of polarons, these peaks reflect transitions from the ‘relaxed excited state’ (RES) of the polaron back to the ground state.

For weak coupling ($\alpha = 1$ or 2), the conductivity shows well-defined peaks at lower frequencies, corresponding to weak electron-phonon interactions. As α increases, the peaks shift to higher frequencies, and new peaks appear, indicating the formation of higher-order FC bands. These peaks correspond to transitions involving multiple phonon modes, reflecting the increasingly complex interaction between the polaron and the lattice.

In the 3D case (bottom row), the peaks are distinct for $\alpha > 6$. The heatmaps in the right column show how these FC peaks evolve as a function of both α and frequency, with sharp peaks in the conductivity corresponding to resonant absorption processes. As the coupling strength α increases, the peaks sharpen and blueshift to higher frequencies, reflecting the increased absorption corresponding to the higher-order multi-phonon processes.

The appearance of multiple peaks in the spectra can be associated with the FC effect, where transitions occur between multiple vibrational states due to strong electron-phonon interactions. These transitions are not limited to the lowest vibrational state but can involve higher vibrational excitations, leading to the emergence of bands at higher frequencies. In the strong coupling regime ($\alpha > 5$), the complexity of the optical absorption spectrum increases significantly due to the many vibrational states involved.

The relation between the 2D and 3D systems is provided by the scaling relations in Eq. (2.142). This is evident from the heatmaps, where the 2D optical absorption is ‘squashed’ to lower α s compared to the 3D system.

Thermal Optical Conductivity

In Figs. 2.11 and 2.12, we analyse the optical absorption spectra of the Fröhlich polaron in both 2D and 3D systems, focusing on the features arising from Franck-Condon (FC) states, relaxed excited states (RES), dissipation, and multi-phonon processes.

The left figure presents the real part of the optical conductivity $\text{Re } \sigma(\Omega)$ as a function of frequency Ω (in units of the phonon frequency ω_0) for various electron-phonon coupling strengths α . The right figure provides contour plots showing the evolution of the conductivity with both frequency and coupling strength.

At weak coupling ($\alpha \approx 1$), we observe a single prominent peak in the optical conductivity at low frequencies ($\Omega \approx 1 \omega_0$). This peak corresponds to the fundamental ‘one-phonon’ polaron absorption, where an electron transitions from the ground state to an excited state by absorbing a phonon. The process involves minimal lattice distortion, and the polaron remains relatively delocalised, allowing band-like transport.

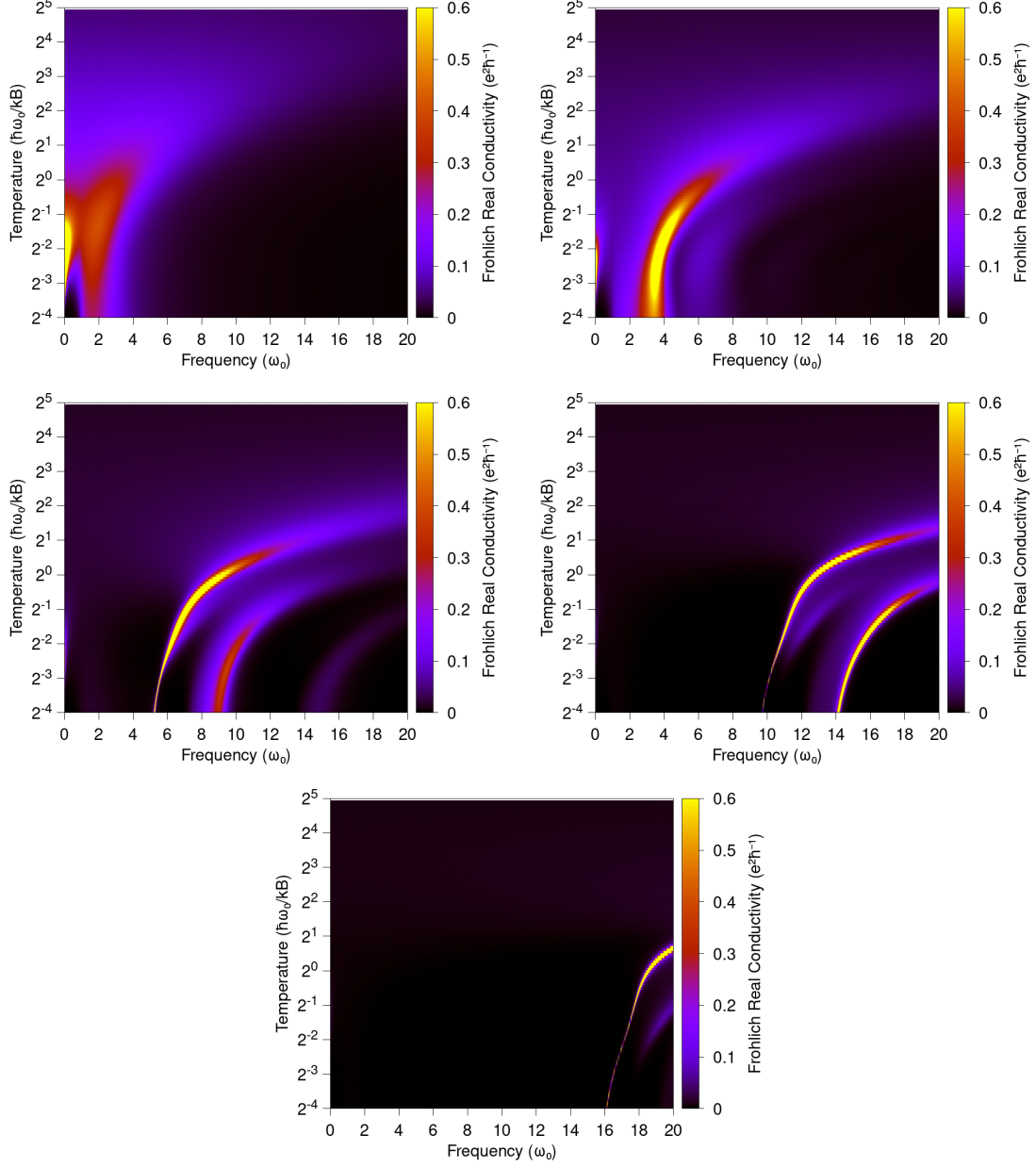


Figure 2.11: The temperature (T in units of $\hbar\omega_0/k_B$)- and frequency-dependence (Ω in units of ω_0) of the real component of the 2D Fröhlich polaron conductivity $\text{Re } \sigma(\Omega)$ (units of $e^2\hbar^{-1}$) for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (middle-left), 4 (middle-right) and 5 (bottom)

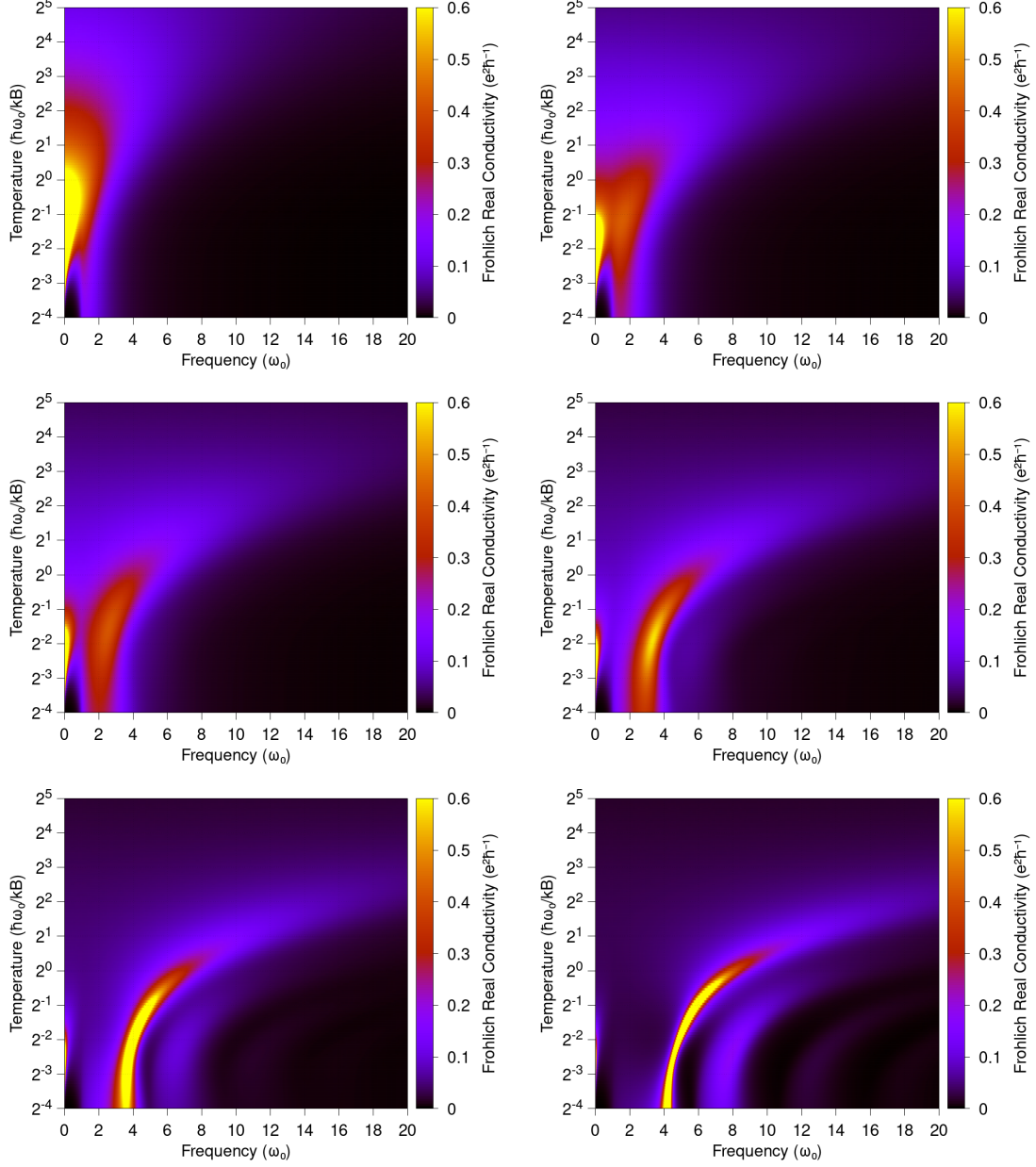


Figure 2.12: The temperature (T in units of $\hbar\omega_0/k_B$)- and frequency-dependence (Ω in units of ω_0) of the real component of the 3D Fröhlich polaron conductivity $\text{Re } \sigma(\Omega)$ (units of $e^2\hbar^{-1}$) for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (middle-left), 4 (middle-right), 5 (bottom-left) and 6 (bottom-right).

As the coupling strength α increases, the optical conductivity spectra exhibit additional peaks at higher frequencies. These are identified as FC peaks, arising from transitions between vibrational states of the polaron that involve multiple phonon excitations. The FC principle explains that optical transitions occur without a change in the position of the nuclei, leading to a spectrum of peaks corresponding to different vibrational levels. In the strong coupling regime ($\alpha > 5$), the polaron becomes more localised due to stronger electron-phonon interactions, resulting in more pronounced FC bands.

The emergence of these multiple peaks indicates the involvement of multi-phonon processes. The polaron absorbs or emits multiple phonons during optical transitions, which becomes increasingly probable at higher coupling strengths. This leads to a richer and more complex absorption spectrum, with peaks shifting to higher frequencies as α increases, reflecting the higher energy required for these multi-phonon excitations.

We also observe RES peaks in the spectra. These peaks occur when the polaron relaxes to a lower-energy excited state before recombining, a process that involves the emission of phonons and contributes to additional features at lower frequencies. The RES peaks become more significant in the strong coupling regime, where strong interactions with the phonon field enhance the polaron's relaxation processes.

As the polaron interacts more strongly with the lattice at higher α , energy is lost through phonon emission and absorption, leading to broader and less sharply defined peaks. This broadening is more pronounced in the 2D system, where reduced dimensionality enhances electron-phonon interactions, resulting in greater dissipation and overlapping spectral features.

Comparing the 2D and 3D systems, we find that the 3D polaron spectra exhibit sharper and more distinct peaks. The increased spatial freedom in 3D allows the polaron to couple to phonons across a wider range of energies with less dissipation. In contrast, the 2D system shows broader peaks and more overlap between FC bands, indicating stronger localisation and higher dissipation due to the confined dimensionality.

2.3.7 Effective Multimode Mobility

Hellwarth and Biaggio [21] extended the Fröhlich model to cases where multiple phonon modes are present in a polar cubic material. They did this by deriving the full classical field Lagrangian that describes one conduction-band electron with charge $-e$, isotropic band mass m_0 and position $\mathbf{r}_{el}(t)$, which is coupled to a polar cubic lattice that possesses many infrared-active modes with varying strengths and frequencies. They derive an effective electron-phonon coupling constant that generalises Fröhlich's α parameter. Then, rather than explicitly incorporating the frequencies of multiple phonon modes into the Feynman path integral polaron model, they propose two different schemes for deriving an effective longitudinal optical phonon frequency. This enables them to directly use Ōsaka's finite-temperature variational principle for determining the temperature-dependent variational parameters v and w needed to evaluate the FHIP mobility.

As usual with Fröhlich polarons, they assume that the lattice unit cell is small compared to the electron wavelength such that the lattice polarisation density $\mathbf{P}(\mathbf{r}, t)$ can be treated as continuous. All other electrons are bound in fully occupied valence bands. The system is then perturbed by a homogeneous electric field $\mathbf{E}(t)$. The polarisation density is composed of many independent terms $\mathbf{P}_j(\mathbf{r}, t)$ where $j = 1, \dots, m; m+1, \dots, m+M$ correspond to the m infrared (lattice) and M ultraviolet (bound electron) modes of the material such that,

$$\mathbf{P}(\mathbf{r}, t) = \sum_{j=1}^{m+M} \mathbf{P}_j(\mathbf{r}, t), \quad (2.224)$$

where it will be useful to separate the transverse (divergence-less) $\mathbf{P}_j^{\text{Tr}}(\mathbf{r}, t)$ and longitudinal (curl-free) $\mathbf{P}_j^{\text{L}}(\mathbf{r}, t)$ parts of the polarisation fields.

Classical Lagrangian and action

Hellwarth's and Biaggio's Lagrangian are presented as

$$\begin{aligned} L = & \int d^3\mathbf{r} \left\{ \sum_{j=1}^{m+M} \frac{2\pi}{\mathcal{K}_j^2} \left[\left(\frac{\partial \mathbf{P}_j(\mathbf{r}, t)}{\partial t} \right)^2 - \mathcal{W}_j^2 \mathbf{P}_j^2(\mathbf{r}, t) \right] + \mathbf{P}_L(\mathbf{r}, t) \cdot \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}(t)) \right. \\ & + \frac{1}{8\pi} \left[\left(\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} \right)^2 - (\nabla \times \mathbf{A}(\mathbf{r}, t))^2 \right] + \frac{1}{c} \mathbf{A}(\mathbf{r}, t) \cdot \frac{\partial \mathbf{P}_{\text{Tr}}(\mathbf{r}, t)}{\partial t} \Big\} \\ & + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \mathbf{P}(\mathbf{r}, t) \cdot \overset{\leftrightarrow}{\mathbf{G}}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}', t) \\ & + \frac{m_0}{2} \left(\frac{d\mathbf{r}_{el}(t)}{dt} \right)^2 + e\mathbf{r}_{el}(t) \cdot \mathbf{E}(t) \end{aligned} \quad (2.225)$$

where $\mathbf{A}(\mathbf{r}, t)$ is the total electric vector potential (assumed purely transverse, i.e. Coulomb gauge), $\mathbf{D}(\mathbf{r}, \mathbf{r}_{el}(t))$ is the longitudinal, un-shielded Coulomb field of the electron given by,

$$\mathbf{D}(\mathbf{r}, \mathbf{r}_{el}(t)) = -e \nabla_{\mathbf{r}} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_{el}(t)|} \right), \quad (2.226)$$

and finally $\vec{\mathbf{G}}(\mathbf{r})$ is the dipole-dipole kernel given by $-\nabla_{\mathbf{r}}^2 |\mathbf{r} - \mathbf{r}'|^{-1}$. The first term in the Lagrangian describes the kinetic and potential energy of the lattice modes where $\mathcal{W}_j$ and $\mathcal{K}_j$ denote the frequencies and oscillator strengths of the isolated lattice modes. The dipole-dipole kernel $\vec{\mathbf{G}}(\mathbf{r} - \mathbf{r}')$ demonstrates a divergent self-interaction as $\mathbf{r} \rightarrow \mathbf{r}'$, so to remove this self-interaction and better imitate the finite size of a unit cell, Hellwarth and Biaggio introduce a cut-off distance $r_0 \sim$ inter-atomic distance. They choose $\vec{\mathbf{G}}(\mathbf{r} - \mathbf{r}')$ to be given by,

$$G_{ab}(\mathbf{r} - \mathbf{r}') = \begin{cases} \frac{3r_a r_b}{|\mathbf{r} - \mathbf{r}'|^5} - \frac{\delta_{ab}}{|\mathbf{r} - \mathbf{r}'|^3}, & |\mathbf{r} - \mathbf{r}'| > r_0, \\ 0, & |\mathbf{r} - \mathbf{r}'| \leq r_0. \end{cases} \quad (2.227)$$

so that it drops to zero at and below this cut-off.

Transforming the action to frequency and reciprocal space

The polarisation $\mathbf{P}_j(\mathbf{r}, t)$ and electric vector potential $\mathbf{A}(\mathbf{r}, t)$ coordinates appear up to second order in the Lagrangian (Eq. (2.225)) but are coupled. Hellwarth and Biaggio seek to uncouple these coordinates by transforming them to normal coordinates, rewriting the action corresponding to Eq. (2.225) in terms of the Fourier transforms of the fields (denoted with a tilde),

$$\tilde{\mathbf{P}}_j^{\text{Tr/L}}(\mathbf{q}, \Omega) = \int dt \int d^3\mathbf{r} \mathbf{P}_j^{\text{Tr/L}}(\mathbf{r}, t) e^{i\Omega t - i\mathbf{q} \cdot \mathbf{r}}, \quad (2.228)$$

$$\tilde{\mathbf{A}}(\mathbf{q}, \Omega) = \int dt \int d^3\mathbf{r} \mathbf{A}(\mathbf{r}, t) e^{i\Omega t - i\mathbf{q} \cdot \mathbf{r}}, \quad (2.229)$$

$$\tilde{\mathbf{D}}(\mathbf{q}, \Omega) = \int dt \int d^3\mathbf{r} \mathbf{D}(\mathbf{r}, \mathbf{r}_{el}(t)) e^{i\Omega t - i\mathbf{q} \cdot \mathbf{r}}, \quad (2.230)$$

$$\tilde{\mathbf{G}}_{ab}(\mathbf{q}) = \int d^3\mathbf{r} \mathbf{G}_{ab}(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}, \quad (2.231)$$

where $\tilde{\mathbf{P}}(\mathbf{q}, \Omega) = \tilde{\mathbf{P}}_L(\mathbf{q}, \Omega) + \tilde{\mathbf{P}}_{\text{Tr}}(\mathbf{q}, \Omega)$. Since the electron wavefunction is assumed larger than the cut-off distance r_0 , Hellwarth and Biaggio keep only the lowest-order terms of the dipole-dipole kernel and write,

$$G_{ab}(\mathbf{q}) = \begin{cases} \frac{4\pi}{3} \left(\delta_{ab} - \frac{3k_a k_b}{q} \right), & q \ll \frac{1}{r_0}, \\ 0, & \text{larger } q. \end{cases} \quad (2.232)$$

Fourier transforming and assuming the absence of any terms where q is not $\ll r_0^{-1}$, Hellwarth and Biaggio obtain the frequency and wave-vector version of the action,

$$\begin{aligned}
 S = & \frac{1}{(2\pi)^4} \int d\Omega \int d^3\mathbf{q} \left\{ \sum_{j=1}^{m+M} 2\pi \frac{\Omega^2 - \mathcal{W}_j^2}{\mathcal{K}_j^2} \left[\left| \tilde{\mathbf{P}}_{\text{Tr}}(\mathbf{q}, \Omega) \right|^2 + \left| \tilde{\mathbf{P}}_{\text{L}}(\mathbf{q}, \Omega) \right|^2 \right] \right. \\
 & + \tilde{\mathbf{P}}_{\text{L}}(\mathbf{q}, \Omega)^* \cdot \tilde{\mathbf{D}}(\mathbf{q}, \Omega) \\
 & + \frac{1}{8\pi} \left(\frac{\Omega^2}{c^2} - q^2 \right) \left| \tilde{\mathbf{A}}(\mathbf{q}, \Omega) \right|^2 \\
 & + i \frac{\Omega}{c} \tilde{\mathbf{A}}(\mathbf{q}, \Omega)^* \cdot \tilde{\mathbf{P}}_{\text{Tr}}(\mathbf{q}, \Omega) \\
 & \left. + \frac{2\pi}{3} \left[\left| \tilde{\mathbf{P}}_{\text{Tr}}(\mathbf{q}, \Omega) \right|^2 - 2 \left| \tilde{\mathbf{P}}_{\text{L}}(\mathbf{q}, \Omega) \right|^2 \right] \right\} + S_{\text{el}}[\mathbf{r}_{\text{el}}(t)],
 \end{aligned} \tag{2.233}$$

where $S^{\text{el}}[\mathbf{r}_{\text{el}}(t)]$ is the action that depends on the electron coordinates $\mathbf{r}_{\text{el}}(t)$ (the last line of the Lagrangian in Eq. (2.225)).

Effective action for the electron-phonon interaction

Hellwarth and Biaggio follow the same procedure as [2] to evaluate the quantum-mechanical unitary transformation matrices $U(\mathbf{r}_{\text{el},f}, \mathbf{P}_f, t_f; \mathbf{r}_{\text{el},i}, \mathbf{P}_{ir}, t_i)$ with path integrals over the polarisation fields $\mathbf{P}(\mathbf{r}, t)$ and electron position $\mathbf{r}(t)$,

$$\begin{aligned}
 U(\mathbf{r}_{\text{el},f}, \mathbf{P}_f, t_f; \mathbf{r}_{\text{el},i}, \mathbf{P}_{ir}, t_i) = & \int_{\mathbf{r}_{\text{el},i}, t_i}^{\mathbf{r}_{\text{el},f}, t_f} D\mathbf{r}(t) \\
 & \times \int_{\mathbf{P}_{ir}, t_i}^{\mathbf{P}_f, t_f} D\mathbf{P}(\mathbf{r}, t) \exp \left\{ \frac{iS[\mathbf{r}(t), \mathbf{P}(\mathbf{r}, t)]}{\hbar} \right\},
 \end{aligned} \tag{2.234}$$

where $S[\mathbf{r}(t), \mathbf{P}(\mathbf{r}, t)]$ is the action functional corresponding to the Lagrangian in Eq. (2.225). The path integral over all trajectories of the polarisation coordinates $\mathbf{P}(\mathbf{r}, t)$ can be done precisely as before since they only appear up to quadratic order in the Lagrangian. Hellwarth and Biaggio evaluate the matrix element $\langle 0 | U(\mathbf{r}_{\text{el},f}, \mathbf{P}_f, t_f; \mathbf{r}_{\text{el},i}, \mathbf{P}_{ir}, t_i) | 0 \rangle$ where the polarisation coordinate paths begin and end in the ground state for all unperturbed polarisation oscillators. The result is an effective model action akin to Feynman's (Eq. (2.83)) where the polarisation coordinates have been replaced by their classical solutions with no external field $\tilde{\mathbf{A}}(\mathbf{q}, \Omega) = 0$. For the transverse part of the polarisation density, the classical solution $\tilde{\mathbf{P}}_{C,j}^{\text{Tr}}(\mathbf{q}, \Omega)$ obeys the equation of motion,

$$4\pi \frac{\Omega^2 - \mathcal{W}_j^2}{\mathcal{K}_j^2} \tilde{\mathbf{P}}_{C,j}^{\text{Tr}}(\mathbf{q}, \Omega) + \frac{4\pi}{3} \tilde{\mathbf{P}}_C^{\text{Tr}}(\mathbf{q}, \Omega) + i \frac{\Omega}{c} \tilde{\mathbf{A}}(\mathbf{q}, \Omega) = 0, \tag{2.235}$$

and the longitudinal part of the polarisation density, the classical solution $\tilde{\mathbf{P}}_{C,j}^L(\mathbf{q}, \Omega)$ obeys the equation of motion,

$$4\pi \frac{\Omega^2 - \mathcal{W}_j^2}{\mathcal{K}_j^2} \tilde{\mathbf{P}}_{C,j}^L(\mathbf{q}, \Omega) - \frac{8\pi}{3} \tilde{\mathbf{P}}_C^L(\mathbf{q}, \Omega) + \tilde{\mathbf{D}}(\mathbf{q}, \Omega) = 0. \quad (2.236)$$

Hellwarth and Biaggio found the solution to these equations of motion to be,

$$\tilde{\mathbf{P}}_C^{\text{Tr}}(\mathbf{q}, \Omega) = \sum_{j=1}^{m+M} \tilde{\mathbf{P}}_{C,j}^{\text{Tr}}(\mathbf{q}, \Omega) = -i \frac{\Omega}{c} \tilde{\mathbf{A}}(\mathbf{q}, \Omega) \frac{\alpha(\Omega)}{1 - (4\pi/3)\alpha(\Omega)}, \quad (2.237)$$

and,

$$\tilde{\mathbf{P}}_C^L(\mathbf{q}, \Omega) = \sum_{j=1}^{m+M} \tilde{\mathbf{P}}_{C,j}^L(\mathbf{q}, \Omega) = \frac{\alpha(\Omega)}{1 + (8\pi/3)\alpha(\Omega)} \tilde{\mathbf{D}}(\mathbf{q}, \Omega), \quad (2.238)$$

where,

$$\alpha(\Omega) = \frac{1}{4\pi} \sum_{j=1}^{m+M} \frac{\mathcal{K}_j^2}{\mathcal{W}_j^2 - \Omega^2}, \quad (2.239)$$

is the polarisability of a single-unit cell. Substituting $\tilde{\mathbf{P}}_C^{\text{Tr}}(\mathbf{q}, \Omega)$ and $\tilde{\mathbf{P}}_C^L(\mathbf{q}, \Omega)$ into the model action S gives the effective model action,

$$S^{\text{eff}} = S^{\text{el}}[\mathbf{r}(t)] + S^{\text{int}} + S^{\text{norm}}, \quad (2.240)$$

where S^{norm} is a normalisation term that cancels in the matrix element $\langle 0 | U | 0 \rangle$. S^{int} is an effective interaction term given by,

$$S^{\text{int}} = \frac{1}{2(2\pi)^4} \int d\Omega \int d^3\mathbf{q} B(\Omega) \tilde{\mathbf{D}}(\mathbf{q}, \Omega)^* \cdot \tilde{\mathbf{D}}(\mathbf{q}, \Omega), \quad (2.241)$$

where $B(\Omega)$ was obtained from the relation $\tilde{\mathbf{P}}_C^L(\mathbf{q}, \Omega) = B(\Omega) \tilde{\mathbf{D}}(\mathbf{q}, \Omega)$ and is,

$$B(\Omega) = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon(\Omega)} \right) = \frac{\alpha(\Omega)}{1 + (8\pi/3)\alpha(\Omega)} = \frac{1}{4\pi} \sum_{j=1}^{m+M} \frac{\kappa_j^2}{\omega_j^2 - \Omega^2}. \quad (2.242)$$

$B(\Omega)$ is the macroscopic polarisability, where each term in the sum of $B(\Omega)$ acts as a harmonic longitudinal lattice mode with a frequency ω_j and coupling constant κ_j that linearly coupled to the conduction electron field $\tilde{\mathbf{D}}$.

Hellwarth and Biaggio use the Born-Oppenheimer approximation as in the original Fröhlich model by assuming that the bound-electrons (ultraviolet oscillators) response speed is near instantaneous. Therefore, the short-wavelength limit ϵ_∞ of the dielectric constant accounts for the electronic contribution when the ions are immobile. Otherwise, the contribution

corresponding to ionic displacements is assumed to be described by the static dielectric constant ϵ_0 . Therefore, the ions slowly follow the harmonic movement of the electron with a time delay. Hellwarth and Biaggio separate $B(\Omega)$ into infrared and optical contributions where the latter is represented by ϵ_∞ so that

$$B(\Omega) = \tilde{B}(\Omega) + \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_\infty} \right) \quad (2.243)$$

where

$$\tilde{B}(\Omega) = \frac{1}{4\pi} \sum_{j=1}^m \frac{\kappa_j^2}{\omega_j^2 - \Omega^2}. \quad (2.244)$$

This $\tilde{B}(\Omega)$ is the infrared contributions of m polar infrared lattice modes and replaces $B(\Omega)$ when neglecting the ultraviolet contributions. Hence, since the zero frequency limit is represented by ϵ_0 , we can obtain the familiar Pekar factor

$$\sum_{j=1}^m \frac{\kappa_j^2}{\omega_j^2} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}. \quad (2.245)$$

Now it is assumed that the ultraviolet contributions are summarised by ϵ_∞ and an effective band mass m_0 that replaces the electron mass m_e in the effective action S^{eff} . The space-time integral action is needed, so Hellwarth and Biaggio transform the effective action by evaluating the integrals over Ω and $\mathbf{q}$. The frequency integral in S^{int} corresponds to a Fourier-like transform

$$\int \frac{d\Omega}{2\pi} \frac{e^{-i\Omega t}}{\omega_j^2 - \Omega^2} = \frac{ie^{-i\omega_j|t|}}{2\omega_j}. \quad (2.246)$$

and the transform $\tilde{\mathbf{D}}(\mathbf{q}, \Omega)$ is calculated from Eq. (2.230) to give

$$\tilde{\mathbf{D}}(\mathbf{q}, \Omega) = 4\pi i e \int dt e^{i\Omega t} \frac{e^{-i\mathbf{q} \cdot \mathbf{r}_{el}(t)}}{q}. \quad (2.247)$$

Substituting these into S^{int} gives

$$\begin{aligned} S^{\text{int}} &= \frac{ie^2}{(2\pi)^2} \int d^3\mathbf{q} \frac{1}{q^2} \int dt \int dt' e^{i\mathbf{q} \cdot [\mathbf{r}_{el}(t) - \mathbf{r}_{el}(t')]} \sum_{j=1}^m \left(\frac{\kappa_j^2}{\omega_j} e^{-i\omega_j|t-t'|} \right) \\ &= i \frac{e^2}{4} \int dt \int dt' \frac{1}{|\mathbf{r}_{el}(t) - \mathbf{r}_{el}(t')|} \sum_{j=1}^m \left(\frac{\kappa_j^2}{\omega_j} e^{-i\omega_j|t-t'|} \right). \end{aligned} \quad (2.248)$$

Hellwarth and Biaggio find the final form of the effective action, akin to Feynman's, to be

$$S^p = \frac{m_0}{2} \int dt \left(\frac{d\mathbf{r}_{el}(t)}{dt} \right)^2 + \int dt \mathbf{E} \cdot \mathbf{r}_{el}(t) + \frac{i\hbar\omega_p}{2\sqrt{2}} \sum_{j=1}^m \alpha_j \int dt \int dt' \frac{e^{-i\omega_j|t-t'|}}{|\mathbf{r}_{el}(t) - \mathbf{r}_{el}(t')|} \quad (2.249)$$

where we have excluded the infinite normalisation term due to the phonon oscillators (this does not affect the electron coordinate $\mathbf{r}_{el}(t)$ and so can be ignored). The effective action is written in terms of “polaron units”: frequencies are measured relative to a standard lattice frequency ω_p , time in units of ω_p^{-1} , energy $\hbar\omega_p$, lengths $\sqrt{\hbar/(m_0\omega_p)}$, temperature $\hbar\omega_p/k_B$ and mobility $e/(m_0\omega_p)$.

The dimensionless coupling constants α_j generalise the Fröhlich version to multiple phonon modes j and is given by

$$\alpha_j = \frac{\kappa_j^2}{\omega_p \omega_j} \frac{e^2}{\hbar} \left(\frac{m_0}{2\hbar\omega_p} \right)^{\frac{1}{2}}. \quad (2.250)$$

For a single phonon branch with frequency $\omega = \omega_p$ and strength κ then this coupling constant reduces to the familiar α ,

$$\alpha = \frac{\kappa^2}{\omega_p^2} \frac{e^2}{\hbar} \left(\frac{m_0}{2\hbar\omega_p} \right)^{\frac{1}{2}} = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{e^2}{\hbar} \left(\frac{m_0}{2\hbar\omega_p} \right)^{\frac{1}{2}}. \quad (2.251)$$

The dielectric function

To compare to the experiment, Hellwarth and Biaggio seek an expression for the dielectric function $\epsilon(\Omega)$. They first obtain the classical solution for the magnetic vector potential $\tilde{\mathbf{A}}_C(\mathbf{q}, \Omega)$ and find that it obeys the equation of motion

$$\frac{1}{4\pi} \left(\frac{\Omega^2}{c^2} - q^2 \right) \tilde{\mathbf{A}}_C(\mathbf{q}, \Omega) - i \frac{\Omega}{c} \tilde{\mathbf{P}}^{\text{Tr}}(\mathbf{q}, \Omega) = 0. \quad (2.252)$$

By substituting the classical solution for $\tilde{\mathbf{P}}_C^{\text{Tr}}(\mathbf{q}, \Omega)$ in Eq. (2.237) into the equation of motion for $\tilde{\mathbf{A}}_C(\mathbf{q}, \Omega)$ in Eq. (2.252) they find that the classical transverse solutions must also obey (for all $\mathbf{q}$)

$$\left[\frac{1}{4\pi} \left(\frac{\Omega^2}{c^2} - q^2 \right) + \frac{\Omega^2}{c^2} \frac{\alpha(\Omega)}{1 - (4\pi/3)\alpha(\Omega)} \right] \tilde{\mathbf{A}}_C(\mathbf{q}, \Omega) = 0, \quad (2.253)$$

from which they obtain the Lorentz-Lorenz relation for the dielectric function $\epsilon(\Omega)$,

$$\epsilon(\Omega) = n^2(\Omega) = \frac{1 + (8\pi/3)\alpha(\Omega)}{1 - (4\pi/3)\alpha(\Omega)}, \quad (2.254)$$

where $n(\Omega) = qc/\Omega$ is the refractive index.

Obtaining a single effective phonon frequency

Hellwarth and Biaggio use the mobility result from FHIP combined with Ōsaka's temperature-dependent variational parameters. To do this, they reduce the many infrared longitudinal phonon mode frequencies to a single effective frequency. They first compare their athermal effective action in Eq. (2.249) to the thermal effective action derived by Ōsaka in Eq. (2.145). From this comparison, they see that the inclusion of multiple phonon modes converts the influence functional phase Φ (Eq. (2.179)) to a sum over terms differing only in the phonon frequencies ω_j and coupling constants α_j

$$\begin{aligned} \Phi = & -\frac{\hbar^2}{2\sqrt{2}\pi^2} \sum_j \alpha_j r_j \omega_j^2 \int_0^\infty dt \int_0^\infty dt' \int \frac{d^3\mathbf{q}}{q^2} \left\{ \left(e^{i\mathbf{q}\cdot\mathbf{r}_{el}(t)} - e^{i\mathbf{q}\cdot\mathbf{r}'_{el}(t)} \right) \right. \\ & \times \left. \left(D_{\omega_j}(t-t') e^{-i\mathbf{q}\cdot\mathbf{r}_{el}(t')} - D_{\omega_j}^*(t-t') e^{i\mathbf{q}\cdot\mathbf{r}'_{el}(t')} \right) \right\}. \end{aligned} \quad (2.255)$$

In [21], they propose two schemes, labelled 'A' and 'B', to reduce this expression to a single term with an effective frequency ω_{eff} and an effective coupling constant κ_{eff} . They then take the "polaron frequency" to be equal to this effective frequency $\omega_p = \omega_{\text{eff}}$.

In the first scheme, 'A', they seek an effective time kernel $H_{\text{eff}}(t)$ defined by,

$$H_{\text{eff}}(t) \sim \alpha_{\text{eff}} D_{\omega_{\text{eff}}}(t) \quad (2.256)$$

which has the properties

$$H_{\text{eff}}(0) = \sum_{j=1}^m H_j(0). \quad (2.257)$$

This is fulfilled by taking,

Hellwarth 'A' Scheme Effective Phonon Mode

$$\frac{\kappa_{\text{eff}}^2}{\omega_{\text{eff}}} \coth\left(\frac{\hbar\omega_{\text{eff}}\beta}{2}\right) = \sum_{j=1}^m \frac{\kappa_j^2}{\omega_j} \coth\left(\frac{\hbar\omega_j\beta}{2}\right), \quad (2.258)$$

and,

$$\left. \frac{dH_{\text{eff}}(t)}{dt} \right|_{t=0} = \sum_{j=1}^m \left. \frac{dH_j(t)}{dt} \right|_{t=0}. \quad (2.259)$$

This requires,

$$\kappa_{\text{eff}}^2 = \sum_{j=1}^m \kappa_j^2. \quad (2.260)$$

The second scheme, ‘B’, seeks to find the single effective frequency ω_{eff} and coupling constant κ_{eff} to match,

$$\int_0^{\hbar\beta} dt H_{\text{eff}}(it) = \sum_{j=1}^m \int_0^{\hbar\beta} dt H_j(it), \quad (2.261)$$

where they now used the imaginary-time kernel $H(it)$. They found that this expression is fulfilled by,

Hellwarth ‘B’ Scheme Effective Phonon Mode

$$\frac{\kappa_{\text{eff}}^2}{\omega_{\text{eff}}^2} = \sum_{j=1}^m \frac{\kappa_j^2}{\omega_j^2}. \quad (2.262)$$

The second scheme also requires that,

$$\left. \frac{dH_{\text{eff}}(it)}{dt} \right|_{t=0} = \sum_{j=1}^m \left. \frac{dH_j(it)}{dt} \right|_{t=0} \quad (2.263)$$

which also requires,

$$\kappa_{\text{eff}}^2 = \sum_{j=1}^m \kappa_j^2. \quad (2.264)$$

Despite considering temperature dependence, the final result of the second ‘B’ scheme is independent of temperature as the temperature terms cancel.

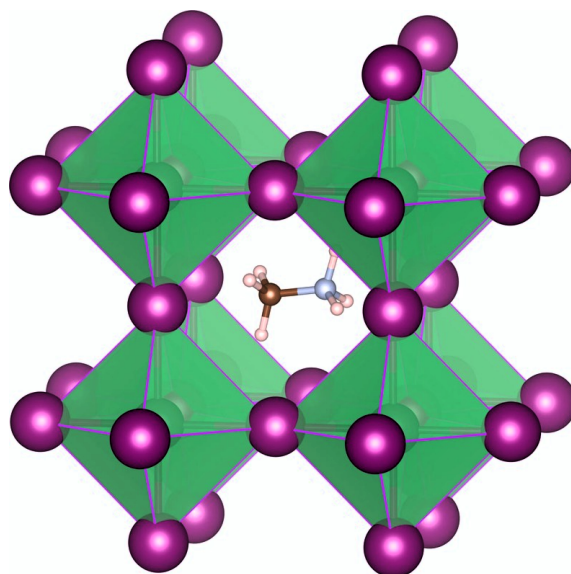


Figure 2.13: Reprinted without permission from ref. [20]. Crystal structure of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskite, referred to here as ‘MAPI’. The green octahedra represents the lead (Pb) atoms at the centre, coordinated by iodine (I) atoms at the vertices. The methylammonium (CH_3NH_3^+) organic cation occupies the spaces between the PbI_3 frameworks, interacting with the inorganic lattice.

2.4 Material Case Studies

2.4.1 Methylammonium Lead Halide Perovskite

Methylammonium lead iodide (MAPI, $\text{CH}_3\text{NH}_3\text{PbI}_3$) is a hybrid organic-inorganic perovskite that has gained significant attention for its remarkable optoelectronic properties, making it a leading material in perovskite solar cells. MAPI crystallises in a perovskite structure (see Fig. 2.13) with the general formula ABX_3 , where A is the organic methylammonium (MA) cation, B is the lead (Pb) cation, and X is the iodide (I) anion. This material exhibits excellent light absorption, long charge carrier diffusion lengths, and high power conversion efficiency in photovoltaic devices. This has driven substantial research into its structural, thermal, and electronic properties.

The structural behaviour of MAPI is temperature-dependent, exhibiting three distinct crystallographic phases: orthorhombic, tetragonal, and cubic. At low temperatures, MAPI adopts an orthorhombic structure, transitions to a tetragonal phase at moderate temperatures, and further transitions into a cubic structure at high temperatures, typically above 327 K. These phase transitions are critical to the material’s properties, as they affect the symmetry, lattice dynamics, and the alignment of the MA cations within the perovskite cage, which, in turn, influence its optoelectronic characteristics.

In the study by Brivio et al. [20], the lattice dynamics and vibrational spectra of MAPbI₃ in its orthorhombic, tetragonal, and cubic phases were analysed using first-principles density functional theory (DFT) calculations. The study focused on understanding how the vibrational modes and phonon interactions evolve across the different phases and how these dynamics contribute to the stability and performance of MAPbI₃ in optoelectronic applications.

In the orthorhombic phase (below ~ 160 K), the MA cations are highly ordered, and the structure is relatively rigid, resulting in distinct vibrational modes characteristic of low symmetry. As the temperature increases and MAPbI₃ transitions into the tetragonal phase (around 160–327 K), the MA cations become more dynamically disordered, allowing for greater rotational freedom. This leads to softening specific phonon modes and lowering the vibrational energy. The study found that in the tetragonal phase, the vibrational spectra show a mix of soft lattice modes and strong coupling between the MA cations and the Pb-I cage.

In the cubic phase, the MA cations exhibit near-complete rotational disorder at high temperatures. The cubic symmetry increases the MA cations' rotational freedom within the Pb-I framework, resulting in further phonon softening and highly anharmonic lattice vibrations. The cubic phase is highly dynamic, with significant coupling between the organic cation motions and the inorganic lattice. Brivio et al. [20] highlighted that this dynamic disorder plays a crucial role in stabilising the cubic phase and impacts the material's electronic properties, such as its bandgap, which slightly changes with temperature.

The vibrational spectra for each phase were analysed in detail to understand the phonon modes contributing to the structural stability and thermal properties of MAPbI₃. The study revealed that the softening of low-frequency phonon modes, particularly in the tetragonal and cubic phases, is associated with the material's propensity for dynamic disorder, affecting the performance of perovskite-based devices. Specifically, the MA cations' dynamic behaviour and the resulting lattice fluctuations can influence charge carrier recombination, affecting the efficiency and stability of solar cells.

2.4.2 Rubrene Organic Crystal

Rubrene, a polycyclic aromatic hydrocarbon, is a well-known organic semiconductor recognized for its high charge-carrier mobility and superior performance in organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs). With a chemical formula of C₄₂H₂₈, rubrene's molecular structure consists of four fused phenyl rings. Its exceptional intrinsic mobility, exceeding $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in single-crystal form [79], makes it one of the most efficient organic materials for electronic devices.

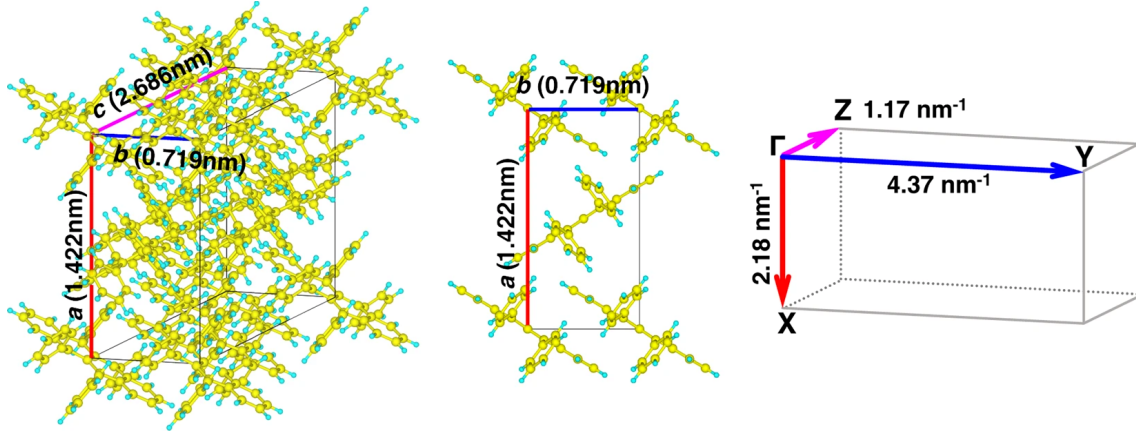


Figure 2.14: Reprinted without permission from ref. [78]. Crystal structure of rubrene showing its orthorhombic unit cell parameters. The unit cell dimensions are $a = 1.422 \text{ nm}$, $b = 0.719 \text{ nm}$, and $c = 2.686 \text{ nm}$. The diagrams highlight the layered molecular arrangement within the unit cell, with the corresponding reciprocal lattice vectors displayed on the right, indicating spatial periodicity in the X, Y, and Z directions.

Rubrene's charge transport properties are highly anisotropic, meaning its mobility depends on the crystallographic direction. This anisotropy is deeply rooted in its crystal packing, where rubrene molecules form π - π stacked columns, facilitating efficient one-dimensional charge transport along specific directions. Fig. 2.14 illustrates the orthorhombic crystal structure of rubrene, highlighting the molecular arrangement and unit cell dimensions, which are critical to understanding its anisotropic behaviour. The figure shows how the π - π stacking occurs along the crystallographic axes, promoting high mobility in certain directions. Meanwhile, weaker van der Waals interactions along the perpendicular directions reduce mobility.

A key factor affecting rubrene's performance in electronic devices is electron-phonon coupling—the interaction between charge carriers (electrons or holes) and lattice vibrational modes (phonons). Strong electron-phonon coupling increases charge carrier scattering, thus reducing mobility. Understanding electron-phonon coupling is crucial for enhancing device efficiency in rubrene, where weak van der Waals forces dominate the intermolecular interactions. The study by Ordejón et al. [22] used ab initio calculations, including density functional theory (DFT), to explore how electron-phonon interactions influence rubrene's charge transport. It focused mainly on low-frequency phonon modes—intermolecular vibrations—that impact mobility.

The study revealed that electron-phonon coupling in rubrene is also anisotropic, with phonon modes coupling to charge carriers differently depending on the transport direction. Phonon modes associated with the π - π stacking direction, which facilitate efficient charge transport, exhibit weaker electron-phonon coupling compared to those in directions per-

pendicular to the stacking. This weaker coupling along the π -stacking direction preserves high carrier mobility, contributing to rubrene's outstanding performance in OFETs.

Low-frequency phonon modes, especially those related to intermolecular vibrations and molecular rotations, were identified as major contributors to electron-phonon coupling. These modes can distort the lattice, increasing charge carrier scattering. The study also showed that electron-phonon coupling in rubrene is weaker than in inorganic semiconductors. However, it still limits the maximum achievable mobility, particularly at higher temperatures where phonon activity increases. Furthermore, lattice dynamics in rubrene contributed to charge localisation effects, where stronger electron-phonon interactions at certain phonon frequencies trap charge carriers, further reducing mobility. This effect becomes more pronounced in disordered or polycrystalline rubrene due to the material's flexibility and weaker intermolecular forces.

2.5 Structure of this Thesis

Chapter 2 introduced foundational methods for modelling polarons, focusing on Feynman’s 1955 variational path integral approximation (FVA) [2] applied to the Fröhlich model [3]. The FVA offers a non-perturbative technique for calculating polaron properties by applying variational principles to a trial action, where a simple harmonic spring coupling models the interaction between an electron and a phonon bath. This was originally used in the Fröhlich polaron model only, which considers the electron-phonon interaction with a parabolic electron band interacting Coulombically with a single optical phonon mode. Building on the FVA, the 1962 Feynman-Hellwarth-Iddings-Platzman (FHIP) [17] approach extends the FVA to calculate dynamic response functions, such as charge-carrier mobility. More recently, Devreese-Sitter-Goovaerts (DSG) [18] provides a framework for calculating optical conductivity.

Several limitations restrict the applicability of these methods to real semiconductors. The Fröhlich Hamiltonian is highly idealised. Real systems have multiple phonon modes, anisotropic and non-parabolic electronic band structures, and phonon dispersion. Notably, the FVA and FHIP methods have not been extended to handle small polarons, which provide a more natural description of polarons in organic crystals where strong localised electron-phonon interactions and significant lattice distortions combine with large effective masses and big unit cells to localise polarons to a single unit cell. Small polaron models, such as the Holstein model [5, 6], are more suitable for describing organic semiconductors.

The FHIP mobility model and DSG theory of optical conductivity are further limited by their oversimplified treatment of the electron-phonon interaction. Both approaches assume the electron is initially in a nonphysical, factorised product state with the phonon bath, simplifying the analysis but introducing inaccuracies. Additionally, they do not incorporate phonon dispersion in the Feynman trial model, a critical aspect of many materials. For instance, while DSG predicts sharp phonon peaks in the optical conductivity due to Franck-Condon (FC) transitions and Relaxed Excited States (RES), these features do not align with the more precise results from Diagrammatic Monte Carlo (DiagMC) simulations. Mishchenko et al. [10] show significant discrepancies from the sharp peaks predicted by DSG, suggesting that the trial action of a single fictitious particle coupled to the electron via a spring is too simple to represent the full spectral function of the phonon bath. Sels [77] and Thornbur [80] highlighted this issue, where they pointed out that the variational principle for the free energy is largely insensitive to distinguishing between different absorption spectra, fundamentally limiting the method’s accuracy in predicting optical conductivity.

Hellwarth and Biaggio [21] illustrate a key limitation in applying FVA. While they extended the FHIP approach to account for multiple phonon modes in polar lattices, their model simplifies complex interactions by reducing them to a single effective phonon mode within the FVA framework. Though computationally expedient, this approximates the spectrum of electron-phonon interaction in real materials as a single mode, where multiple phonon branches with distinct characteristics contribute to the transport properties. A simple semi-classical analysis suggests that in a material such as lead-halide perovskite, these spectral functions would be observed in a frequency-dependent mobility measurement [81].

Such limitations motivate the method development presented in the rest of this thesis. Chapters 3 and 4 introduce significant improvements to the FVA and FHIP methods to address these issues, particularly by incorporating more realistic descriptions of electron-phonon interactions in large and small polarons. The FVA framework is generalised to account for multimode phonon systems and anisotropic effective masses. Additionally, adapting the FVA to the Holstein model allows for a more accurate solution than simply reusing the electron-phonon matrix elements in the Fröhlich FVA. The variational equation itself is improved by generalising to multiple fictitious particles in the trial model, and eventually to a general variational self-energy function. Likewise, we derive a cumulant expansion that gives a tighter variational bound to the free energy, generalising the Feynman-Jensen approach. We present some preliminary theoretical results for generalising these methods to many-body systems and to non-parabolic band electrons using coherent state path integrals and techniques borrowed from many-body Green function methods and quantum field theory.

In chapter 5, these new models are validated by comparisons with DiagMC simulations, ensuring their accuracy for predicting mobility and optical conductivity in complex materials. Finally, in chapter 6 we apply these models to MAPbI₃, Rubrene and 1258 other materials from the Liege dataset [14] to predict their polaronic properties and investigate the applicability of these models.

Finally, in chapter 7, I conclude this dissertation and discuss how this research could be expanded upon in future. These developments aim to overcome the limitations of the historic methods discussed in chapter 2, providing more robust theoretical tools for understanding polaron transport and optical properties in real-world systems and validated and efficient computer codes to model the semiconductors required for renewable energy systems in the 21st century.

CHAPTER 3

GENERALISING THE FEYNMAN ‘MODEL’ ACTION

Greensite “. . . in a sense God did hand us the exact wave function . . . - it’s a Feynman path integral, and the only question is . . .”

Feynman “. . . how to do the integral, yeah!”

—Jeff Greensite and Richard Feynman, *Variational Calculations in Quantum Field Theory*, 1988

In this chapter, I focus on generalising the *model* path integral to more complicated systems beyond the original Fröhlich Hamiltonian. To extend the applicability of the variational method to more materials, I generalise the model path integral to multiple phonon modes in the Fröhlich Hamiltonian; lattice polaron as described by the Holstein Hamiltonian; general electron-phonon interactions for a (possibly anisotropic) parabolic-band electron; and many polarons using coherent-state path integrals.

3.1 Multiple Phonon Modes

IN simple polar materials with two atoms in the basis, the single triply-degenerate optical phonon branch is split by dielectric coupling into the singly-degenerate longitudinal-optical mode and doubly-degenerate transverse-optical modes. Only the longitudinal-optical mode is infrared active and contributes to the Fröhlich dielectric electron-phonon interaction.

The infrared activity of this mode drives the formation of the polaron. Similarly, a range of infrared active modes contributes to polaron stabilisation in more complex polar materials. This relationship is, however, slightly obscured by the algebra in Eq. (2.34), and instead, this electron-phonon coupling seems to emerge from bulk phenomenological quantities, the Pekar factor, $\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}$ being particularly opaque. Rearranging the Pekar factor as

$$\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) = \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_\infty \epsilon_0} = \frac{\epsilon_j^{\text{ionic}}}{\epsilon_\infty \epsilon_0}, \quad (3.1)$$

we can now see that the Fröhlich α is proportional to the ionic dielectric contribution $\epsilon_j^{\text{ionic}}$, as would be expected from appreciating that this is the driving force for polaron formation.

3.1.1 Multimodal Fröhlich Hamiltonian

The relative static dielectric constant is composed out of the high-frequency optical component (from the response of the electronic structure), and then the THz scale vibrational motion of the ions, $\epsilon_0 = \epsilon_\infty + \sum_j \epsilon_j$. This vibrational contribution is typically calculated by summing the infrared activity of the individual harmonic modes as Lorentz oscillators [82]. This infrared activity can be calculated by projecting the Born effective charges along the dynamic matrix (harmonic phonon) eigenvectors from electric-structure calculations. The overall dielectric function across the phonon frequency range can then be written as

$$\epsilon_{\alpha\beta}^0(\omega) = \epsilon_{\alpha\beta}^\infty + \sum_j^{\text{modes}} \epsilon_{\alpha\beta j}^{\text{ionic}}(\omega) = \epsilon_{\alpha\beta}^\infty + \frac{4\pi e^2}{V_0} \sum_{j\nu\mu} \frac{\sum_{\alpha'} Z_{\alpha\alpha'}^{*\mu} u_{\mu j}^{\alpha'} \sum_{\beta'} Z_{\beta\beta'}^{*\nu} u_{\nu j}^{\beta'}}{(\omega_j^2 - \omega^2)} \quad (3.2)$$

where e is the electron charge, V_0 the unit cell volume, $Z_{\alpha\beta}^{*\nu}$ is the Born effective charge tensor at atom ν , $u_{\mu j}^\alpha$ is the dynamic matrix eigenvector at atom μ for the j th phonon branch, ω_j is the dispersionless LO phonon frequency for the j th phonon branch and ω is the reduced frequency. α and β denote Cartesian components. This is the standard approach to predict static dielectric constants computationally.

Considering the isotropic case (and therefore picking up a factor of $\frac{1}{3}$ for the averaged interaction with a dipole) and expressing the static (zero-frequency) dielectric contribution in terms of the infrared activity of a mode, $\epsilon_j^{\text{ionic}}$ is,

$$\epsilon^{\text{ionic}}(\hat{\mathbf{q}}) = \sum_j^{\text{modes}} \epsilon_j^{\text{ionic}}(\hat{\mathbf{q}}) = \frac{4\pi e^2}{3V_0} \sum_j^{\text{modes}} \frac{\left(\sum_{\nu\alpha\beta} q^\alpha Z_{\alpha\beta}^{*\nu} u_{\nu j}^\beta \right)^2}{q^2 \omega_j^2}, \quad (3.3)$$

where $\hat{\mathbf{q}}$ is the unit vector for $\mathbf{q}$ and $q \equiv |\mathbf{q}|$. This provides a clear route to defining α_j for individual phonon branches, with the simple constitutive relationship that $\alpha = \sum_j \alpha_j$,

$$|M_{\mathbf{q}}|^2 = \sum_j^{\text{modes}} \frac{4\pi\hbar(\hbar\omega_j)^{3/2}}{\sqrt{2m_0}V_0q^2} \alpha_j(\hat{\mathbf{q}}) = \frac{2\pi\hbar}{V_0q^2} \sum_j^{\text{modes}} \frac{\omega_j \epsilon_j^{\text{ionic}}(\hat{\mathbf{q}})}{\epsilon_{\infty}(\hat{\mathbf{q}}) \epsilon_0(\hat{\mathbf{q}})} \quad (3.4)$$

where

Multimode Fröhlich Dimensionless Coupling

$$\alpha_j = \frac{1}{4\pi\epsilon_0} \frac{\epsilon_j^{\text{ionic}}}{\epsilon_{\infty}\epsilon_0} \frac{e^2}{\hbar} \left(\frac{m_0}{2\hbar\omega_j} \right)^{\frac{1}{2}}. \quad (3.5)$$

This concept of decomposing α into constituent pieces associated with individual phonon modes is implicit in the effective mode scheme of Hellwarth and Biaggio (Eqs. (2.258) and (2.262)), and has also been used by Verdi, [83] and Devreese [54].

Whilst the effective phonon mode schemes A (Eq. (2.258)) and B (Eq. (2.262)) of Hellwarth and Biaggio are commonly used, including by myself [4], one issue is the effective phonon frequency obtained from the schemes violates the constitutive relationship of the electron-phonon coupling α ,

$$\alpha = \sum_j \alpha_j. \quad (3.6)$$

Instead, we may use this constitutive relationship and the definition of the static dielectric function in Eq. (3.2) to obtain the effective phonon frequency from the ionic dielectric contribution and phonon frequency for each mode j ,

$$\omega_{\text{eff}} = \left[\frac{\sum_j \epsilon_j^{\text{ionic}}}{\sum_j \epsilon_j^{\text{ionic}} \omega_j^{-1/2}} \right]^2, \quad (3.7)$$

which is consistent with Eqs. (3.6) and (3.2). In chapter 6 I use this method to calculate the effective phonon frequency for lead-halide perovskites.

In 1992 [83], Verbist proposed an extended Fröhlich model Hamiltonian in Eq. (2.38) with a sum over multiple (m) phonon branches,

Multimode Fröhlich Polaron Hamiltonian

$$\hat{H} = \frac{p^2}{2m_0} + \sum_{\mathbf{q},j} \hbar \omega_j b_{\mathbf{q},j}^\dagger b_{\mathbf{q},j} + \sum_{\mathbf{q},j} (M_{\mathbf{q},j} b_{\mathbf{k},j} e^{i\mathbf{q}\cdot\mathbf{r}} + M_{\mathbf{q},j}^* b_{\mathbf{q},j}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}}). \quad (3.8)$$

Here, the index j indicates the j^{th} phonon branch. The interaction coefficient is given by

$$M_{\mathbf{q},j} = i \frac{2\hbar\omega_j}{|\mathbf{q}|} \left(\sqrt{\frac{\hbar}{2m_0\omega_j}} \frac{\alpha_j \pi}{V_0} \right)^{1/2}, \quad (3.9)$$

with α_j as in Eq. (3.5).

3.1.2 Multiple Phonon Mode Path Integral

From the Multimodal Fröhlich Hamiltonian, we can write the following extended model action to use within the Feynman variational theory,

$$S_j[\mathbf{r}(\tau)] = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \left(\frac{d\mathbf{r}(\tau)}{d\tau} \right)^2 - \frac{\hbar^{3/2}}{2\sqrt{2m_0}} \alpha_j \omega_j^{3/2} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma \frac{D_{\omega_j}(\tau - \sigma)}{|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|}. \quad (3.10)$$

where $D_{\omega_j}(\tau)$ is the phonon Green function for a phonon with frequency ω_j ,

$$D_{\omega_j}(\tau) = n_{\omega_j} e^{\omega_j|\tau|} + (n_{\omega_j} + 1) e^{-\omega_j|\tau|}. \quad (3.11)$$

This form of action is consistent with Hellwarth and Biaggio's deduction that multiple phonon branches result in the interaction term simply becoming a sum over terms with phonon frequency ω_j and coupling constant α_j dependencies as shown in Eq. (2.249). It is also suggested by the linear nature of the electron-phonon coupling — it has to be additive.

3.2 Small Polarons on a Discrete Lattice

In 1983-1985 [38, 39], Hans De Raedt and Ad Lagendijk derived the discrete path integral for a polaron on a discrete lattice, which was then further developed by Pavel Kornilovitch [45–51] in 1997-2007. Kornilovitch derived the continuous path integral limit of the polaron on a lattice and developed a Continuous-time Path Integral Monte Carlo method (CT-PIMC) for calculating properties of small polarons, focusing on the Holstein model and a lattice-restricted version of the Fröhlich model (which allows for long-range electron-phonon coupling).

The path integral for the partition function of a system is a sum of all possible position and momentum paths in phase space. In the continuum large-polaron model, the sum over all momentum paths can be made as the momentum paths are continuous and unbounded, and the parabolic electronic dispersion is quadratic in momentum. Therefore, the corresponding momentum path integral is an evaluable Gaussian functional integral.

For the small polaron on a lattice, the electronic dispersion is that of a tight-binding model and is not quadratic. Likewise, the momentum and position paths are discrete, and the ‘path-integral’ becomes an infinite summation rather than a functional integral.

In the following section, I re-derive the discrete-time path integral for the Holstein model following the approach taken by De Raedt and Lagendijk [38, 39]. I then present my derivation of the continuous-time limit for the Holstein path integral and approximate the discrete lattice as a continuum and in the limit of an infinite number of lattice sites (the thermodynamic limit). I show that the continuous-time path integral has the same form as the standard phase-space path integral but with the continuum Holstein Hamiltonian.

3.2.1 Discrete-Time Path Integral

We begin with the Holstein Hamiltonian in a mixed representation:

$$\begin{aligned}
 H &= H_0 + H_1 + H_2, \\
 H_0 &= \frac{1}{2M} \sum_{n=1}^N p_n^2, \\
 H_1 &= \frac{M\omega_0^2}{2} \sum_{n=1}^N x_n^2 + g \sum_{n=1}^N x_n c_n^\dagger c_n, \\
 H_2 &= -J \sum_{n=1}^N \left(c_n^\dagger c_{n+1} + c_{n+1}^\dagger c_n \right),
 \end{aligned} \tag{3.12}$$

where the phonons are expressed in their momenta p_n and positions x_n , with n labelling the corresponding lattice site. M is the mass of one lattice site (here, we assume all of them to have the same mass), and ω_0 is the dispersionless phonon frequency, which we assume to have only one mode (i.e. an Einstein mode). The electron description remains in terms of the creation and annihilation operators $c_n^\dagger, c_n$ on lattice-site n .

In deriving the path integral, a system's quantum statistical partition function may be obtained by inserting successive resolutions of identity within the definition of a quantum trace. In the limit of an infinite number of insertions, the Trotter-Suzuki expression [84, 85] gives a direct equality between this discretised partition function Z_M and the total partition function Z :

$$\begin{aligned} Z &\equiv \text{Tr} \left\{ e^{-\beta H} \right\} = \lim_{M \rightarrow \infty} Z_M, \\ Z_M &= \text{Tr} \left\{ \left[e^{-\Delta\tau H_0} e^{-\Delta\tau H_1} e^{\Delta\tau H_2} \right]^M \right\}, \end{aligned} \quad (3.13)$$

where $\Delta\tau = \beta/M$ is the amount of imaginary-time between time-slices.

For the case of a lattice polaron, we have the time-discretised partition function,

$$Z_M = c_1 \Delta\tau^{-\frac{MN}{2}} \sum_{\{r_j\}} \int \left\{ \prod_{j=1}^M \prod_{n=1}^N dx_{n,j} \right\} e^{S_{\text{ph}}} \prod_{i=1}^M I_{\Delta r_i}(2\tau J), \quad (3.14)$$

where $\Delta r_i = r_{i+1} - r_i$ is the change in the electron position across one time-slice and is an integer multiple of the lattice spacing a .

The discretised boson action is

$$S_{\text{ph}} = \sum_{j=1}^M \sum_{n=1}^N \left(\frac{(\Delta x_{n,j})^2}{2\Delta\tau} + \frac{\Delta\tau \omega^2 x_{n,j}^2}{2} + g_H \Delta\tau x_{n,j} \delta_{n,r_j} \right). \quad (3.15)$$

The kinetic portion of the discretised action for the fermion on a lattice is [38]

$$I_{\Delta r_i}(z) = \frac{1}{N} \sum_{n=1}^N \cos \left(\frac{2\pi n \Delta r_i}{Na} \right) \exp \left(-z \cos \left(\frac{2\pi n}{N} \right) \right), \quad (3.16)$$

which is a discrete form of the modified Bessel function of the first-kind $I_m(z)$ [86, (10.32.3)] where here we have $m = \Delta r_i = r_{i+1} - r_i$ and $z = 2J\Delta\tau$. This becomes the normal modified Bessel function of the first-kind $I_m(z)$ in the thermodynamic limit $N \rightarrow \infty$.

The bosonic integrals are Gaussian, and so have closed-form expressions. By expanding the bosonic coordinates in Fourier modes,

$$x_{n,j} = \frac{1}{\sqrt{M}} \sum_{q=0}^{M-1} v_{n,j} \exp\left(\frac{2\pi j q}{M}\right), \quad (3.17)$$

we can diagonalise the bosonic action

$$S_{\text{ph}} = \sum_{n=1}^N \sum_{q=0}^{M-1} \left(\frac{|v_{n,j}|^2}{\Delta\tau D_q^{-1}} + \frac{\Delta\tau g_H v_{n,q}}{\sqrt{M}} \sum_{j=1}^M \delta_{n,r_j} \exp\left(\frac{2\pi j q}{M}\right) \right), \quad (3.18)$$

where

$$D_q^{-1} = 1 - \cos\left(\frac{2\pi q}{M}\right) + \frac{\Delta\tau^2 \omega_0^2}{2} \quad (3.19)$$

is the inverse of the free-phonon Green function.

Integrating over $v_{n,q}$ gives,

$$\begin{aligned} Z_M &= c_2 Z_M^{ph} Z_M^{\text{el}}, \\ Z_M^{ph} &= \left(\prod_{q=0}^{M-1} D_q^{1/2} \right)^N, \\ Z_M^{\text{el}} &= \sum_{\{r_j\}} \left(\prod_{j=1}^M I_{\Delta r_j}(2\Delta\tau J) \right) \exp\left(\Delta\tau^2 \sum_{i=1}^M \sum_{j=1}^M F(i-j) \delta_{r_i, r_j} \right), \end{aligned} \quad (3.20)$$

where c_2 is a coalescence of normalisation factors which will drop out of any expectation values and,

$$F(l) = \frac{\Delta\tau g_H^2}{4M} \sum_{q=0}^{M-1} D_q \cos\left(\frac{2\pi q l}{M}\right) \quad (3.21)$$

is the memory function that fully encodes the electron-phonon interaction over all imaginary times.

Now the kinetic portion of the action is

$$K_M[r_j] = \sum_{j=1}^M \ln \left\{ I_{\Delta r_j}(2J\Delta\tau) \right\}. \quad (3.22)$$

This path integral has no closed-form solution, even for a free electron. Regardless, we could choose the kinetic part of the trial action to be quadratic with an effective mass m_e ,

$$K_{M,\text{trial}}[r_j] = \frac{m_e}{2a^2} \sum_{j=1}^M \left(\frac{\Delta r_j}{\Delta \tau} \right)^2 \Delta \tau. \quad (3.23)$$

The quasi-particle mass term m_e is a variational parameter that minimises the difference between the trial and model actions. However, as the electron positions are discrete (restricted to the lattice sites), the trial path integral would be a discrete Gaussian sum, not a Gaussian integral,

$$Z_{M,\text{trial}} \sim \sum_{\{r_j\}} \exp(K_{M,\text{trial}}[r_j]). \quad (3.24)$$

This sum has no closed-form solution and would have to be evaluated numerically, defeating my goal of using the Feynman variational method to leverage computationally efficient analytic solutions. I would not be able to apply the FHIP theory directly.

Therefore, I will take the continuum limit since we aim to use the Feynman variational method. First, I go to the continuous-time limit of the Holstein path integral.

3.2.2 Continuous-Time Path Integral for the Holstein Model

To obtain the continuous-time limit of the partition function, we first explicitly write out the summation over N lattice sites from the kinetic action (Eq. (3.16)) in the partition function (Eq. (3.20)). Due to the product over the time slices, we now have a product of lattice-site summations from the kinetic action for each time slice,

$$Z_M^{\text{el}} = \frac{1}{(2N)^M} \sum_{\{r_j\}} \sum_{\{n_j\}} \exp \left\{ i \sum_{j=1}^M \frac{2\pi n_j}{Na} \Delta r_j - 2\Delta \tau J \sum_{j=1}^M \cos \left(\frac{2\pi n_j}{N} \right) \right\}, \quad (3.25)$$

where n_j now depends on j . I have used the fact that the kinetic action is even with respect to n and that $\cos(x) = (\exp(ix) + \exp(-ix))/2$ to change the limits of the n_j summations from $\{n_j \mid n_j \in [1, N]\}$ to $\{n_j \mid n_j \in [-N, N], n_j \neq 0\}$. Note that the summations over n_j exclude $n_j = 0$.

We now have a summation of all possible paths a particle can take on the lattice within M time-steps. From the kinetic action, we can see that $2\pi n_j/Na \equiv \Delta k_j$ plays the role of a discrete lattice-momentum multiplying the changes in the electron position Δr_j .

Our electronic partition function is in the form of a discrete phase-space path integral. Therefore, in the continuous-time limit $M \rightarrow \infty$ and $\Delta \tau \rightarrow 0$, the partition function may

be written as

$$Z = CZ_{\text{ph}} \sum_{r(\tau)} \sum_{k(\tau)} \exp\{S_{\text{eff}}\}, \quad (3.26)$$

where C is the accumulation of normalisation factors. The positions $r(\tau)$ and lattice-momenta $k(\tau)$ are still restricted to N discrete values. The effective action is

$$\begin{aligned} S_{\text{eff}} &= K[k(\tau), r(\tau)] - V_{\text{eff}}[r(\tau)], \\ K &= -\frac{2J}{\hbar} \int_0^{\hbar\beta} d\tau \cos(ak(\tau)) + i \int_0^{\hbar\beta} d\tau k(\tau) \dot{r}(\tau), \\ V_{\text{eff}} &= \frac{g_H^2}{4\hbar} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' D_{\omega_0}(\tau - \tau') \delta_{r(\tau), r(\tau')}, \end{aligned} \quad (3.27)$$

where the summations over j have become imaginary-time integrals and

$$\begin{aligned} \lim_{\Delta\tau \rightarrow 0} \{r_j\} &\rightarrow r(\tau), \\ \lim_{\Delta\tau \rightarrow 0} \{\Delta r_j / \Delta\tau\} &\rightarrow dr(\tau)/d\tau \equiv \dot{r}(\tau), \\ \lim_{\Delta\tau \rightarrow 0} \{\Delta k_j\} &\rightarrow k(\tau) \equiv 2\pi n(\tau)/Na. \end{aligned} \quad (3.28)$$

Here $D_{\omega_0}(\tau)$ is the thermal (imaginary-time) phonon Green's function.

To summarise, we have derived the discrete-time Holstein path integral (Eq. (3.20)) by starting with the Holstein Hamiltonian in a mixed representation (Eq. (3.12)), including phonon, electron-phonon coupling, and electronic components. We used the Trotter-Suzuki expression (Eq. (3.13)) to discretise the quantum statistical partition function (Eq. (3.14)) into a form suitable for path integral methods. We then expressed the partition function in terms of bosonic (Eq. (3.15)) and fermionic (Eq. (3.16)) actions, and evaluated the Gaussian integration over the bosonic coordinates. We also discussed how the discrete nature of the Holstein path integral stops us defining an analytically evaluable trial partition function. Finally, we transitioned towards the continuum limit by reformulating the partition function in terms of continuous imaginary-time integrals, leading to an effective action (Eq. (3.27)) that encapsulates the interactions and dynamics of the electron-phonon system.

3.2.3 Thermodynamic and Continuum Limits

In the thermodynamic limit $N \rightarrow \infty$, the summation over all discrete k paths becomes continuous and can be identified with the electron quasi-momentum $k(\tau)$. The discrete sums over k become continuous functional (path) integrals over quasi-momentum paths confined to the first Brillouin Zone.

$$Z = CZ_B \int_{r \in a\mathbf{Z}} Dr(\tau) \int_{k \in [-\frac{\pi}{a}, \frac{\pi}{a}]} Dk(\tau) e^{S_{\text{eff}}}. \quad (3.29)$$

The electron position is still restricted to the lattice, represented above by the set of integers, $\mathbf{Z}$, multiplied by the lattice constant, a .

In the continuum limit $a \rightarrow 0$, the electron position can take any real value $r \in \mathbf{R}$, and the momentum is unbounded, $k \in (-\infty, \infty)$. Here, I assume that $ka \ll 1$ so that these conditions on the electron position and momentum are approximately satisfied. Physically, this describes an electron whose momentum is restricted to magnitudes small compared to those of the reciprocal lattice vectors and in which the electron couples to a single phonon branch (e.g. the longitudinal optical modes in a polar crystal).

The partition function can now be written in the Hamiltonian formulation of the (phase-space) path integral,

$$Z = C \int Dr(\tau) \int Dk(\tau) \exp \left\{ i \int_0^{\hbar\beta} d\tau k(\tau) \dot{r}(\tau) - \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau H_{\text{eff}}[r(\tau), k(\tau)] \right\}, \quad (3.30)$$

where the Hamiltonian is the tight-binding Hamiltonian with an additional non-local effective interaction term,

Holstein Hamiltonian with an Effective Interaction

$$H_{\text{eff}} \approx 2J \cos(ak(\tau)) + g_H^2 \int_0^{\hbar\beta} d\tau' D_{\omega_0}(\tau - \tau') \delta_{r(\tau), r(\tau')}. \quad (3.31)$$

Now, we discover that we could have started with this Hamiltonian (phase-space) path integral, substituted in the Holstein Hamiltonian and performed the path integration over the lattice coordinates to arrive at the same result. This offers an alternative avenue where instead of starting from the Lagrangian (configuration) formulation of the path integral (typically derived by integrating over the momentum coordinates in the Hamiltonian path integral), we may use the Hamiltonian formulation instead. The benefit is that we can now write more general kinetic actions that do not assume the electron bands to be parabolic (the effective mass approximation).

To generalise, we realise that we may substitute a higher-dimensional tight-binding Hamiltonian to generalise to the higher-dimensional effective (meaning the phonons have been integrated to give an effective non-local interaction) Holstein action. The effective interaction term will be similar but with a generalised Kronecker-Delta dependent on vector positions $\mathbf{r}(\tau)$.

3.2.4 The Effective Mass (Parabolic-Band) Approximation

We still face difficulty in applying the variational method. The presence of the cosine in the kinetic action (from the tight-binding band structure) renders the overall action non-convex, even in imaginary time, so Jensen's inequality does not hold.

To make progress, we assume that $ak \ll 1$ and thereby make a parabolic (effective-mass) approximation. Since we have made the continuum approximation, this is a reasonable assumption. From the cosine form of the tight-binding band structure, and using the small-angle approximation $\cos(\theta) = 1 - \theta^2/2$,

$$\epsilon_{\mathbf{k}} = 2J \cos(ak(\tau)) \approx 2J - Ja^2[k(\tau)]^2. \quad (3.32)$$

In one dimension, the kinetic action is approximated by,

$$K = 2J\hbar\beta - \frac{1}{2m_0} \int_0^{\hbar\beta} d\tau [k(\tau)]^2 + i \int_0^{\hbar\beta} d\tau k(\tau) \dot{r}(\tau), \quad (3.33)$$

where the band-mass is $m_0 = \hbar^2/2Ja^2$. By making this approximation, the functional integral over $k(\tau)$ is the same Gaussian form as for a free particle and can be solved exactly.

Overall, I get a parabolic-band Holstein effective action in n -dimensions,

Parabolic Holstein *Model* Action

$$S_{\text{eff}}^{(H)} = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2 - \frac{g_H^2}{\hbar} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' D_{\omega_0}(\tau - \tau') \delta_{\mathbf{r}(\tau), \mathbf{r}(\tau')}. \quad (3.34)$$

I have excluded the $2nJ\hbar\beta$ term since this is band-minimum energy that will be absorbed into the partition function's normalisation factor C .

I reiterate the approximations used to derive this action. First, I went to the thermodynamic limit, which means I do not expect this model to capture any finite-size effects. Second, I make the continuum approximation so that the electron paths can be assumed to be continuous and the electron quasi-momenta unbounded. Third, I approximate the tight-binding (cosine) band with a parabolic band, which is only correct for small crystal quasi-momentum ($ka \ll 1$) and misses contributions when I integrate across reciprocal space; I expect it to break down entirely near the Brillouin-Zone boundaries.

Nonetheless, the model has a genuinely short-range electron-phonon coupling. Upon integrating out the phonons, the short-range electron-phonon coupling presents a non-local point-like interaction of the electron with itself through imaginary time, which is only non-zero when the electron crosses its prior path.

Since the effective model has a Kronecker-delta-like interaction, the *phonon* momentum is (correctly) bounded to remain within the first Brillouin zone. We can see this from the integral representation of the Kronecker delta,

$$\delta_{r,r'} = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dq e^{iq(r-r')}. \quad (3.35)$$

Therefore, the effective model includes the correct discrete lattice description regarding the phonons.

We can generalise the Kronecker-delta to arbitrary dimensions n in Cartesian coordinates

$$\delta_{\mathbf{r},\mathbf{r}'} = \frac{V_n}{(2\pi)^n} \int_{-\pi/a}^{\pi/a} d\mathbf{q} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}, \quad (3.36)$$

where, for example, a cubic unit cell $V_3 = a^3$.

Alternatively, the methodology used by Feynman for the Fröhlich Hamiltonian uses a spherical coordinate representation of the Kronecker-delta in n -dimensions:

$$\delta_{\mathbf{r},\mathbf{r}'} = \frac{V_n S_{n-1}}{(2\pi)^n} \int_0^{\Lambda_n} dq q^{n-1} e^{iq(r-r')}, \quad (3.37)$$

where Λ_n is some momentum cutoff. I assume that the system has rotational invariance so that the angular components of $\mathbf{q} \cdot \mathbf{r}$ can be integrated over to give $S_{n-1} = 2\pi^{n/2}/\Gamma(n/2)$ the surface-“area” of an n -dimensional sphere where $\Gamma(x)$ is the Gamma function.

From this work on the Holstein model, we serendipitously found everything we need to establish the machinery for a general variational method for polarons—one that we can apply to an arbitrary electron-phonon Hamiltonian.

3.3 A General Parabolic Polaron

The Hamiltonian for a general polaron model [87] can be written in momentum-basis second-quantisation form as

General Polaron Hamiltonian

$$H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \sum_{\mathbf{k}, \mathbf{q}} M_{\mathbf{k}, \mathbf{q}} c_{\mathbf{k}+\mathbf{q}}^{\dagger} c_{\mathbf{k}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}}), \quad (3.38)$$

where $\epsilon_{\mathbf{k}}$ is the electron band energy for momentum $\mathbf{k}$, $c_{\mathbf{k}}^{\dagger}$ and $c_{\mathbf{k}}$ are the electron creation and annihilation operators for an electron with momentum $\mathbf{k}$, $\omega_{\mathbf{q}}$ is the phonon frequency for momentum $\mathbf{q}$, $b_{\mathbf{q}}^{\dagger}$ and $b_{\mathbf{q}}$ are the creation and annihilation operators for a phonon with momentum $\mathbf{q}$, $M_{\mathbf{k}, \mathbf{q}}$ is the electron-phonon coupling matrix which describes the strength of the interaction.

For a model describing a parabolic band electron linearly coupled to harmonic phonons, the electron-phonon coupling matrix is independent of the electron momentum, $M_{\mathbf{k}, \mathbf{q}} \rightarrow M_{\mathbf{q}}$. The path integrals over electron momentum and the phonon operators are then Gaussian and can be evaluated analytically. The resultant electron action is only a functional of the electron position, $\mathbf{r}$, and describes a temporally non-local self-interaction acting on the electron,

$$S[\mathbf{r}(\tau)] = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2(\tau) - \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' D_{\omega_0}(\tau - \tau') \Phi[\mathbf{r}(\tau), \mathbf{r}(\tau')], \quad (3.39)$$

where $D_{\omega_0}(\tau)$ is the imaginary-time thermal phonon propagator.

The electron self-interaction functional is

$$\Phi[\mathbf{r}(\tau), \mathbf{r}(\tau')] = \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \rho_{\mathbf{q}}[\mathbf{r}(\tau)] \rho_{-\mathbf{q}}[\mathbf{r}(\tau')]. \quad (3.40)$$

Here $\rho_{\mathbf{q}}[\mathbf{r}(\tau)] = e^{i\mathbf{q} \cdot \mathbf{r}(\tau)}$ is a Fourier component of the electron density derived from corresponding first-quantisation density operator and $M_{\mathbf{q}}$ is a general electron-phonon coupling matrix element. The polaron self-interaction functional is where the specific electron-phonon coupling presents itself in this mathematical machinery.

For the Fröhlich model, this electron self-interaction functional is,

$$\begin{aligned}
 \Phi_F [\mathbf{r}(\tau), \mathbf{r}(\tau')] &= \sum_{\mathbf{q}} \frac{g_F^2}{V_n q^{n-1}} e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))}, \\
 &= g_F^2 \int \frac{d^n q}{(2\pi)^n} \frac{e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))}}{q^{n-1}}, \\
 &= \frac{g_F^2 S_{n-1}}{(2\pi)^n} \frac{1}{|\mathbf{r}(\tau) - \mathbf{r}(\tau')|},
 \end{aligned} \tag{3.41}$$

where $S_{n-1} = 2\pi^{n/2}/\Gamma(n/2)$ is the hypervolume of the unit $(n-1)$ -sphere and the phonon momentum is unbounded, $0 \leq q < \infty$. The Fröhlich model makes the continuum approximation of the lattice, $\lim_{V_n \rightarrow \infty} V_n^{-1} \sum_{\mathbf{q}} \sim \int d^n q / (2\pi)^n$, where V_n is the n -dimensional crystal volume.

For the Holstein model in n isotropic dimensions (n -dimensional hypercube), the self-interaction functional is

$$\begin{aligned}
 \Phi_H [\mathbf{r}(\tau), \mathbf{r}(\tau')] &= g_H^2 \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))}, \\
 &= g_H^2 a^n \int \frac{d^n q}{(2\pi)^n} e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))}, \\
 &= g_H^2 \delta_{\mathbf{r}(\tau)\mathbf{r}(\tau')}^n,
 \end{aligned} \tag{3.42}$$

where δ_{ij}^n is the n -dimensional Kronecker Delta functional and $-\pi/a \leq q \leq \pi/a$. This could be adapted to any Brillouin-Zone geometry. We could also use spherical coordinates as in the Fröhlich model where instead $0 \leq q \leq \Lambda_n$ with Λ_n a momentum cutoff given by the radius of an n -ball with volume $\frac{(2\pi)^n}{V_n}$:

$$\Lambda_n = 2\sqrt{\pi} \left(V_n \Gamma\left(\frac{n}{2} + 1\right) \right)^{1/n}. \tag{3.43}$$

3.3.1 General Phonon-Band Polarons

We can now develop the variational path integral method for this generalised polaron action and specialise to a specific case by using an explicit expression for the electron-phonon coupling in the self-interaction functional as we have above for the Fröhlich and Holstein models. I will assume that we are working with only one parabolic-band electron so that the self-interaction functional, depends on the electron position through the term $e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))}$ only. If this is true, we can use Feynman's variational path integral method.

At this point, I would like to discuss the potential for direct numeric evaluation of the momentum integrals. The momentum integral can be evaluated numerically by substituting an explicit form for the electron-phonon matrix $|M_{\mathbf{q}}|^2$ and phonon dispersion $\omega_{\mathbf{q}}$, then using a numerical integration algorithm like Gauss-Kronrod. Many closed-forms for the electron-phonon matrix $|M_{\mathbf{q}}|^2$ and phonon dispersion $\omega_{\mathbf{q}}$ are known, such as for acoustic phonons, Bogoliubov-Fröhlich polaron, impurities etc [87, 88]. We could use such an analytic expression in our integrals, which may then admit closed-form solutions or be evaluated numerically.

For real materials, we could instead use electronic structure methods to evaluate $|M_{\mathbf{q}}|^2$ and $\omega_{\mathbf{q}}$ on a standard reciprocal space grid. These would then enter the variational method as arrays evaluated at the electron/hole band-extremum (e.g. the gamma-point $\mathbf{k} = \mathbf{0}$). Our q -integrands above would become tensor products concatenated overall q -points.

I have done some work implementing and validating these general phonon-band approaches in the computer codes [11] associated with this thesis. Still, I do not have numeric results to present.

3.3.2 Effective-mass anisotropy

In the degenerate anisotropic uni-axial case, we can incorporate the anisotropy into the Feynman approach (which is one-dimensional due to the underlying isotropy of the Fröhlich Hamiltonian) by treating the two directions independently with effective masses $m_{\perp}$ and $m_{\parallel}$.

We can then use the variational principle separately in each direction to find the variational parameters $v_{\perp/\parallel}$ and $w_{\perp/\parallel}$ which give the lowest upper-bound to the ground-state energy $E_{\perp/\parallel}$ for each direction.

The variational parameters can then be used to obtain the effective polaron masses $M_{\perp}$ and $M_{\parallel}$ using Eq. (2.130) and polaron radii $R_{\perp}$ and $R_{\parallel}$ using Eq. (2.132).

To make a comparison with the isotropic case, we can define an effective ground-state energy by taking the arithmetic mean of the uniaxial components of the ground-state energy,

$$E = \frac{2E_{\perp} + E_{\parallel}}{3}. \quad (3.44)$$

Similarly, we can define an effective radius of the anisotropic polaron by finding the radius of a sphere with the same volume as the ellipsoidal anisotropic polaron. This means taking the geometric mean of the uni-axial components of the polaron radius,

$$R = \left(R_{\perp}^2 R_{\parallel} \right)^{1/3}. \quad (3.45)$$

The two averaging methods are justified as they give a ground-state energy and polaron radius consistent with those evaluated by Feynman's original 1955 model [2] when applied to an isotropic material.

3.4 Many Polarons Beyond the Parabolic Approximation

So far, we have derived path integrals using the eigenvalues of the position and momenta operators of the Hamiltonian. However, there is another construction based on the eigenvalues of the Fock-space annihilation operators resulting in the so-called *Coherent-State Path Integrals* (CSPI) [88]. I have provided more details on the definitions of coherent states and the derivation of the coherent state path integral in appendix C.

Intuitively, CSPI allows us to construct a path integral directly from the second-quantised form of the Hamiltonian rather than the first-quantised form. Statistically, this corresponds to constructing the *grand-canonical* ensemble partition function in the path integral formalism compared to the canonical ensemble partition function we have been using previously. Thus, CSPIs allow us to construct path integrals for systems with varying particle numbers. Since the dispersion relationship does not depend on the coherent state variables, CSPIs offer us a way to generalise the variational principle to electron dispersions beyond the effective-mass approximations, as the tight-binding Hamiltonian describes.

In this derivation, we construct the coherent state path integral to the electron-phonon model. We begin by defining the system's Hamiltonian, proceed to express the transition amplitude using coherent states for both electrons and phonons and finally derive the path integral expression by discretising time and integrating over the coherent state variables.

3.4.1 The Electron-Phonon Hamiltonian

The electron-phonon Hamiltonian encompasses the kinetic energy of electrons, the energy of phonons, and their mutual interaction. It is typically expressed as

$$\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{int}} \quad (3.46)$$

Here, $\hat{H}_{\text{el}}$ represents the electronic Hamiltonian, $\hat{H}_{\text{ph}}$ the phononic Hamiltonian, and $\hat{H}_{\text{int}}$ the electron-phonon interaction.

For electrons in a lattice, the electronic Hamiltonian is given by

$$\hat{H}_{\text{el}} = \sum_{\mathbf{k}, \sigma} \epsilon_{\mathbf{k}} \hat{c}_{\mathbf{k}\sigma}^{\dagger} \hat{c}_{\mathbf{k}\sigma}, \quad (3.47)$$

where $\epsilon_{\mathbf{k}}$ denotes the energy of an electron with momentum $\mathbf{k}$ and spin σ , while $\hat{c}_{\mathbf{k}\sigma}^{\dagger}$ and $\hat{c}_{\mathbf{k}\sigma}$ are the fermionic creation and annihilation operators, respectively.

Phonons, being quantised lattice vibrations, are described by bosonic operators. The phononic Hamiltonian is expressed as

$$\hat{H}_{\text{ph}} = \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} \left(\hat{b}_{\mathbf{q}}^{\dagger} \hat{b}_{\mathbf{q}} + \frac{1}{2} \right), \quad (3.48)$$

where $\omega_{\mathbf{q}}$ is the frequency of a phonon with momentum $\mathbf{q}$, and $\hat{b}_{\mathbf{q}}^{\dagger}$, $\hat{b}_{\mathbf{q}}$ are the bosonic creation and annihilation operators for phonons.

The interaction between electrons and phonons is modelled by

$$\hat{H}_{\text{int}} = \sum_{\mathbf{k}, \mathbf{q}, \sigma} M_{\mathbf{k}, \mathbf{q}} \left(\hat{c}_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger} \hat{c}_{\mathbf{k}\sigma} \hat{b}_{\mathbf{q}} + \hat{c}_{\mathbf{k}\sigma}^{\dagger} \hat{c}_{\mathbf{k}+\mathbf{q}\sigma} \hat{b}_{-\mathbf{q}}^{\dagger} \right), \quad (3.49)$$

where $M_{\mathbf{k}, \mathbf{q}}$ represents the electron-phonon coupling matrix element. The first term describes electron scattering by absorbing a phonon, while the second term accounts for electron scattering by emitting a phonon.

3.4.2 Coherent States for Electrons and Phonons

We employ coherent states for both electrons and phonons to construct the path integral. Coherent states provide an overcomplete basis that simplifies the evaluation of transition amplitudes.

Bosonic Coherent States (Phonons)

A bosonic coherent state $|\phi\rangle$ for phonons is defined as an eigenstate of the phonon annihilation operator

$$\hat{b}_{\mathbf{q}} |\phi\rangle = \phi_{\mathbf{q}} |\phi\rangle, \quad (3.50)$$

where $\phi_{\mathbf{q}}$ is a complex number. These coherent states satisfy the resolution of identity

$$\int \prod_{\mathbf{q}} \frac{d^2 \phi_{\mathbf{q}}}{\pi} e^{-\sum_{\mathbf{q}} \bar{\phi}_{\mathbf{q}} \phi_{\mathbf{q}}} |\{\phi_{\mathbf{q}}\}\rangle \langle \{\phi_{\mathbf{q}}\}| = \hat{I}_{\text{ph}} \quad (3.51)$$

Fermionic Coherent States (Electrons)

Fermionic coherent states are constructed using Grassmann numbers due to the anticommuting nature of fermions. A fermionic coherent state $|\psi\rangle$ satisfies

$$\hat{c}_{\mathbf{k}\sigma} |\psi\rangle = \psi_{\mathbf{k}\sigma} |\psi\rangle, \quad (3.52)$$

where $\psi_{\mathbf{k}\sigma}$ are Grassmann numbers. These coherent states obey the resolution of identity

$$\int \prod_{\mathbf{k},\sigma} d\bar{\psi}_{\mathbf{k}\sigma} d\psi_{\mathbf{k}\sigma} e^{-\sum_{\mathbf{k},\sigma} \bar{\psi}_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}} |\{\psi_{\mathbf{k}\sigma}\}\rangle \langle \{\psi_{\mathbf{k}\sigma}\}| = \hat{I}_{\text{el}} \quad (3.53)$$

3.4.3 Constructing the Coherent State Path Integral

The transition amplitude between an initial state $|\psi_i, \{\phi_i\}\rangle$ and a final state $|\psi_f, \{\phi_f\}\rangle$ over a time interval T is given by

$$\langle \psi_f, \{\phi_f\} | e^{-i\hat{H}T} | \psi_i, \{\phi_i\} \rangle. \quad (3.54)$$

We discretise the time interval T into M small slices of duration $\Delta t = T/M$ to express this amplitude as a path integral. We insert identity resolutions between each time slice for electrons and phonons.

The discretised amplitude becomes

$$\begin{aligned} \langle \psi_f, \{\phi_f\} | e^{-i\hat{H}T} | \psi_i, \{\phi_i\} \rangle &= \lim_{M \rightarrow \infty} \int \prod_{j=1}^{M-1} \left(\prod_{\mathbf{q}} \frac{d^2 \phi_{\mathbf{q},j}}{\pi} \prod_{\mathbf{k},\sigma} d\bar{\psi}_{\mathbf{k}\sigma,j} d\psi_{\mathbf{k}\sigma,j} \right) \\ &\times \prod_{j=1}^M \langle \psi_j, \{\phi_j\} | e^{-i\hat{H}\Delta t} | \psi_{j-1}, \{\phi_{j-1}\} \rangle, \end{aligned} \quad (3.55)$$

where $\psi_0 = \psi_i$, $\psi_M = -\psi_f$, $\phi_0 = \phi_i$, and $\phi_M = \phi_f$. The index j labels the time slices.

For each small time slice, we approximate the matrix element $\langle \psi_j, \{\phi_j\} | e^{-i\hat{H}\Delta t} | \psi_{j-1}, \{\phi_{j-1}\} \rangle$ by expanding the exponential to first order in Δt ,

$$\begin{aligned} \langle \psi_j, \{\phi_j\} | e^{-i\hat{H}\Delta t} | \psi_{j-1}, \{\phi_{j-1}\} \rangle &\approx \langle \psi_j, \{\phi_j\} | \psi_{j-1}, \{\phi_{j-1}\} \rangle \\ &\times \left(1 - i\Delta t \frac{\langle \psi_j, \{\phi_j\} | \hat{H} | \psi_{j-1}, \{\phi_{j-1}\} \rangle}{\langle \psi_j, \{\phi_j\} | \psi_{j-1}, \{\phi_{j-1}\} \rangle} \right). \end{aligned} \quad (3.56)$$

The overlaps are given by

$$\langle \psi_j, \{\phi_j\} | \psi_{j-1}, \{\phi_{j-1}\} \rangle = e^{\sum_{\mathbf{q}} \bar{\phi}_{\mathbf{q},j} \phi_{\mathbf{q},j-1} + \sum_{\mathbf{k},\sigma} \bar{\psi}_{\mathbf{k}\sigma,j} \psi_{\mathbf{k}\sigma,j-1}}. \quad (3.57)$$

Assuming that the Hamiltonian does not change rapidly over the small time slice, we approximate

$$\langle \psi_j, \{\phi_j\} | \hat{H} | \psi_{j-1}, \{\phi_{j-1}\} \rangle \approx H(\bar{\psi}_j, \psi_{j-1}; \bar{\phi}_j, \phi_{j-1}), \quad (3.58)$$

where $H(\bar{\psi}_j, \psi_{j-1}; \bar{\phi}_j, \phi_{j-1})$ is the expectation value of the Hamiltonian in the coherent states.

In the continuum limit $M \rightarrow \infty$, the product over time slices transforms into an exponential of the action. The action S comprises contributions from the kinetic terms of both electrons and phonons and the interaction terms. Specifically, for each mode, we obtain terms involving $\bar{\psi}\dot{\psi}$ for electrons and $\bar{\phi}\dot{\phi}$ for phonons, along with the Hamiltonian contributions.

The final path integral expression is

$$\langle \psi_f, \{\phi_f\} | e^{-i\hat{H}T} | \psi_i, \{\phi_i\} \rangle = \int D\bar{\psi} D\psi D\bar{\phi} D\phi \exp(iS[\bar{\psi}, \psi; \bar{\phi}, \phi]), \quad (3.59)$$

where the action S is given by

$$S[\bar{\psi}, \psi; \bar{\phi}, \phi] = \int_0^T dt \left(\sum_{\mathbf{k}, \sigma} \bar{\psi}_{\mathbf{k}\sigma}(t) i \partial_t \psi_{\mathbf{k}\sigma}(t) + \sum_{\mathbf{q}} \bar{\phi}_{\mathbf{q}}(t) i \partial_t \phi_{\mathbf{q}}(t) - \hat{H}(\bar{\psi}, \psi; \bar{\phi}, \phi) \right). \quad (3.60)$$

The terms $i\bar{\psi}\partial_t\psi$ and $i\bar{\phi}\partial_t\phi$ arise from the logarithm of the coherent state overlaps and represent the kinetic parts of the action, often referred to as the Berry phase or geometric phase.

3.4.4 Integrating Out Phonon Degrees of Freedom

A common approach in the electron-phonon model is to integrate out the phonon degrees of freedom to obtain an effective action for the electrons. This procedure simplifies the problem, especially in regimes where phonon dynamics can be treated perturbatively.

Assuming that the phonon part of the action is quadratic (for non-interacting phonons), the integration over phonon coherent states can be performed exactly. The phonon kinetic and potential energy terms allow us to complete the square, leading to a Gaussian integration.

The effective electron action after integrating out the phonons incorporates mediated electron-electron interactions arising from the exchange of phonons. This leads to quartic terms in the fermionic Grassmann variables, effectively generating attractive interactions essential for superconductivity in the BCS theory.

The integration over phonons yields an effective electron action of the form

$$S_{\text{eff}}[\bar{\psi}, \psi] = \int_0^T dt \sum_{\mathbf{k}, \sigma} \bar{\psi}_{\mathbf{k}\sigma}(t) (i \partial_t - \epsilon_{\mathbf{k}}) \psi_{\mathbf{k}\sigma}(t) - \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \sigma} M_{\mathbf{k}, \mathbf{q}}^* M_{\mathbf{k}', \mathbf{q}} \int_0^T \int_0^T dt dt' \bar{\psi}_{\mathbf{k}+\mathbf{q}\sigma}(t) \psi_{\mathbf{k}\sigma}(t) D_{\omega_{\mathbf{q}}}(t-t') \bar{\psi}_{\mathbf{k}'-\mathbf{q}\sigma}(t') \psi_{\mathbf{k}'\sigma}(t'), \quad (3.61)$$

where $D_{\omega_{\mathbf{q}}}$ is the phonon propagator. This effective action encapsulates the mediated interactions between electrons via phonon exchange.

In imaginary time, the absence of spin, and lack of electron momentum dependence in the electron-phonon coupling matrix, this becomes,

$$S_{\text{eff}}[\bar{\psi}, \psi] = \int_0^{\hbar\beta} dt \sum_{\mathbf{k}} \bar{\psi}_{\mathbf{k}}(\tau) (\partial_{\tau} - \epsilon_{\mathbf{k}}) \psi_{\mathbf{k}}(\tau) - \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \rho_{\mathbf{q}}(\tau) D_{\omega_{\mathbf{q}}}(\tau - \tau') \bar{\rho}_{\mathbf{q}}(\tau'), \quad (3.62)$$

where $\rho_{\mathbf{q}}(\tau) = \sum_{\mathbf{k}} \bar{\psi}_{\mathbf{k}+\mathbf{q}}(\tau) \psi_{\mathbf{k}}(\tau)$ is a Fourier component of the electron density.

The coherent state path integral formulation offers a robust and elegant framework for analysing the electron-phonon model. By employing coherent states for both electrons and phonons, the path integral approach facilitates the exact integration of phonon fields, leading to effective electron-electron interactions that are useful for understanding polarons, superconductivity and other many-body phenomena in condensed matter systems.

CHAPTER 4



IMPROVING THE TRIAL PATH INTEGRAL MODEL AND VARIATIONAL APPROXIMATION

[The] [m]ost important part of doing physics is the knowledge of approximation.

—Lev Landau, *Unknown, Unknown*

In this chapter, I extend the trial polaron Lagrangian beyond Feynman's original spring-mass harmonic model (while retaining the analytic solution) to try and increase the accuracy of the variational approximation and the predicted response functions. These extensions include developing the variational method for the multimode Fröhlich polaron and small Holstein polaron, as well as generalising the trial action to couple the electron to multiple spring masses, a general bath spectral-function with self-consistent equations, general many-body polarons approximated by an effective trial Green function, and extending the Feynman-Jensen inequality with an infinite series of cumulant corrections.

4.1 Multiple Phonon Mode Variational Solution

With multiple phonon modes, the energy of the trial system S_0 and the internal energy $\langle S_0 \rangle_{S_0}$ remains unchanged and are as presented by Ōsaka [27]. However, as the model action S has been generalised to include multiple phonon modes, I derive a multiple phonon mode extension to the internal energy of the model action,

Multiple Phonon Mode Model Action Expectation

$$\langle S \rangle_{S_0} = \sum_{j=1}^m \frac{\hbar \alpha_j \omega_j^2}{\sqrt{\pi}} \int_0^{\hbar\beta} d\tau \frac{D_{\omega_j}(\tau)}{\sqrt{G(\tau)}}, \quad (4.1)$$

These are similar to Hellwarth and Biaggio's single mode versions, but with the single effective phonon frequency ω_0 substituted with the branch dependent phonon frequencies ω_j . There are m phonon branches indexed by the integer j .

Summing F_0 in Eq. (2.170), $\langle S_0 \rangle_{S_0}$ in Eq. (2.165), and $\langle S \rangle_{S_0}$ in Eq. (4.1), I obtain a generalised variational inequality for the contribution to the free energy of the polaron from the m phonon branches, each with phonon frequency ω_j and coupling constant α_j ,

$$F(\beta) \leq F_0 - \langle S_0 \rangle_{S_0} - \sum_{j=1}^m \langle S_j \rangle_{S_0}. \quad (4.2)$$

Since the trial system S_0 is unchanged from Eq. (2.145), I obtain two variational parameters v and w that minimise the free energy expression and will be used in evaluating the polaron mobility. Considering only one phonon branch ($m = 1$), this simplifies to Ōsaka's free energy. Feynman's original athermal version can be obtained by taking the zero-temperature limit ($\beta \rightarrow \infty$).

4.2 A Variational Approach to the Holstein Small Polaron Model

There are two main difficulties for the small Holstein polaron. First, the electronic dispersion is that of a tight-binding model and is not quadratic. Second, the momentum and position paths are discrete, and the ‘path-integral’ is an infinite summation rather than a functional integral. Therefore, the corresponding ‘path-integral’ is a non-Gaussian summation rather than a typical Gaussian functional integral. To apply the Feynman variational approximation, the trial path integral must have the same measure as the original system, but since the paths are discrete, even if the trial path integral were Gaussian, a Gaussian sum does not have a closed-form expression, unlike a Gaussian integral. Even if we approximate the paths to be continuous to bypass this issue, unlike for the Fröhlich model, we cannot choose the kinetic action of the trial path-integral to be identical to the Holstein kinetic action as it is non-Gaussian. We would then have an additional term, the difference between the trial and actual kinetic actions. To apply the Feynman-Jensen inequality, we need this term to be convex; this is no longer guaranteed.

To circumnavigate these issues in pursuit of tangible results, I instead chose to approximate the Holstein kinetic action with an approximate parabolic form with an effective band mass, much like the Fröhlich model. I will refer to this version of the Holstein model as the “*parabolic-Holstein*” model. I then allow the electron paths to be unconstrained such that the momentum integrals for the electron are unbounded (e.g. we have improper integrals over the electron momentum) and can be evaluated to give the standard Gaussian kinetic action. I could keep the momentum integrals bounded to the first Brillouin zone and still have a closed-form expression for the kinetic action; however, in addition to the standard Gaussian form, there are error functions that make it unclear how the resulting path integral could be evaluated — if this is even possible.

We can follow the usual variational procedure with the same trial action as the Fröhlich model by making these approximations. I should note that the Holstein electron-phonon interaction is still treated correctly, and the phonon quasi-momentum is still confined to the first Brillouin zone.

4.2.1 The Parabolic-Holstein Variational Equation

Here, I derive a variational inequality for the parabolic-Holstein polaron free energy that fully accounts for the lattice electron-phonon integral despite allowing the electron not to be confined to individual lattice sites. Despite the latter approximation, this model still captures many typical features of small Holstein polarons.

If we choose the kinetic part of the trial action to be the same as in the parabolic-Holstein action (Eq. (3.27)), then the expectation of the parabolic-Holstein action with respect to the trial action, $\langle S \rangle_{S_0}$, is

$$\langle S \rangle_{S_0} = g_H^2 \sum_{\mathbf{q}} \iint_0^{\hbar\beta} d\tau d\sigma D_{\omega_0}(\tau - \sigma) \left\langle e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\sigma))} \right\rangle_{S_0}, \quad (4.3)$$

where $D_{\omega_0}(\tau)$ is the phonon Green function (Eq. (2.2.1)), $g_H = \sqrt{2Jn\hbar\omega_0\alpha_H/V}$ is the Holstein electron-phonon coupling element (where J is the transfer integral, n the number of dimensions, ω_0 the Holstein phonon frequency, α_H the dimensionless Holstein coupling and V the unit cell volume), and $\mathbf{q}$ is the phonon wavevector which is restricted to the first Brillouin-zone, $-\pi/a \leq q \leq \pi/a$.

For the parabolic-Holstein model with a hypercubic lattice (i.e. cubic in 3D), the self-interaction functional is

$$\begin{aligned} \langle S \rangle_{S_0} &= g_H^2 \left(\frac{a}{2\pi} \right)^n \iint_0^{\hbar\beta} d\tau d\sigma D_{\omega_0}(\tau - \sigma) \int d^n q \left\langle e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\sigma))} \right\rangle_{S_0} \\ &= g_H^2 \iint_0^{\hbar\beta} d\tau d\sigma D_{\omega_0}(\tau - \sigma) \left[\frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dq e^{-\hbar q^2 G(\tau)/2m_0} \right]^n \\ &= 2n\alpha_H J \hbar \omega_0 \iint_0^{\hbar\beta} d\tau d\sigma D_{\omega_0}(\tau - \sigma) \left[\frac{\text{erf}(\pi \sqrt{G(\tau)J/\hbar})}{\sqrt{4\pi G(\tau)J/\hbar}} \right]^n, \end{aligned} \quad (4.4)$$

where $\gamma = \hbar\omega_0/J$ is the adiabaticity, m_0 is the Holstein band mass $m_0 = \hbar^2/2Ja^2$ and $G(\tau)$ is the polaron Green function from Eq. (2.164). $V = a^3$ has been cancelled. To go from the first to the second line we have used the form of the density-density function for the trial system derived in Eq. (2.113).

Summing the free energy F_0 (Eq. (2.170)) and internal energy $\langle S_0 \rangle_{S_0}$ (Eq. (2.165)) of the trial system with the internal energy of the parabolic-Holstein model $\langle S \rangle_{S_0}$ in Eq. (4.4) gives the variational inequality for the parabolic-Holstein model as

$$F_H \leq F_0(\beta) + \frac{1}{\beta} \langle S_0 \rangle_0 - \frac{4n\alpha_H J \omega_0}{\beta} \int_0^{\hbar\beta} d\tau (\hbar\beta - \tau) D_{\omega_0}(\tau) \left[\frac{\text{erf}(\pi \sqrt{G(\tau)J/\hbar})}{\sqrt{4\pi G(\tau)J/\hbar}} \right]^n, \quad (4.5)$$

where we have simplified the double-time integral using its symmetry property (see Eq. (2.94)).

A critical difference between the Holstein and Fröhlich models is the domain of the reciprocal-space integral for the phonon wavevector $\mathbf{q}$. For the Fröhlich model, this is over all of reciprocal space and has spherical symmetry, whereas the Holstein model integral is

bounded (by the error function) to the first Brillouin Zone (and formally reflects the crystal symmetry). Physically, this is an ultraviolet momentum cutoff due to the discrete lattice in the Holstein model, without which the integrals (in all spatial dimensions) catastrophically diverge.

The Fröhlich model also diverges in 1D, whereas the Holstein converges for all dimensionalities. This can be seen from the fact that the integrand of the q -space integral for the Holstein model is always proportional to a Gaussian multiplied by q^m where m is a positive integer for all dimensions.

I provide results for the parabolic-Holstein model in one- to three dimensions and compare these results to Ragni's DiagMC [89] results for both the original Holstein model (with a tight-binding electron dispersion) and the parabolic-band Holstein model. I also compare some results to the Fröhlich Hamiltonian. To compare and contrast these models, I consider:

1. The energy and character (e.g. a bound state or a small polaron) of the athermal quasi-particle (polaron) state versus coupling.
2. The temperature dependence of the polaron mobility and polaron energy.
3. The frequency dependence of the polaron mobility and optical conductivity.

4.2.2 Athermal Holstein Polaron

I start with the zero temperature polaron in one, two and three dimensions for the parabolic-Holstein model and compare it to the three-dimensional Fröhlich model. I present the models in a unitless presentation with an adiabaticity of $\gamma = 1$ ($\omega_0 = J = 1$). I assume that the two dimensionless coupling alpha parameters, α_H and α_F , used in the parabolic-Holstein and Fröhlich models produce similar physical regimes within either model. Therefore, I will compare these two models to a single alpha parameter $\alpha \equiv \alpha_H = \alpha_F$.

Polaron Variational Parameters

In Fig. 4.1 are the polaron variational parameters v and w of the Holstein and Fröhlich polarons as a function of the electron-phonon dimensionless coupling parameter α . The Holstein model has a noticeably different variational solution than the Fröhlich model, with a distinct discontinuity in three dimensions. This transition is smoother for one- and two-dimensions and occurs at $\alpha \approx 2n$, where n is the dimensionality of the model. I interpret this transition as physically corresponding to forming the small-polaron state.

In both models, w asymptotes to the phonon frequency $\omega_0 = 1$ at large electron-phonon coupling α , with a more abrupt transition in the parabolic-Holstein model. The v parameters have a different strong coupling dependency on α . In the Fröhlich model at large α , $v_F \sim \alpha^2$

whereas in the Holstein model $v_H \sim \sqrt{\alpha}$. Another noticeable difference is the weak coupling limit ($\alpha \rightarrow 0$) where the Fröhlich model parameters asymptotes are $v_F = w_F = 3$, whereas Holstein are $v_H = w_H \approx 2n$.

Polaron Ground-state Energy & Mass

Fig. 4.1 is the variational solution for the free energy of the one-, two- and three-dimensional parabolic-Holstein model (with $J = \omega_0 = 1$ in this unitless presentation) with respect to the electron-phonon coupling parameter α . I also compare the variational solution to the three-dimensional Fröhlich model ($\omega_0 = 1$).

As required, the athermal polaron energy at $\alpha = 0$ corresponds to the band extrema for both models. In the Fröhlich model, this is zero $E_F(\alpha = 0) = 0$, and for the Holstein model, this is $E_H(\alpha = 0) = 2nJ$ with n the dimensionality. The athermal energy in the Fröhlich model is approximately linear for small alpha $E_F \sim -\hbar\omega_0\alpha$ and quadratic for large alpha $E_F \sim -\hbar\omega_0\alpha^2$. The athermal energy in the parabolic-Holstein model is also linear for small alpha $E_H + 2nJ \sim -J\alpha/2$ (which is the same for all dimensions), but the large alpha behaviour is not quadratic and is instead linear and dependent on the number of dimensions $E_H + 2nJ \sim -Jn\alpha$.

In Fig. 4.2, I now vary the adiabaticity $\gamma = \hbar\omega_0/J = 0.1, 0.3$ and 0.5 in the parabolic-Holstein model for dimensions $n = 1, 2$ and 3 and compare these variational results with DiagMC results for an identical parabolic model provided by Ragni (for values of $\alpha = 0$ to 5 which are shown more closely in the inset figures). These variational solutions agree with Ragni's DiagMC results for all dimensions and adiabaticities. The adiabaticity affects the lower alpha energy of the polaron below the small polaron transition around $\alpha = 2n$ and increases the sharpness of this transition for smaller adiabaticity.

We note that in three dimensions with $\gamma < 1$, this transition momentarily *reduces* the polaron binding energy in the variational solution, which is not replicated in the DiagMC results — more DiagMC data for $\alpha > 5$ may be required to determine if this is an artefact of the parabolic-Holstein model or just the variational solution.

In Fig. 4.2 we also show (top-left panel) a comparison of the DiagMC results for the *parabolic-band* Holstein model with the original *tight-binding-band* Holstein model where we see that the two models predict similar energies below the small-polaron transition, but the tight-binding model shows a sharper, dimension-independent transition at $\alpha = 2$ and larger polaron-binding energy above this transition.

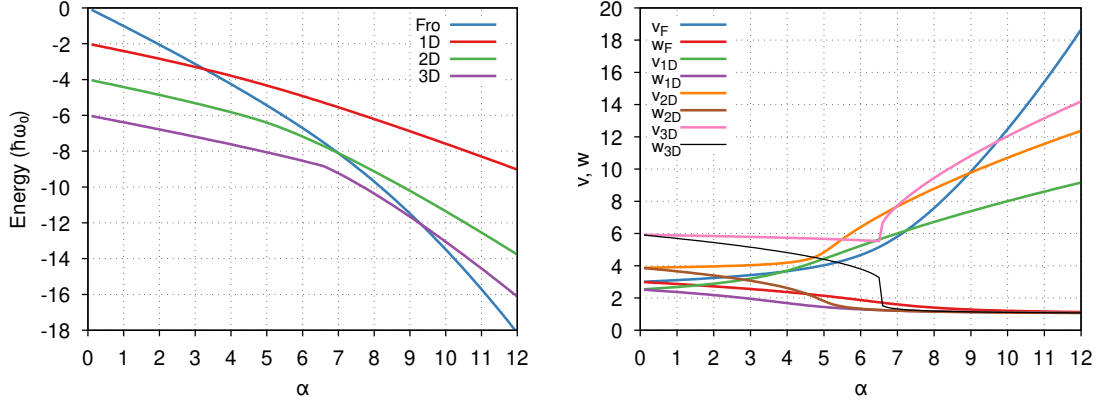


Figure 4.1: Left: The electron-phonon coupling α dependence of the ground-state energy E (in units of $\hbar\omega_0$) of the 3D Fröhlich model (blue) and the parabolic-Holstein model in 1D (red), 2D (green) and 3D (purple). Right: The electron-phonon coupling α dependence of the variational parameters v and w (in units of ω_0) for the 3D Fröhlich model (v blue, w red) and the parabolic-Holstein model in 1D (v green, w purple), 2D (v orange, w brown) and 3D (v pink, w black).

4.2.3 Thermal polarons

We now look at the finite temperature dependence of the polaron in one-, two- and three-dimensions for the parabolic-Holstein model (top sub-figures) and the three-dimensional Fröhlich model (bottom sub-figure), for values of the electron-phonon coupling $\alpha = 0.1, 2, 4, 6, 8, 10, 12$. Here we take a unitless presentation with $\omega_0 = J = 1$.

Polaron Free Energy

Fig. 4.3 shows the temperature dependence of the parabolic Holstein polaron free energy (left) and the effective polaron mass (right) for the 1D (top), 2D (middle), and 3D (bottom) systems. Each plot shows results for varying electron-phonon coupling strengths $\alpha = 0.1, 2, 4, 6, 8, 10, 12$, expressed in units of $\hbar\omega_0$.

In the left panels, the polaron binding energy decreases with temperature in all cases, with stronger electron-phonon coupling α leading to deeper binding energies. This trend is consistent across all dimensions, but the magnitude of the binding energy is larger for higher-dimensional systems (2D and 3D). For example, in the 1D system at $\alpha = 12$, the binding energy reaches as low as $-40\hbar\omega_0$, while in 3D, it bottoms out around $-120\hbar\omega_0$.

The right panels show that the effective polaron mass exhibits a non-monotonic dependence on temperature, with the mass increasing at low temperatures ($T < \hbar\omega_0/k_B$), peaking at intermediate temperatures ($T \approx \hbar\omega_0/k_B$) and then decreasing to the electron band mass at higher temperatures ($T > \hbar\omega_0/k_B$). This demonstrates the stripping of the phonon cloud from the polaron quasi-particle by the thermally excited lattice phonons. For stronger coupling $\alpha \gg 1$, the peak in mass becomes more pronounced, indicating stronger polaron localisation.

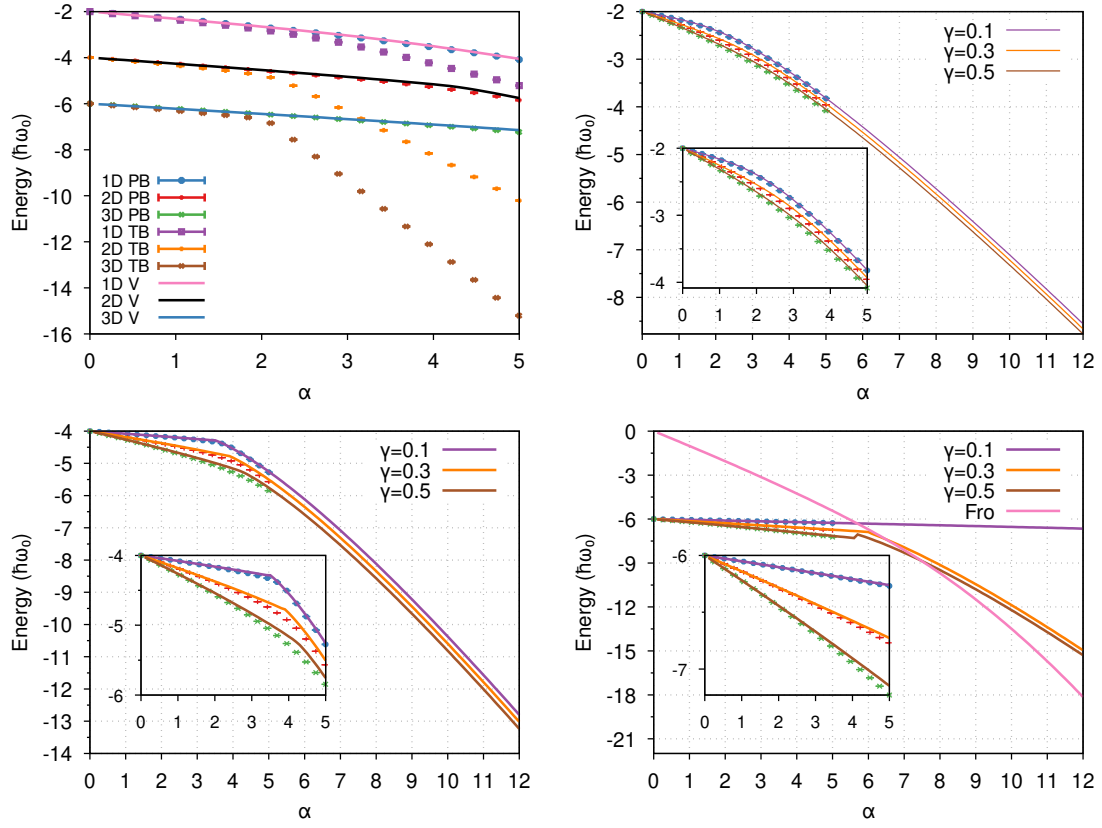


Figure 4.2: Polaron binding energy (in units of $\hbar\omega_0$) for the Holstein model with respect to the electron-phonon dimensionless coupling parameter α and adiabaticity $\gamma = \hbar\omega_0/J$.

Top left: Comparison between the variational solution for the parabolic-Holstein model (1D pink, 2D black and 3D light blue) to the DiagMC solution for the parabolic-Holstein model (1D blue points, 2D red points and 3D green points) and tight-binding Holstein model (1D purple points, 2D orange points and 3D brown points).

Top right: Comparison for the 1D parabolic-Holstein model between the variational solution ($\gamma = 0.1$ purple, 0.3 orange and 0.5 brown) and the DiagMC solution ($\gamma = 0.1$ blue points, 0.3 red points and 0.5 green points).

Bottom left: Comparison for the 2D parabolic-Holstein model between the variational solution ($\gamma = 0.1$ purple, 0.3 orange and 0.5 brown) and the DiagMC solution ($\gamma = 0.1$ blue points, 0.3 red points and 0.5 green points).

Bottom right: Comparison for the 3D parabolic-Holstein model between the variational solution ($\gamma = 0.1$ purple, 0.3 orange and 0.5 brown) and the DiagMC solution ($\gamma = 0.1$ blue points, 0.3 red points and 0.5 green points). I also include the variational solution to the 3D Fröhlich model for comparison (pink).

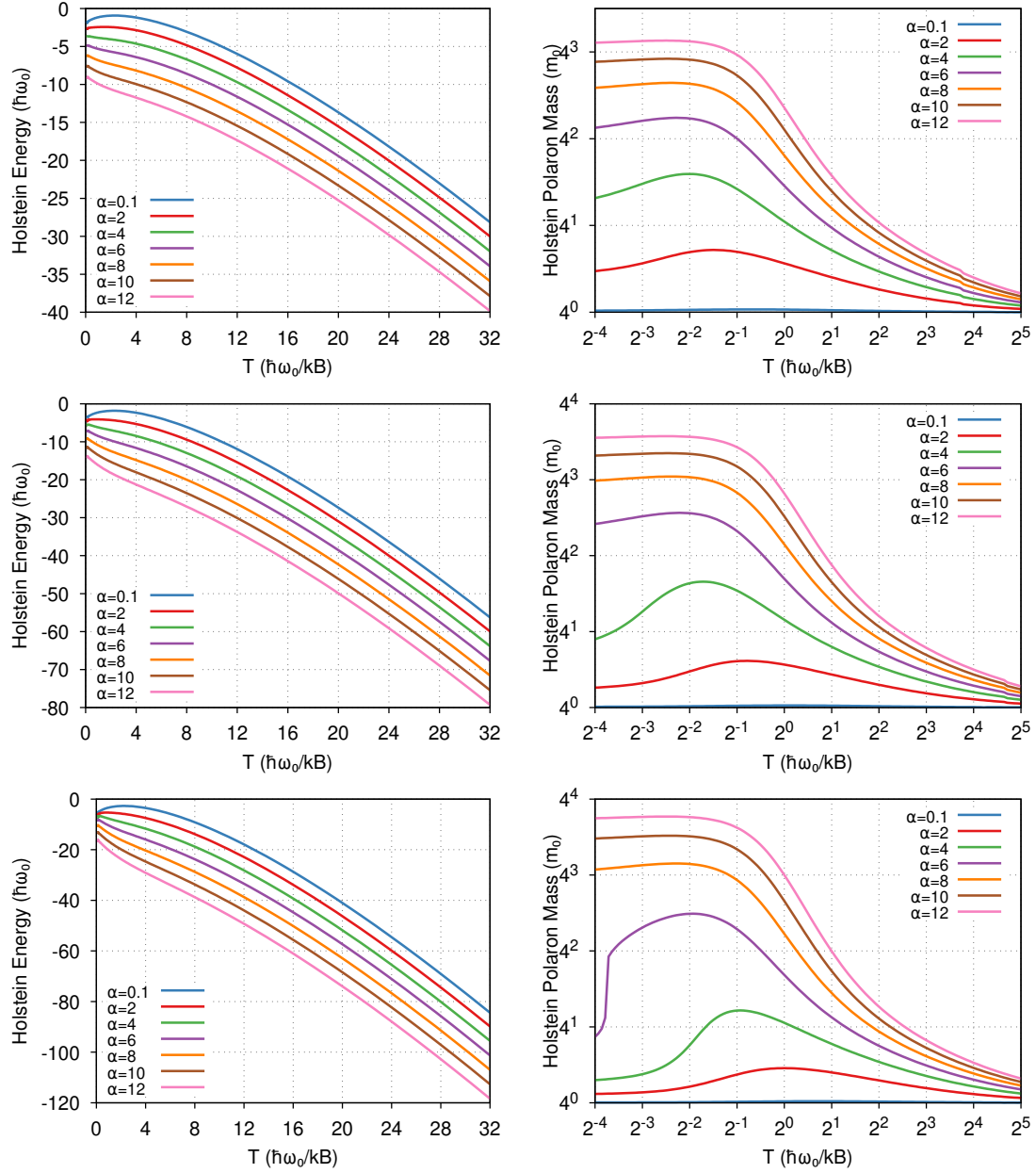


Figure 4.3: Polaron binding energy (left) and effective mass (right) for the Holstein model in 1D (top), 2D (middle) and 3D (bottom) with respect to temperature (in units of the phonon frequency $\hbar\omega_0$), for values of the Holstein electron-phonon coupling $\alpha = 0.1, 2, 4, 6, 8, 10, 12$

4.3 A General Parabolic Polaron Variational Approach

Following the procedure for the Fröhlich model [2, 4], we derive a variational inequality for a general *parabolic-band* polaron, moving the model-specific evaluation into the self-interaction function.

The variational method for the polaron developed by Feynman gives a lower upper-bound to the polaron free energy,

$$\begin{aligned} F &\leq F_0(\beta) - \frac{1}{\hbar\beta} \langle S_{\text{pol}} - S_0 \rangle_{S_0}, \\ &\leq F_0(\beta) - \frac{1}{\hbar^2\beta} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' D_{\omega_0}(\tau - \tau') \langle \Phi_{\text{pol}} - \Phi_0 \rangle_{S_0}, \end{aligned} \quad (4.6)$$

where the expectation $\langle O \rangle_{S_0}$ is defined as

$$\langle O \rangle_{S_0} \equiv \frac{\int D^3 r(\tau) O e^{-S_0[\mathbf{r}(\tau)]}}{\int D^3 r(\tau) e^{-S_0[\mathbf{r}(\tau)]}}. \quad (4.7)$$

Here $S_0[\mathbf{r}(\tau)]$ is a trial action that is chosen to best approximate the polaron model-action $S_{\text{pol}}[\mathbf{r}(\tau)]$, with the requirement that the path integral for S_0 can be analytically evaluated. The trial-action is chosen to be at most quadratic in the electron coordinate $\mathbf{r}(\tau)$ for this reason. We use the original 1955 quasi-particle trial action of Feynman,

$$S_0[\mathbf{r}(\tau)] = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}^2(\tau) + \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' D_w(\tau - \tau') \Phi_0[\mathbf{r}(\tau), \mathbf{r}(\tau')], \quad (4.8)$$

where the trial self-interaction functional is a simple quadratic,

$$\Phi_0[\mathbf{r}(\tau), \mathbf{r}(\tau')] = \hbar w \kappa [\mathbf{r}(\tau) - \mathbf{r}(\tau')]^2. \quad (4.9)$$

The κ and w variational parameters have a direct interpretation as the spring-constant and oscillation frequency of the polaron quasi-particle. We have integrated out the interaction with the phonon field and replaced it with a fictitious mass coupled to our electron by a spring, representing the phonon drag. This trial model (the quasi-particle) is often stated in terms of v and w variational parameters where $\kappa = m_0(v^2 - w^2)$.

The expectation value of the trial action $\langle S_0 \rangle_{S_0}$ and the free energy of the trial system $F_0(\beta)$ are as given by Ōsaka [27]

$$\langle S_0 \rangle_{S_0} = \frac{n\hbar\beta}{4} \frac{v^2 - w^2}{v} \left(\frac{2}{v\hbar\beta} - \coth\left(\frac{v\hbar\beta}{2}\right) \right), \quad (4.10)$$

$$F_0(\beta) = \frac{n}{\beta} \log \left(\frac{w \sinh(\hbar\beta v/2)}{v \sinh(\hbar\beta w/2)} \right). \quad (4.11)$$

All the expectation values in the variational expression can be evaluated from $\langle e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))} \rangle_{S_0}$, which for the trial model has a closed-form expression,

$$\langle e^{i\mathbf{q} \cdot (\mathbf{r}(\tau) - \mathbf{r}(\tau'))} \rangle_{S_0} = \exp \left[-\hbar q^2 G(\tau - \tau') / 2m_0 \right], \quad (4.12)$$

where the imaginary-time thermal polaron Green function $G(\tau)$ is

$$G(\tau) = \tau \left(1 - \frac{\tau}{\hbar\beta} \right) + \frac{v^2 - w^2}{v^3} \left[D_v(0) - D_v(\tau) - v\tau \left(1 - \frac{\tau}{\hbar\beta} \right) \right], \quad (4.13)$$

with D is the phonon propagator from Eq. (2.2.1).

In n -dimensions, from Eq. (4.6) we have

$$F \leq F_0(\beta) + \frac{1}{\hbar\beta} \langle S_0 \rangle_0 - \frac{2}{\hbar\beta} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \int_0^{\hbar^2\beta} d\tau (\hbar\beta - \tau) D_{\omega_0}(\tau) e^{-\hbar q^2 G(\tau)/2m_0}, \quad (4.14)$$

where we have used the symmetry property of the double-time integral (see Eq. (2.94)).

To evaluate the remaining phonon wavevector $\mathbf{q}$ integral, we could either use Cartesian coordinates, or we can transform the q -space summation into a spherical integral over the n -dimensional ball

$$\begin{aligned} \langle \Phi_{\text{pol}} \rangle_{S_0} &= \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 e^{-\hbar q^2 G(\tau)/2m_0}, \\ &= \frac{V S_{n-1}}{(2\pi)^n} \int_0^R dq |M_q|^2 q^{n-1} e^{-\hbar q^2 G(\tau)/2m_0}, \end{aligned} \quad (4.15)$$

with $S_{n-1} = 2\pi^{n/2}/\Gamma(n/2)$ the hypervolume of the unit $(n-1)$ -sphere and R the radius of the ball.

For closed-form expressions for the electron-phonon matrix $M_{\mathbf{q}}$, we can numerically evaluate this phonon wavevector integral using standard methods such as adaptive Gauss-Kronrod quadrature. Alternatively, suppose the electron-phonon matrix $M_{\mathbf{q}}$ has been calculated numerically using electron-structure methods over a grid of $\mathbf{q}$ values (e.g. using Density Functional Theory). We can numerically evaluate the phonon wavevector *sum* over this $\mathbf{q}$ -grid.

As an example, for the Fröhlich self-interaction functional, we have

$$\begin{aligned}\langle \Phi_F \rangle_{S_0} &= \frac{g_F^2 S_{n-1}}{(2\pi)^n} \int_0^\infty dq e^{-\hbar q^2 G(\tau)/2m_0}, \\ &= \alpha_F \hbar^2 \omega_0^{3/2} \frac{\Gamma(\frac{n-1}{2})}{2\Gamma(\frac{n}{2})} \frac{1}{\sqrt{G(\tau)}}.\end{aligned}\quad (4.16)$$

The variational inequality for the Fröhlich model is,

$$F_F \leq F_0(\beta) - \frac{1}{\beta} \langle S_0 \rangle_{S_0} - \alpha_F \hbar \omega_0^{3/2} \frac{\Gamma(\frac{n-1}{2})}{\Gamma(\frac{n}{2})} \int_0^{\hbar\beta} d\tau \frac{D_{\omega_0}(\tau)}{\sqrt{G(\tau)}}. \quad (4.17)$$

For the parabolic-Holstein model with a hypercubic lattice (i.e. cubic in 3D), the self-interaction functional is,

$$\begin{aligned}\langle \Phi_H \rangle_{S_0} &= g_H^2 \left[\frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dq e^{-\hbar q^2 G(\tau)/2m_0} \right]^n, \\ &= 2n\alpha_H J \hbar \omega_0 \left[\frac{\text{erf}(\pi \sqrt{G(\tau)J/\hbar})}{\sqrt{4\pi G(\tau)J/\hbar}} \right]^n,\end{aligned}\quad (4.18)$$

where $\gamma = \hbar \omega_0/J$ is the adiabaticity.

Substituting the Holstein self-interaction functional into Eq. (4.6) gives the variational inequality for the Holstein model as

$$F_H \leq F_0(\beta) + \frac{1}{\beta} \langle S_0 \rangle_{S_0} - 4n\alpha_H J \omega_0 \int_0^{\hbar\beta} d\tau D_{\omega_0}(\tau) \left[\frac{\text{erf}(\pi \sqrt{G(\tau)J/\hbar})}{\sqrt{4\pi G(\tau)J/\hbar}} \right]^n. \quad (4.19)$$

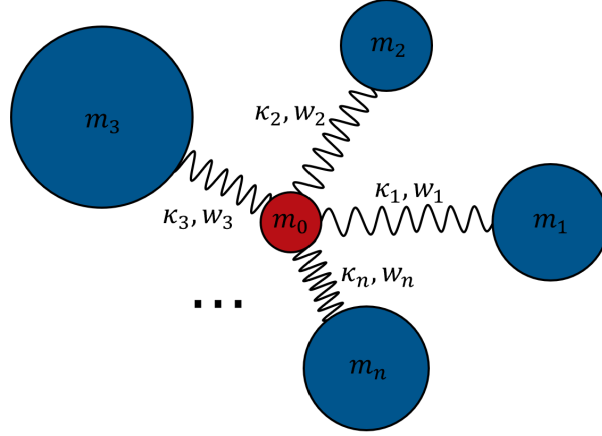


Figure 4.4: Schematic representation of a multiple spring-mass trial system. The electron with mass m_0 is coupled to multiple harmonic oscillators. The electron interacts with the surrounding particles of masses $m_1, m_2, \dots, m_n$ through springs characterised by spring constants $\kappa_1, \kappa_2, \dots, \kappa_n$ and natural frequencies $\omega_1, \omega_2, \dots, \omega_n$.

4.4 Multiple Fictitious Particles in the Trial Action

The first way I tried to improve the trial action was to couple the electron to more than one fictitious particle, each with its respective mass and spring constant, which added multiple pairs of variational parameters in the model. This was previously done for one additional fictitious mass by Abe and Okamoto in 1971 [90].

Extending to more fictitious particles in the trial action, I generalised Feynman's trial action to represent a particle (the charge-carrier) coupled to N massive fictitious particles. This results in $2 \times N$ variational parameters (one for the coupling strength and one for the coupling frequency of each fictitious particle).

The Lagrangian for this trial model is

$$L = \frac{m_0}{2} \dot{\mathbf{r}}(t)^2 + \frac{1}{2} \sum_{p=1}^N m_p \dot{\mathbf{x}}_p(t)^2 - \frac{1}{2} \sum_{p=1}^N \kappa_p (\mathbf{r}(t) - \mathbf{x}_p(t))^2, \quad (4.20)$$

where $\mathbf{r}(t)$ is the position of the electron with band-mass m_0 , $\mathbf{x}_p(t)$ is the position of the p^{th} fictitious particle with mass m_p , and κ_p is the spring constant for the spring connecting the electron with the p^{th} fictitious particle. The frequency of the p^{th} spring is $w_p = \sqrt{\kappa_p/m_p}$. A visualisation of this trial system is shown in Fig. 4.4.

This generalised polaron trial action is

$$S_0[\mathbf{r}(\tau)] = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \left(\frac{d\mathbf{r}(\tau)}{d\tau} \right)^2 + \frac{1}{8} \sum_{p=1}^N \kappa_p w_p \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\sigma D_{w_p}(\tau - \sigma) (\mathbf{r}(\tau) - \mathbf{r}(\sigma))^2. \quad (4.21)$$

Here κ_p is the spring constant associated with the p^{th} fictitious particle, and w_p is the corresponding oscillation frequency. In 1992 [91], Poulter and Sa-yakanit evaluated the partition function for this action.

Following Feynman [2] and Ōsaka [27] (see section 2.2), I extend the trial free energy F_{S_0} and the expectation of the trial action $\langle S_0 \rangle_{S_0}$ to the case of multiple fictitious particles,

$$F_{S_0} = \frac{3}{\beta} \left[\sum_{p=1}^N \log \left(\frac{v_p \sinh(w_p \hbar\beta/2)}{w_p \sinh(v_p \hbar\beta/2)} \right) + \frac{1}{2} \log \left(2\pi \hbar^2 \beta / m_0 \right) \right], \quad (4.22a)$$

$$\langle S_0 \rangle_{S_0} = \frac{3}{4} \sum_{p,l=1}^N \frac{C_{pl}}{v_l w_p} \left(\coth \left(\frac{v_l \hbar\beta}{2} \right) - \frac{2}{v_l \hbar\beta} \right), \quad (4.22b)$$

where

$$C_{pl} = w_p \frac{\kappa_p h_l}{v_l^2 - w_p^2}, \quad (4.23a)$$

$$\kappa_p = \left(v_p^2 - w_p^2 \right) \prod_{\substack{l=1 \\ l \neq p}}^N \frac{v_l^2 - w_p^2}{w_l^2 - w_p^2}, \quad (4.23b)$$

$$h_p = \left(v_p^2 - w_p^2 \right) \prod_{\substack{l=1 \\ l \neq p}}^n \frac{w_l^2 - v_l^2}{v_l^2 - v_l^2}. \quad (4.23c)$$

C_{pl} are the components of a generalised $(N \times N)$ matrix version of Feynman's C variational parameter. The cross (off-diagonal) terms give the coupling (interaction) between the fictitious particles.

A generalisation of the polaron (quasiparticle) Green function is

$$G(\tau) = \tau \left(1 - \frac{\tau}{\hbar\beta} \right) + \sum_{p=1}^N \frac{h_p}{v_p^3} \left(D_{v_p}(0) - D_{v_p}(\tau) - v_p \tau \left(1 - \frac{\tau}{\hbar\beta} \right) \right). \quad (4.24)$$

If $N = 1$ (a single fictitious particle) and $\tau \rightarrow it$, $G(\tau)$ becomes the same as $D(t)$ in Eq. (2.200).

From this trial Green function $G(\tau)$ I arrive at a generalisation to Osaka's $\langle S \rangle_{S_0}$ with multiple (N with index p) variational parameters v_p and w_p ,

$$\langle S \rangle_{S_0} = \frac{\hbar \alpha \omega_0^2}{\sqrt{\pi}} \int_0^{\hbar \beta} d\tau D_{\omega_0}(\tau) [G(\tau)]^{-\frac{1}{2}}. \quad (4.25)$$

I then obtain length vectors N for the variational parameters v_p and w_p that correspond to the minimum upper bound to the free energy, which will be used in evaluating the polaron mobility. Considering only two variational parameters ($N = 1$) simplifies to Ōsaka's free energy expression in Eq. (2.167). Feynman's original athermal version can be obtained by taking the zero-temperature limit ($\beta \rightarrow \infty$) in Eq. (2.118).

4.4.1 Numerical Implementation

In this section, I present my numerical investigations into the result of the trial model generalised to multiple fictitious particles in the case of the Fröhlich polaron model. Adding fictitious particles adds two more variational parameters per particle to the trial model, representing each new particle's mass and frequency (or the spring constant) coupled to the electron. These can be transformed into corresponding v_p and w_p parameters where p labels each fictitious particle. The ordering of these parameters can be fixed such that $w_1 < v_1 < w_2 < v_2 < \dots$ [91]. Enforcing this constraint dramatically improves the convergence of the correct upper bound on the free energy. However, the absolute value of the optimal v_N and w_N corresponding to the N th fictitious particle increases exponentially with N . Thus, we are limited by numerical precision to $N \leq 6$. The v_N and w_N exceed 10^{12} and the corresponding relative improvement on the free energy is less than $10^{-8}\%$ compared to the $N = 5$ approximation of the free energy. Arbitrary precision numerics could improve the variational bound on the free energy by enabling convergence for $N > 6$ but would significantly increase the computational cost.

4.4.2 Discussion of Analytic Results

Adamowski et al. [37], Saitoh [92] and Rosenfelder et al. [93] considered the optimal self-consistent solution to Feynman's variational approach using a general memory function. At small alpha α , they derived the optimal weak coupling approximation to the polaron energy as

$$\begin{aligned} \frac{E}{\hbar \omega_0} &= -\alpha - \frac{1}{6} \left(\frac{1}{2} - \frac{4}{3\pi} \right) \alpha^2 + \mathcal{O}(\alpha^3) \\ &\approx -\alpha - 0.0125978 \alpha^2. \end{aligned} \quad (4.26)$$

Smondirev [69] derived the best perturbative weak coupling result using a fourth-order perturbative expansion of the polaron self-energy. Smondirev calculated the α^2 coefficient to be $2 \ln(\sqrt{2} + 1) - \frac{3}{2} \ln 2 - \frac{\sqrt{2}}{2} \approx -0.01591962$.

So, despite minor improvements in the variational bound on the polaron free energy, the optimal variational result does not coincide with the best perturbative result, at least for the Fröhlich model. The Feynman variational method can be improved by including higher-order cumulant corrections in the difference between the polaron model and trial actions $\langle (S - S_0)^n \rangle_{S_0}$. Marshall and Mills [94], and Lu and Rosenfelder [95] calculated the second-order cumulant correction to the Feynman variational approach and found that this reproduces the fourth-order perturbation result. The second-order cumulant correction is only a perturbative correction; it violates the variational principle for the free energy as this correction term is typically negative and does not preserve the upper bound to the free energy. However, in section 4.6, we present an arbitrary cumulant expansion to all orders that also preserves the variational bound.

Despite minor improvements in the energy bound of the variational method, Thornber [80] and Sel [77] showed that the corresponding dynamical theory changes significantly, likely due to the high sensitivity of analytic continuation to the optimal variational result. We investigate this further in section 5.4.

4.4.3 Numerical Results for the Additional Variational Parameters

In Fig. 4.5, I present the coupling-dependence of the optimal v and w parameters for the Fröhlich model, for a sequence of different numbers of fictitious particles in the trial model from $N = 1$ to $N = 6$. In the top-right figure ($N = 2$), I have co-plotted the results calculated by Abe and Okamoto in 1971 [90] for the two fictitious particle trial action.

Notably for $N > 1$, $w_{p>1}$ have a different α coupling dependence to w_1 , which asymptotes to $w_1 = \omega_0$ at strong coupling. Instead, $w_{p>1}$ shows a similar coupling dependence to the $v_{p>2}$ parameters. The gap between $v_{p>2}$ and $w_{p>2}$ becomes significantly smaller until it is unperceivable in the plots. This suggests that each successive particle asymptotically approaches the electron band mass with a larger spring constant. Looking at the energy, we will see that each additional particle contributes diminishingly to the system's free energy.

In Fig. 4.6, I present the temperature-dependence of the optimal v_p and w_p parameters for the Fröhlich model for coupling $\alpha = 6$ and $N = 1$ to 4 (for $N > 4$ and $T > \hbar\omega_0/k_B$ we found similar convergence difficulties due to limited precision as for $N > 6$ at zero temperature). The relative difference between v_p and w_p (for a given p) is largest at low temperatures, $T < 0.5\hbar\omega_0/k_B$, and decreases when $T > \hbar\omega_0/k_B$. The additional fictitious masses are less sensitive to changes in temperature but still show a similar trend to the

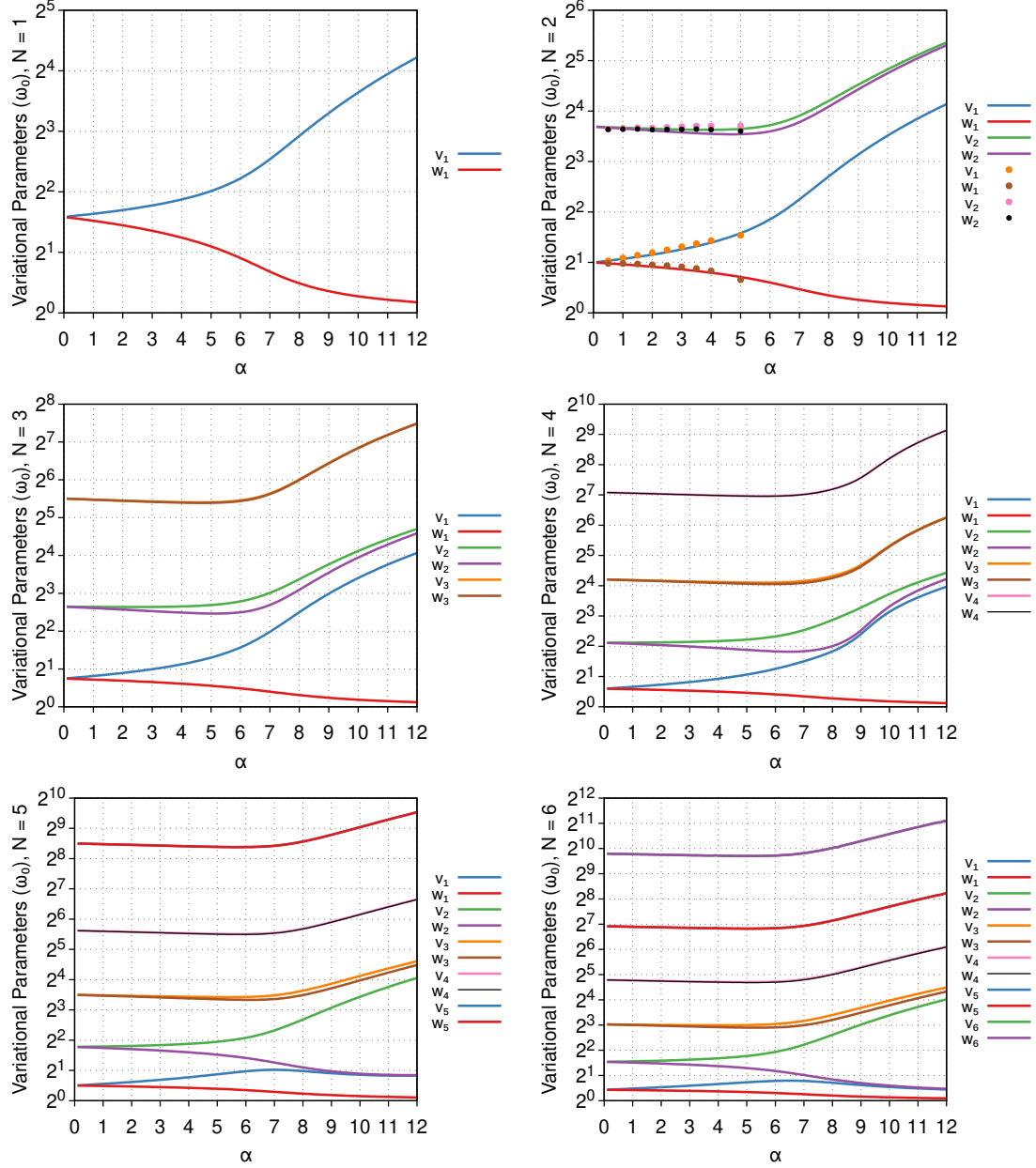


Figure 4.5: The thermal ($T = 0$) coupling-dependence (α) of the variational parameters v_p and w_p for the Fröhlich model, corresponding to additional fictitious particles in the trial model. The first figure (top-left) is Feynman's original variational solution $N = 1$. The result for additional fictitious particles are shown in top-right ($N = 2$, co-plotted with Abe and Okamoto's [90] results), middle-left ($N = 3$), middle-right ($N = 4$), bottom-left ($N = 5$) and bottom-right ($N = 6$)

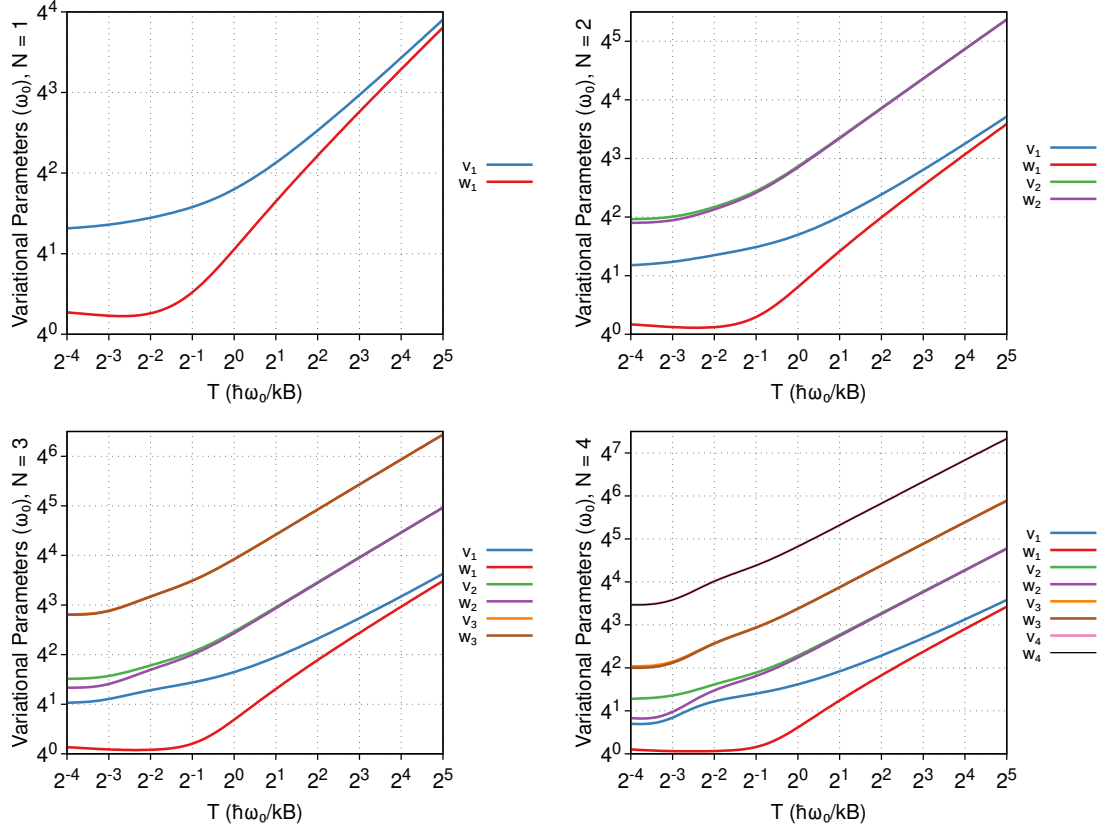


Figure 4.6: The temperature-dependence of the variational parameters v_p and w_p for the Fröhlich model, corresponding to additional fictitious particles in the trial model for coupling $\alpha = 6$. The first figure (top-left) is Feynman’s original variational solution $N = 1$. The result for additional fictitious particles are shown in top-right ($N = 2$), bottom-left ($N = 3$) and bottom-right ($N = 4$).

original single spring mass of Feynman’s trial model, where their mass asymptotes to the electron band mass at high temperatures and their spring stiffens.

4.4.4 Numerical Results of the Improved Energy Bound

In Fig. 4.7, I show in the top-left figure the absolute shift in the free energy for $N > 1$ compared to the free energy result for $N = 1$ as a function of the electron-phonon coupling from $\alpha = 0$ to $\alpha = 12$. There are two key observations. First, the greatest improvement to the free energy bound can be seen at intermediate coupling around $\alpha \approx 7$. Second, there is rapid convergence to the optimal free energy bound with no discernible difference between the results for $N > 2$ fictitious particles. We have co-plotted the ‘best’ variational result calculated by Sels [77] corresponding to the $N \rightarrow \infty$ limit. We see that the variational solution converges to the optimal results as soon as $N = 4$.

In the top-right figure, I show how these variational free energy bound improvements depend on different temperatures for $\alpha = 6$. Again, we see rapid convergence to the optimal solution by $N = 4$. The maximum improvement occurs for low temperatures $T \ll \hbar\omega_0/k_B$,

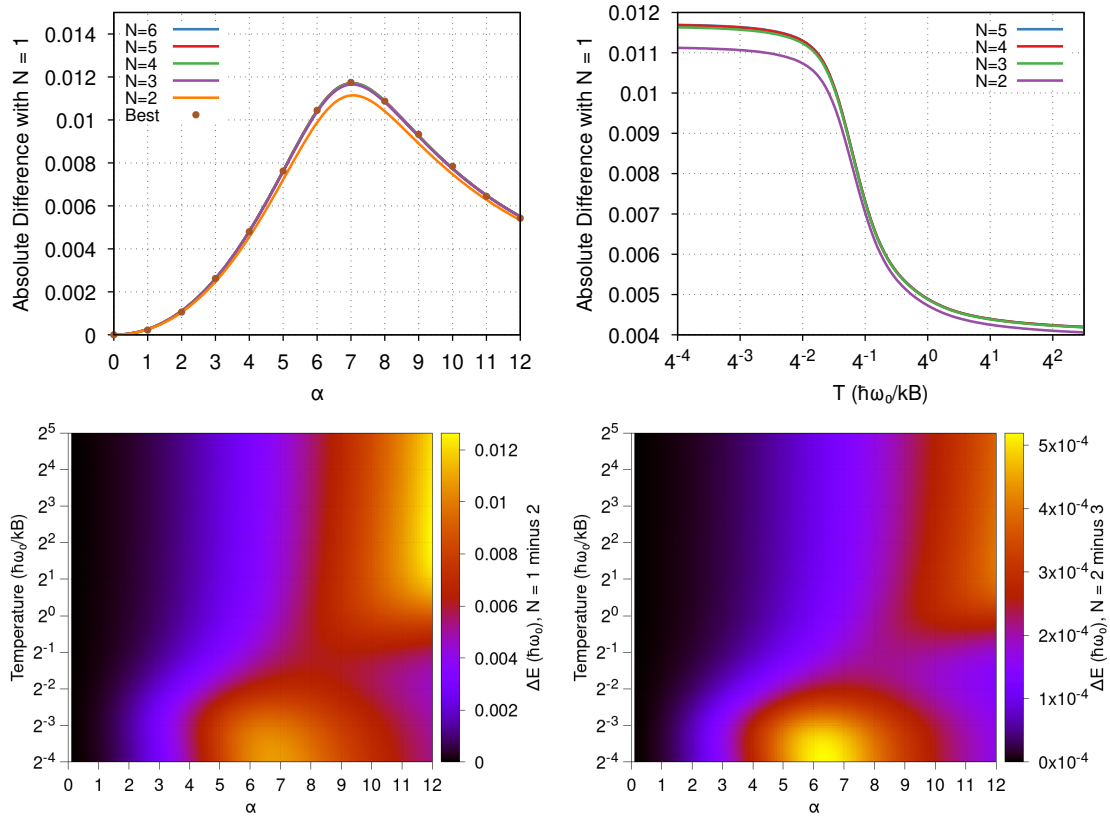


Figure 4.7: The polaron free energy for the Fröhlich model for increasing number N of fictitious particles in the trial model. top-left The absolute change in the free energy for $N = 2$ to 6 compared to the free energy result for $N = 1$ for different couplings. The dots correspond to the ‘best’ ($N \rightarrow \infty$ limit) variational solution reproduced without permission from Sels [77]. top-right The absolute change in the free energy for $N = 2$ to 5 compared to $N = 1$ for different temperatures and $\alpha = 6$. Bottom-left: A heatmap showing the absolute energy difference between $N = 1$ and $N = 2$ for different temperatures and couplings. Bottom-right: A heatmap showing the next absolute energy difference between $N = 2$ and $N = 3$ for different temperatures and couplings.

and we see a transition through the Debye temperature $T_D = \hbar\omega_0/k_B$ to a regime that converges more rapidly, such that even $N = 3$ appears to coincide with the optimal solution.

In the lower two figures in Figs. (4.7), I show heatmaps of the combined temperature and coupling dependence of the absolute shift in the free energy for $N = 2$ compared to $N = 1$ (left) and $N = 3$ compared to $N = 2$ (right). First, we consider changing the coupling where two regimes are evident at constant T . At low temperatures, below the Debye temperature ($T < T_D = \hbar\omega_0/k_B$), the most improvement in the variational bound occurs around $\alpha = 6$ to 7. Above the Debye temperature, the greatest energy difference coincides with stronger coupling. Second, from the perspective of changing temperature, we see three regimes. For $\alpha < 7$, the greatest energy difference coincides with lower temperatures as in the top-right panel of Fig. 4.7. Then, at $\alpha \approx 9$, there is minimal temperature dependence on the energy difference. For large coupling $\alpha > 9$, the temperature dependence flips so that the greatest energy difference coincides with higher temperatures. Finally, we observe that the energy difference between $N = 3$ and $N = 2$ is 100 times smaller than the energy difference between $N = 2$ and $N = 1$. This trend continues: the additional energy corrections decrease by a factor of 100 for each additional fictitious particle $N > 3$.

Overall, including multiple fictitious particles in the trial action shows considerable improvement in the free energy bound whilst maintaining rapid convergence and computational efficiency for all couplings and temperatures. We note that the analysis of this improved trial action has only been applied to the Fröhlich model. Other Hamiltonians may show different results, as demonstrated for the optimal variational solution applied to the Bogoliubov-Fröhlich Hamiltonian by Ichmoukhamedov and Tempere [63], who had to include the second-order cumulant correction to obtain an accurate bound on the free energy. While numerical analysis of improved trial actions for the Fröhlich model already exists, these are only for zero temperature. Here, I present the analysis for finite temperatures, too and believe that this choice of trial action aids a mechanistic interpretation of the quasi-particle model of the polaron that more general variational solutions (such as a general memory function) may lack.

4.5 The General Functional Variational Approach

In this section, I present the functional generalisation of the Feynman variational approach to the Fröhlich model by introducing a general ‘memory function’. This memory function represents a more general temporally non-local interaction potential due to the fictitious bath (i.e. the $N \rightarrow \infty$ limit of multiple fictitious particles in the trial action as in section 4.4) interacting with the electron. This generalisation is not new and has been derived previously in 1980 and 1984 by Adamowski et al. [36, 37], 2001 by Rosenfelder [93] and in 2022 by Ichmoukhamedov and Tempere [63], each using their own notation and interpretations.

Here, I present my notation and interpretation. I analogueise this general ‘memory function’ with a trial *self-energy* function Σ and make comparisons of the generalised variational principle with other many-body diagrammatic methods such as GW and Density Mean-Field Theory.

Later, in section 4.7, I push this analogy further when I derive a variational principle for fields using coherent state path integrals and establish the connection to dynamical properties like the polaron mobility in section 5.4.

4.5.1 A Trial Action with a General Self-Energy

The most general quadratic, isotropic, two-time trial action for a generalised function variational approach is

$$S_0 = \frac{m_0}{2} \int_0^{\hbar\beta} [\dot{\mathbf{r}}(\tau)]^2 - \frac{1}{2} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \Sigma(\tau - \tau') \mathbf{r}(\tau) \cdot \mathbf{r}(\tau'), \quad (4.27)$$

where $\Sigma(\tau)$ is a trial ‘self-energy’ and is a real, continuous function defined for $|\tau| \leq \hbar\beta$ and can be assumed to be symmetric $\Sigma(-\tau) = \Sigma(\tau)$. If the trial action S_0 is translationally invariant, the self-energy must obeys the sum-rule,

$$\int_0^{\hbar\beta} \Sigma(\tau - \tau') d\tau' = 0 \quad \forall \tau \in [0, \hbar\beta]. \quad (4.28)$$

Since the polaron model action S is typically translationally invariant, we require this of the trial action too. A consequence of imposing Eq. (4.28) is that the self-energy is β -periodic,

$$\Sigma(\tau - \hbar\beta) = \Sigma(\tau) \quad \forall \tau \in [0, \hbar\beta]. \quad (4.29)$$

In what follows, we assume that the self-energy is always β -periodic, but many of the following results do not necessarily require it to follow the sum-rule in Eq. (4.28) [37].

Using integration-by-parts on the kinetic part of the trial action, we can rewrite the trial action as

$$S_0 = \frac{1}{2} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \mathbf{r}(\tau) G^{-1}(\tau, \tau') \mathbf{r}(\tau'), \quad (4.30)$$

where we define the ‘kernel’ function $G^{-1}(\tau, \tau') \equiv m_0 \frac{\partial^2}{\partial \tau^2} \delta(\tau - \tau') - \Sigma(\tau - \tau') = G^{-1}(\tau - \tau')$. We have explicitly analogised this kernel with the inverse of the polaron quasiparticle Green function $G(\tau, \tau')$ where we identify $G_0^{-1}(\tau, \tau') = m_0 \frac{\partial^2}{\partial \tau^2} \delta(\tau - \tau')$ as the inverse of the *bare* (non-interacting) Green function of the electron.

4.5.2 The Free Energy Functional Expression

Instead of optimising for the values of the variational parameters v and w that give the lowest upper bound to the polaron free energy, we now optimise for the best ‘self-energy’ $\Sigma(\tau)$. Thus, our free energy becomes a functional of this trial self-energy function

$$F \leq F_{\text{trial}}[\Sigma] = F_{\text{ph}} + F_{S_0[\Sigma]} + \frac{1}{\hbar\beta} \langle S - S_0[\Sigma] \rangle_{S_0[\Sigma]}, \quad (4.31)$$

with F_{ph} the free energy of the non-interacting phonon system.

The Model Action Internal Energy

For the model action S , we use the general polaron action defined in Eq. (3.39). Assuming the kinetic part of the model and trial actions are the same and cancel; we evaluate $\langle S \rangle_{S_0}$ from

$$\langle S \rangle_{S_0} = - \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' D_{\omega_{\mathbf{q}}}(\tau - \tau') \left\langle e^{i\mathbf{q} \cdot [\mathbf{r}(\tau) - \mathbf{r}(\tau')]} \right\rangle_{S_0}. \quad (4.32)$$

To evaluate this functional, we need to evaluate the density-density correlation function

$$\left\langle \rho^\dagger(\tau) \rho(\tau') \right\rangle = \left\langle e^{i\mathbf{q} \cdot [\mathbf{r}(\tau) - \mathbf{r}(\tau')]} \right\rangle_{S_0}. \quad (4.33)$$

To evaluate the density-density correlation function, we introduce the generating functional

$$Z[\mathbf{J}] = \left\langle \exp \left\{ \int_0^{\hbar\beta} d\tau \mathbf{J}(\tau) \cdot \mathbf{r}(\tau) \right\} \right\rangle_{S_0}, \quad (4.34)$$

where $\mathbf{J}(\tau)$ is an arbitrary source term. This generating functional reduces to the density-density correlation function if we substitute $\mathbf{J}(\sigma) = i\mathbf{q} [\delta(\sigma - \tau) - \delta(\sigma - \tau')]$. From this field integral, we can derive all correlation functions, and subsequently, we can calculate both $\langle S - S_0 \rangle_{S_0}$ and F_{S_0} .

We recognise that the expectation $\langle \cdot \rangle_{S_0}$ indicates averaging with respect to an isotropic Gaussian stochastic process $\mathbf{r}(\tau)$ with zero mean and so is uniquely characterised by its covariance $\langle \mathbf{r}(\tau) \cdot \mathbf{r}(\tau') \rangle_{S_0}$. Consequentially, the functional integral implicit in Eq. (4.34) is evaluable and must be a Gaussian functional,

$$Z[\mathbf{J}] = \exp \left\{ \frac{m_0}{2n\hbar\beta} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \mathbf{J}(\tau) \cdot \langle \mathbf{r}(\tau) \cdot \mathbf{r}(\tau') \rangle_{S_0} \cdot \mathbf{J}(\tau') \right\}, \quad (4.35)$$

where n is the dimensionality.

Building on our analogy to many-body methods, this covariance is the single-polaron quasiparticle Green function $G(\tau, \tau') \equiv \langle \mathbf{r}(\tau) \cdot \mathbf{r}(\tau') \rangle$. It can be determined from the Dyson equation $G^{-1}(\tau - \tau') = G_0^{-1}(\tau - \tau') - \Sigma(\tau - \tau')$ and the equation of motion of the polaron Green function

$$\int_0^{\hbar\beta} d\tau'' G(\tau - \tau'') G^{-1}(\tau' - \tau'') = n\delta(\tau - \tau'), \quad (4.36)$$

where $\delta(\tau)$ is a periodic delta function which has a Fourier representation

$$\delta(\tau) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} e^{i\omega_n \tau}, \quad (4.37)$$

with $\omega_n = 2\pi n/\hbar\beta$ the “even” Matsubara frequencies.

Under the assumption of translation invariance,

$$\int_0^{\hbar\beta} \Sigma(\tau) d\tau \neq 0, \quad (4.38)$$

the polaron Green function is then given in Fourier representation as

$$G(\tau - \tau') = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} \frac{e^{i\omega_n(\tau - \tau')}}{m_0\omega_n^2 - \Sigma_n}, \quad (4.39)$$

where we can identify the Fourier coefficients as $G_n = (m_0\omega_n^2 - \Sigma_n)^{-1}$ where Σ_n is the n -th Fourier coefficient of the self-energy function

$$\Sigma_n = \frac{1}{\beta} \int_0^{\hbar\beta} \Sigma(\tau) e^{-i\omega_n \tau} d\tau = \Sigma_{-n}. \quad (4.40)$$

If $\Sigma_0 = 0$ and we no longer have a translation-invariant system, the equation of motion for the Green function is still valid, provided we omit the term at $n = 0$ in Eq. (4.39).

Now equipped with the polaron quasiparticle Green function and the generating functional, we can compute all the averages required in the free energy inequality. Setting the source term to be,

$$\mathbf{J}(\tau) = i\mathbf{q} [\delta(\tau - \sigma) - \delta(\tau - \sigma')] \equiv \mathbf{J}_{\mathbf{q},\sigma,\sigma'}(\tau). \quad (4.41)$$

we find the density-density correlation function,

$$\left\langle e^{i\mathbf{q} \cdot [\mathbf{r}(\tau) - \mathbf{r}(0)]} \right\rangle_{S_0} = \exp \left(-q^2 r_0^2 [G(0) - G(\tau)] \right). \quad (4.42)$$

Thus, for $\langle S \rangle_{S_0}$ we obtain

$$\frac{1}{\beta} \langle S \rangle_{S_0} = -\frac{1}{\beta} \sum_{\mathbf{q}} |\mathbf{M}_{\mathbf{q}}|^2 \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' D_{\omega_{\mathbf{q}}}(\tau - \tau') e^{q^2 r_0^2 [G(\tau - \tau') - G(0)]}. \quad (4.43)$$

The Trial Model Free Energy

The free energy for the trial system can be evaluated from its partition function Z_{S_0} ,

$$Z_{S_0} = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(\hbar\beta)=0} D\mathbf{r}(\tau) \exp \left(-\frac{m_0}{2\hbar} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \mathbf{r}(\tau) G^{-1}(\tau - \tau') \mathbf{r}(\tau') \right). \quad (4.44)$$

This is just a Gaussian functional integral for a real-valued function and can be readily evaluated as

$$Z_0 = \left[\det(G^{-1}) \right]^{-1/2}. \quad (4.45)$$

Note that we have absorbed the mass term into G for simplicity.

Using the relationship between the partition function and the free energy $Z_{S_0} = e^{-\beta F_{S_0}}$, we get the free energy for the trial system as

$$\begin{aligned} F_{S_0} &= -\frac{1}{2\beta} \ln \det(G) \\ &= -\frac{1}{2\beta} \text{Tr} \ln(G). \end{aligned} \quad (4.46)$$

The Trial Model Internal Energy

We can evaluate the trial system internal energy $\frac{1}{\beta} \langle S_0 \rangle_{S_0}$ by using the “coupling constant” integration trick [37] in which we extract a multiplicative constant λ from the self-energy function $\Sigma \rightarrow \lambda \Sigma$. For a translation-invariant system, we can evaluate the free energy from

$$F_{S_0}(\lambda) = F_{S_0}(0) + \int_0^\lambda d\lambda' \frac{\partial F_{S_0}(\lambda')}{\partial \lambda'}. \quad (4.47)$$

The partial derivative is then

$$\frac{\partial F_{S_0}(\lambda)}{\partial \lambda} = \frac{1}{\beta} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \Sigma(\tau - \tau') G(\tau - \tau'), \quad (4.48)$$

which implies

$$F_{S_0}(0) = -\frac{1}{\beta} \ln \left\{ V_n \left(\frac{m_0}{2\pi\hbar^2\beta} \right)^{n/2} \right\} = \frac{1}{\beta} \text{Tr} \ln \left(G_0^{-1} \right), \quad (4.49)$$

which is just the free energy of the free electron. Note we have defined a short-hand ‘trace’, Tr , which we consider to include the double imaginary-time integration of the ‘functional matrices’ (infinite-dimensional matrices) and any other indices the self-energy and Green function may depend on.

Thus, we can evaluate $\langle S_0 \rangle_{S_0}$ using $F_{S_0}(\lambda)$ in Eq. (4.47) and setting $\lambda = 1$ [63],

$$\begin{aligned} \frac{1}{\beta} \langle S_0 \rangle_{S_0} &= \left. \frac{\partial F_{S_0}(\lambda)}{\partial \lambda} \right|_{\lambda=1} \\ &= \frac{1}{\beta} \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' \Sigma(\tau - \tau') G(\tau - \tau') \\ &\equiv \frac{1}{\beta} \text{Tr} (\Sigma G). \end{aligned} \quad (4.50)$$

The Total Free Energy Functional Expression

Overall, by combining all the terms, we obtain the variational expression for the free energy,

$$F \leq F_{ph} + F_{S_0} + \frac{1}{\beta} \text{Tr} (\Sigma G) + \Phi[G], \quad (4.51)$$

where I have defined

$$\begin{aligned} \Phi[G] &= \frac{1}{\hbar^2\beta} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \int_0^{\hbar\beta} \int_0^{\hbar\beta} d\tau d\tau' D_{\omega_{\mathbf{q}}}(\tau - \tau') e^{q^2 r_0^2 [G(\tau - \tau') - G(0)]} \\ &= \frac{2}{\hbar^2\beta} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \int_0^{\hbar\beta} d\tau (\hbar\beta - \tau) D_{\omega_{\mathbf{q}}}(\tau) e^{q^2 r_0^2 [G(\tau) - G(0)]}. \end{aligned} \quad (4.52)$$

To go from line one to line two, I used the symmetry property of the double integral (see Eq. (2.94)).

We note that this takes on a similar form to the expression for the grand potential obtained by Luttinger and Ward [96] where $\Phi[G]$ is an approximation to the Luttinger-Ward functional; the sum of all closed, bold, two-particle irreducible diagrams. Other approximations to this function include GW theory, where it is truncated to include just ring diagrams

$\Phi[G] \approx GUG + GUGGUG + \dots$, and Density Mean-Field Theory (DMFT), where only local diagrams are accounted for.

For the n -dimensional Fröhlich polaron model, we have to evaluate the expectation of the two-time Coulomb interaction, which we do in the Fourier representation where we use the result from the density-density correlation,

$$\begin{aligned} \left\langle \frac{1}{|\mathbf{r}(\sigma) - \mathbf{r}(\sigma')|} \right\rangle_{S_0} &= \frac{4\pi S_{n-1}}{(2\pi)^n} \int d^n q \frac{1}{q^2} Z[\mathbf{J}_{\mathbf{q},\sigma,\sigma'}], \\ &= \left(\frac{2n}{\pi \langle |\mathbf{r}(\sigma) - \mathbf{r}(\sigma')|^2 \rangle_{S_0}} \right)^{1/2}, \end{aligned} \quad (4.53)$$

with S_{n-1} the volume of an n -ball. For the n -dimensional Fröhlich model, this reduces to

$$\Phi^{(F)}[G] = -\frac{8\pi S_{n-1}|M_0|^2}{(2\pi)^n} \int_0^{\hbar\beta} d\tau \left(\frac{\tau}{\hbar\beta} - 1 \right) \frac{D_{\omega_0}(\tau)}{\sqrt{G(\tau)}}. \quad (4.54)$$

4.5.3 Self-consistent Equations

To find the best trial-self energy, in analogy to the Luttinger-Ward theorem [96], we choose to evaluate the stationarity condition on the free energy with respect to the trial Green function $\delta F[G]/\delta G(\tau) = 0$, which should vanish for the full interacting Green function and corresponds with the ‘optimal’ self-energy. We get

$$\Sigma(\tau) = \frac{2}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 (\hbar\beta - \tau) D_{\omega_{\mathbf{q}}}(\tau) e^{q^2 r_0^2 [G(\tau) - G(0)]}. \quad (4.55)$$

This is consistent with the Luttinger-Ward theorem, where we can alternatively evaluate the self-energy from the Luttinger-Ward functional,

$$\begin{aligned} \Sigma(\tau) &= \frac{\delta \Phi}{\delta G(\tau)} \\ &= \frac{2}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 (\hbar\beta - \tau) D_{\omega_{\mathbf{q}}}(\tau) e^{q^2 r_0^2 [G(\tau) - G(0)]}, \end{aligned} \quad (4.56)$$

which gives the same answer as the stationarity condition with our definition of self-energy and the Luttinger-Ward functional. More generally, the self-energy would have off-diagonal terms. However, as we assumed a translational invariant system and have no other ‘indices’, we can express this self-energy as a function of one imaginary-time variable.

The equation for the self-energy must be solved self-consistently since the polaron Green function is a functional of the self-energy $G[\Sigma]$. From the equation of motion for the polaron Green function (Eq. (4.36)), we have

$$\int_0^{\hbar\beta} d\tau'' G(\tau - \tau'') \left[G_0^{-1}(\tau' - \tau'') - \Sigma(\tau' - \tau'') \right] = n\delta(\tau - \tau'), \quad (4.57)$$

or in the Matsubara (Fourier) representation,

$$G(\tau) = \frac{1}{\beta} \sum_{i\omega_n} \frac{e^{i\omega_n\tau}}{-m_0(i\omega_n)^2 - \Sigma_n}. \quad (4.58)$$

These equations reduce to Osaka's [27] and Feynman's [2] trial action by choosing the self-energy

$$\Sigma_F(\tau) = \frac{M_w^3}{4} D_w(\tau), \quad (4.59)$$

with D the phonon Green function (Eq. (2.2.1)). This does not follow the stationarity condition for the free energy, so Feynman's trial action does not give the lowest possible upper bound to the free energy of the Fröhlich polaron at the level of Jensen's inequality.

4.6 Cumulant Expansion Corrections

In this section, we seek to generalise the variational approximation beyond the first-order cumulant corresponding to the Feynman-Jensen inequality (Eq. (4.6)). We begin with a simple perturbative expansion akin to that derived by Peeters et al. [97], where the trial action just corresponds to the free electron action. We then generalise this procedure to the more general trial action defined by the trial polaron Green function G (Eq. (4.30)). Finally, we investigate an alternative cumulant expansion for which the variational bound on the free energy is preserved when additional cumulant correction terms are included.

4.6.1 The Perturbative Expansion

The partition function for the polaron system described by the action S can be rewritten in terms of another action S_0 as

$$Z = e^{-\beta F} = e^{-\beta F_{S_0}} \langle e^{\Delta S[\mathbf{r}(\tau)]} \rangle_{S_0}, \quad (4.60)$$

with $\Delta S \equiv S - S_0$.

The exponential can then be expanded to give

$$Z = e^{-\beta F_{S_0}} \sum_{n=0}^{\infty} \frac{1}{n!} \langle (\Delta S[\mathbf{r}(\tau)])^n \rangle_{S_0}. \quad (4.61)$$

If S_0 is chosen to be the action of the free particle,

$$S_0 = \frac{1}{2} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' \mathbf{r}(\tau) G_0^{-1}(\tau, \tau') \mathbf{r}(\tau') = \frac{m_0}{2} \int_0^{\hbar\beta} d\tau \dot{\mathbf{r}}(\tau)^2, \quad (4.62)$$

where

$$G_0^{-1}(\tau, \tau') = G_0^{-1}(\tau - \tau') = -m_0 \frac{\partial^2}{\partial \tau^2} \delta(\tau - \tau') \quad (4.63)$$

is the differential operator for the free particle with periodic boundary conditions (in imaginary time), then $\Delta S = S_{\text{int}}$ will only depend on the particle self-interaction.

The expansion of the partition function is equivalent to a perturbative expansion since $S_{\text{int}} \propto \alpha$ is linearly proportional to the electron-phonon coupling. In this case,

$$\begin{aligned} \langle (\Delta S[\mathbf{r}(\tau)])^n \rangle_{S_0} &= \langle (S_{\text{int}}[\mathbf{r}(\tau)])^n \rangle_{S_0} \\ &= \prod_{j=1}^n \sum_{\mathbf{q}_j} |M_{\mathbf{q}_j}|^2 \int_0^{\hbar\beta} d\tau_j \int_0^{\hbar\beta} d\tau'_j D_{\omega_{\mathbf{q}_j}}(\tau_j - \tau'_j) \left\langle e^{i \sum_{j=1}^n \mathbf{q}_j \cdot [\mathbf{r}(\tau_j) - \mathbf{r}(\tau'_j)]} \right\rangle_{S_0}, \end{aligned} \quad (4.64)$$

where the expectation value can be evaluated with respect to S_0 to give

$$\begin{aligned} \langle (S_{\text{int}}[\mathbf{r}(\tau)])^n \rangle_{S_0} &= \prod_{j=1}^n \sum_{\mathbf{q}_j} |M_{\mathbf{q}_j}|^2 \int_0^{\hbar\beta} d\tau_j \int_0^{\hbar\beta} d\tau'_j D_{\omega_{\mathbf{q}_j}}(\tau_j - \tau'_j) e^{-q_j^2 G_0(\tau_j - \tau'_j)} \\ &\times e^{-\frac{1}{2} \sum_{i=0}^n \sum_{j=1}^{i-1} \mathbf{q}_i \cdot \mathbf{q}_j [G_0(\tau_i - \tau'_j) + G_0(\tau_j - \tau'_i) - G_0(\tau_i - \tau_j) - G_0(\tau'_i - \tau'_j)]}, \end{aligned} \quad (4.65)$$

with the free electron Green function $G_0(\tau) = \frac{|\tau|}{2m_0} \left(1 - \frac{|\tau|}{\hbar\beta}\right)$.

4.6.2 An Improved Perturbative Expansion

More generally, we may want to consider the trial polaron action,

$$S_0 = \frac{1}{2} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' \mathbf{r}(\tau) G_{S_0}^{-1}(\tau, \tau') \mathbf{r}(\tau') \quad (4.66)$$

for some general trial Green function $G_{S_0}(\tau)$ which satisfies the equation of motion

$$\int_0^{\hbar\beta} d\sigma G_{S_0}^{-1}(\tau, \sigma) G_{S_0}(\sigma, \tau') = \delta(\tau - \tau'). \quad (4.67)$$

With this general polaron Green function, we consider

$$\begin{aligned} \Delta S &= \frac{1}{2} \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' \left\{ \mathbf{r}(\tau) \left[G_0^{-1}(\tau, \tau') - G_{S_0}^{-1}(\tau, \tau') \right] \mathbf{r}(\tau') \right. \\ &\quad \left. + 2 \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 \rho_{\mathbf{q}}(\tau) D_{\omega_{\mathbf{q}}}(\tau - \tau') \rho_{-\mathbf{q}}(\tau') \right\}, \end{aligned} \quad (4.68)$$

where $\rho_{\mathbf{q}}(\tau) = e^{i\mathbf{q} \cdot \mathbf{r}(\tau)}$ is the electron density.

Choosing $G_{S_0}^{-1} = G_0^{-1}$ reproduces the perturbative expansion above.

More generally, the n -th term of the expansion is

$$\begin{aligned} \langle (\Delta S[\mathbf{r}(\tau)])^n \rangle_{S_0} &= \sum_{k=0}^n \binom{n}{k} 2^{k-n} \prod_{i=1}^{n-k} \prod_{j=1}^k \sum_{\mathbf{q}_j} |M_{\mathbf{q}_j}|^2 \int_0^{\hbar\beta} d\tau_i d\tau'_i d\sigma_j d\sigma'_j \\ &\times \Sigma_{S_0}(\tau_i, \tau'_i) D_{\omega_{\mathbf{q}_j}}(\sigma_i, \sigma'_i) \left\langle \prod_{i=1}^{n-k} \prod_{j=1}^k \mathbf{r}(\tau_i) \cdot \mathbf{r}(\tau'_i) \rho_{\mathbf{q}_j}(\sigma_j) \rho_{-\mathbf{q}_j}(\sigma'_j) \right\rangle_{S_0}, \end{aligned} \quad (4.69)$$

where we define the self-energy $\Sigma_{S_0}(\tau, \tau') \equiv G_0^{-1}(\tau, \tau') - G_{S_0}^{-1}(\tau, \tau')$.

The expectation within the integrand for the n -th cumulant can be evaluated from the generating functional,

$$\begin{aligned} Z_{S_0}[\mathbf{J}(t)] &= \left\langle \exp \left(\int_0^{\hbar\beta} dt \mathbf{J}(t) \cdot \mathbf{r}(t) \right) \right\rangle_{S_0} \\ &= \exp \left(\frac{1}{2} \int_0^{\hbar\beta} dt \int_0^{\hbar\beta} dt' \mathbf{J}(t) \cdot G_{S_0}(t, t') \cdot \mathbf{J}(t') \right), \end{aligned} \quad (4.70)$$

where we assume periodic boundary conditions $\mathbf{r}(0) = \mathbf{r}(\hbar\beta)$.

The generating functional $Z[\mathbf{J}]$ allows us to evaluate the correlation functions corresponding to products of the electron position at different times $\langle \mathbf{r}(\tau_1) \mathbf{r}(\tau'_1) \dots \mathbf{r}(\tau_n) \mathbf{r}(\tau'_n) \rangle_{S_0}$. This is typically done by differentiating the generating functional with respect to the source term at different times $J(\tau_i)$, one for each position function in the expectation. We would then set $J = 0$ afterwards.

To evaluate the expectation

$$\left\langle \prod_{i=1}^{n-k} \prod_{j=1}^k \mathbf{r}(\tau_i) \cdot \mathbf{r}(\tau'_i) \rho_{\mathbf{q}_j}(\sigma_j) \rho_{-\mathbf{q}_j}(\sigma'_j) \right\rangle_{S_0}, \quad (4.71)$$

we can use the standard method of differentiating the generating function with respect to the source term J , but instead of setting $J = 0$, we will set

$$\mathbf{J}(t) = i \sum_j \mathbf{q}_j \left[\delta(t - \sigma_j) - \delta(t - \sigma'_j) \right] \quad (4.72)$$

to account for all the electron density terms within the expectation.

For example, the first cross-term involving electron positions $\mathbf{r}$ and densities $\rho_{\mathbf{q}}$ can be evaluated from

$$\begin{aligned} \langle \mathbf{r}(\tau) \cdot \mathbf{r}(\tau') \rho_{\mathbf{q}}(\sigma) \rho_{-\mathbf{q}}(\sigma') \rangle_{S_0} &= \frac{\delta^2 Z_{S_0}[\mathbf{J}(t)]}{\delta \mathbf{J}(\tau) \delta \mathbf{J}(\tau')} \bigg|_{\mathbf{J}(t)=i\mathbf{q}[\delta(t-\sigma)-\delta(t-\sigma')]} \\ &= \left(G_{S_0}(\tau, \tau') - q^2 [G_{S_0}(\tau, 0)G_{S_0}(\tau', 0) - G_{S_0}(\tau, \sigma)G_{S_0}(\tau', \sigma')] \right) e^{-q^2 [G_{S_0}(0) - G_{S_0}(\sigma, \sigma')]}, \end{aligned} \quad (4.73)$$

where we assume the trial system is translation invariant such that $G_{S_0}(\tau, \tau') = G_{S_0}(|\tau - \tau'|)$ which implies $G_{S_0}(\tau, \tau') = G_{S_0}(\tau', \tau)$ and $G_{S_0}(\tau, \tau) = G_{S_0}(0)$. Higher-order terms can be determined similarly.

We may choose S_0 as a trial action that better approximates the polaron action S over the free particle action. For example, we may choose Feynman's trial action, for which the

trial Green function is,

$$G_F(\tau) = \frac{|\tau|}{2m_0} \left(1 - \frac{|\tau|}{\hbar\beta} \right) - \frac{1}{2m_0} \frac{v^2 - w^2}{v^3} \left[D_v(\tau) - \frac{|\tau|}{\hbar\beta} \right]. \quad (4.74)$$

Or, we may choose the ‘variationally optimal’ trial action with the corresponding Green function derived self-consistently following the method in the previous section (4.5).

4.6.3 A Variational Bound Preserving Expansion

Truncating the series expansion presents an approximation to the partition function of the polaron:

$$Z = \sum_{n=0}^{\infty} \frac{1}{n!} \langle (\Delta S[\mathbf{r}(\tau)])^n \rangle_{S_0} \approx Z_N = \sum_{n=0}^N \frac{1}{n!} \langle (\Delta S[\mathbf{r}(\tau)])^n \rangle_{S_0}. \quad (4.75)$$

Alternatively, we could take a mean-field approximation such that

$$\langle (\Delta S[\mathbf{r}(\tau)])^n \rangle_{S_0} \approx \left(\langle \Delta S[\mathbf{r}(\tau)] \rangle_{S_0} \right)^n, \quad (4.76)$$

which gives

$$Z \approx e^{-\beta F_{S_0}} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\langle \Delta S[\mathbf{r}(\tau)] \rangle_{S_0} \right)^n = e^{-\beta F_{S_0} + \langle \Delta S \rangle_{S_0}}, \quad (4.77)$$

which is just the Feynman-Jensen approximation.

We may attempt to combine this series expansion (Eq. (4.75)) with the variational approximation. Rather than expanding the partition function in terms of the *raw* moments $\mu'_n = \langle (\Delta S)^n \rangle_{S_0}$, we can rewrite the expansion for the partition function in terms of the *central* moments $\mu_n = \langle (\Delta S - \langle \Delta S \rangle_{S_0})^n \rangle_{S_0}$

$$\begin{aligned} Z &= Z_{S_0} \left\langle e^{\Delta S} \right\rangle_{S_0} \\ &= Z_{S_0} e^{\langle \Delta S \rangle_{S_0}} \left\langle e^{\Delta S - \langle \Delta S \rangle_{S_0}} \right\rangle_{S_0} \\ &= e^{-\beta F_{S_0} + \langle \Delta S \rangle_{S_0}} \sum_{n=0}^{\infty} \frac{1}{n!} \langle (\Delta S - \langle \Delta S \rangle_{S_0})^n \rangle_{S_0}, \end{aligned} \quad (4.78)$$

where we extract the average contribution from the mean-field Feynman-Jensen inequality.

We note the first term ($n = 0$) is 1 and the second term ($n = 1$) is zero, so we have

$$Z = e^{-\beta F_{S_0} + \langle \Delta S \rangle_{S_0}} \left[1 + \sum_{n=2}^{\infty} \frac{1}{n!} \langle (\Delta S - \langle \Delta S \rangle_{S_0})^n \rangle_{S_0} \right]. \quad (4.79)$$

From this we can recover the Feynman-Jensen inequality noting that since $\frac{d^2}{dx^2}e^x \geq 0$, then $e^X \geq e^{\langle X \rangle} [1 + (X - \langle X \rangle)]$.

Näively, we could directly include higher-order terms in this expansion. However, generally, this destroys the variational bound as the residual of the truncated Taylor expansion $R_N(X)$ for the exponential function is not strictly positive for all orders of the expansion,

$$R_N(X) = e^X - e^{\langle X \rangle} \sum_{n=0}^N \frac{(X - \langle X \rangle)^n}{n!} \not\geq 0 \quad \forall \quad X \in \mathcal{R}, \quad N \in \mathcal{N}_0, \quad (4.80)$$

since $R_N(X) \leq 0$ for $X \leq \langle X \rangle$ and N even.

However, if we instead group the expansion in pairs of terms, i.e. $n = 0$ with $n = 1$, $n = 2$ with $n = 3$ etc., we can write,

$$R_N(X) = e^X - e^{\langle X \rangle} \sum_{n=0}^{2N-1} \frac{(X - \langle X \rangle)^n}{n!} \geq 0 \quad \forall \quad X \in \mathcal{R}, \quad N \in \mathcal{N}_0, \quad (4.81)$$

which is strictly convex.

We can then approximate the partition function as

$$\begin{aligned} Z &= e^{-\beta F_{S_0} + \langle \Delta S \rangle_{S_0}} \left[1 + \sum_{n=1}^{\infty} \sum_{m=2n}^{2n+1} \frac{1}{m!} \langle (\Delta S - \langle \Delta S \rangle_{S_0})^m \rangle_{S_0} \right] \\ Z &\geq Z_N = e^{-\beta F_{S_0} + \langle \Delta S \rangle_{S_0}} \left[1 + \sum_{n=2}^{2N-1} \frac{1}{n!} \langle (\Delta S - \langle \Delta S \rangle_{S_0})^n \rangle_{S_0} \right]. \end{aligned} \quad (4.82)$$

We then obtain a generalised upper-bound to the free energy as

$$F \leq F_{S_0} - \frac{1}{\beta} \langle \Delta S \rangle_{S_0} - \frac{1}{\beta} \ln \left[1 + \sum_{n=2}^{2N-1} \frac{1}{n!} \langle (\Delta S - \langle \Delta S \rangle_{S_0})^n \rangle_{S_0} \right] \quad (4.83)$$

which presents an alternative cumulant-type expansion that preserves the variational bound on the free energy.

Thus, we could include higher-order cumulant corrections, the terms of which can be evaluated using Eq. (4.69), and systematically derive an improved variational inequality for the polaron free energy rather than including perturbative corrections in terms of the mean-field Feynman-Jensen variational solution.

I do not present numerical results from this improved inequality in this thesis but provide it as a potential new theoretical derivation.

4.7 Variational Principle for Coherent State Path Integrals

In this section, we derive a variational principle for coherent state path integrals using a trial Green function, G . This approach is beneficial for interacting fermionic systems where exact solutions are not feasible. We will introduce the self-energy corrections, first calculate the moments (disconnected Green functions), and then generalise the expansion to include cumulants requiring connected Green functions. To facilitate this, we introduce two generating functionals: $Z[J]$ for moments (disconnected Green functions) and $Z[K]$ for cumulants (connected Green functions). Additionally, we address the physical motivation for choosing this formalism and discuss its applicability to specific fermionic models.

We begin with the full partition function for an interacting fermionic system,

$$Z = \int D\bar{\psi} D\psi \exp \left(-\bar{\psi}_i G_{0,ij}^{-1} \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right), \quad (4.84)$$

where G_0 is the bare Green function, and V_{ijkl} represents the interaction vertex tensor. In this section we use the Einstein summation convention where repeated indices are implicitly summed over. The partition function Z captures the full interacting fermionic system. We aim to introduce a trial Green function G and derive a variational approximation to this partition function that accounts for the interaction corrections.

4.7.1 First Order Feynman-Jensen Variational Approximation

We now derive the first variational approximation using the trial Green function G . The partition function associated with this trial Green function is given by

$$\begin{aligned} Z_0[G] &= \int D\bar{\psi} D\psi \exp \left(-\bar{\psi}_i G_{ij}^{-1} \psi_j \right) \\ &= \det \left[G^{-1} \right]. \end{aligned} \quad (4.85)$$

To facilitate a variational approach, we rewrite the original partition function by splitting the terms involving the trial Green function and the difference between the interacting and trial Green functions. This yields the expression,

$$Z = \int D\bar{\psi} D\psi \exp \left(-\bar{\psi}_i [G_{0,ij}^{-1} - G_{ij}^{-1}] \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right) e^{-\bar{\psi}_i G_{ij}^{-1} \psi_j}. \quad (4.86)$$

Using the definition of Z_0 , we factor out the non-interacting part:

$$Z = Z_0[G] \left\langle \exp \left(-\bar{\psi}_i \Sigma_{ij}[G] \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right) \right\rangle_G, \quad (4.87)$$

where $\Sigma_{ij}[G] = G_{0,ij}^{-1} - G_{ij}^{-1}$ represents the self-energy correction and the average $\langle \cdot \rangle_G$ is,

$$\langle \cdot \rangle_G \equiv \int D\bar{\psi} D\psi (\cdot) \exp \left(-\bar{\psi}_i G_{ij}^{-1} \psi_j \right). \quad (4.88)$$

Since the exponential function is convex, we apply Jensen's inequality $\langle e^X \rangle \geq e^{\langle X \rangle}$ to derive a variational bound to obtain a tractable approximation to the partition function. This gives

$$Z \geq Z_0[G] \exp \left(\Sigma_{ij}[G] \langle \psi_j \bar{\psi}_i \rangle_G - V_{ijkl} \langle \psi_k \psi_l \bar{\psi}_i \bar{\psi}_j \rangle_G \right). \quad (4.89)$$

4.7.2 Moment Generating Functional $Z[J]$ for Disconnected Green Functions

To calculate the two-point $\langle \psi_j \bar{\psi}_i \rangle_G$ and four-point $\langle \psi_k \psi_l \bar{\psi}_i \bar{\psi}_j \rangle_G$ correction functions, we first introduce the moment generating functional $Z[J]$, which allows for calculating these 'moments' (disconnected Green functions). This functional is defined by adding a source term J_i and $\bar{J}_i$ that couples to the fermionic fields,

$$\begin{aligned} Z[J] &= \int D\bar{\psi} D\psi \exp \left(-\bar{\psi}_i G_{ij}^{-1} \psi_j + \bar{J}_i \psi_i + \bar{\psi}_i J_i \right) \\ Z[J] &= Z_0 \exp \left(\bar{J}_i G_{ij} J_j \right) \end{aligned} \quad (4.90)$$

The disconnected Green functions (moments) are obtained by differentiating the generating functional with respect to the source terms,

$$\langle \psi_i \bar{\psi}_j \rangle = \frac{1}{Z_0} \frac{\delta^2 Z[J]}{\delta \bar{J}_i \delta J_j} \Big|_{J=0}, \quad (4.91)$$

and higher-order disconnected Green functions (moments) are computed similarly,

$$\langle \psi_1 \bar{\psi}'_1 \cdots \psi_n \bar{\psi}'_n \rangle = \frac{1}{Z_0} \frac{\delta^{2n} Z[J]}{\delta \bar{J}_1 \delta J'_1 \cdots \delta \bar{J}_n \delta J'_n} \Big|_{J=0}. \quad (4.92)$$

For higher-order Green functions, the moments are expressed in terms of the determinant of the Green function matrix,

$$\langle \psi_1 \cdots \psi_n \bar{\psi}'_1 \cdots \bar{\psi}'_n \rangle_G = \det \begin{bmatrix} G_{11'} & \cdots & G_{1n'} \\ \vdots & \ddots & \vdots \\ G_{n1'} & \cdots & G_{nn'} \end{bmatrix}, \quad (4.93)$$

which accounts for all the possible exchanges of pairs of fermions as from Wick's theorem. These moments describe the disconnected contributions to the Green functions and are necessary for calculating statistical averages but do not account for the full structure of interactions in the system.

Substituting these Green functions into the variational expression leads to the variational expression for the thermodynamic potential $\Omega[G]$,

$$\Omega[G] \leq -\frac{1}{\beta} \ln \det[G^{-1}] - \frac{1}{\beta} \Sigma_{ij}[G] G_{ji} + \frac{1}{\beta} V_{ijkl} (G_{ki} G_{lj} - G_{kj} G_{il}). \quad (4.94)$$

The stationary condition for $\Omega[G]$ gives a self-consistent equation for the optimal G solution,

$$\frac{\delta \Omega[G]}{\delta G_{ab}} = G_{ba}^{-1} - G_{0,ba}^{-1} + 2 (V_{ibaj} - V_{biaj}) G_{ji} = 0, \quad (4.95)$$

leading to the self-energy expression,

$$\Sigma_{ba} = G_{0,ba}^{-1} - G_{ba}^{-1} = 2 (V_{ibaj} - V_{biaj}) G_{ji}. \quad (4.96)$$

which are just the Hartree-Fock self-energy diagrams.

4.7.3 Full Cumulant Expansion and Generalised Expression for the Thermodynamic Potential

Having derived the first-order approximation via the Feynman-Jensen bound, we now generalise the expression to include higher-order corrections via the cumulant expansion. Following Kubo [98], the partition function can be formally expressed as:

$$Z = Z_0[G] \exp \left\{ \left\langle \exp \left(-\bar{\psi}_i \Sigma_{ij}[G] \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right) - 1 \right\rangle_{c,G} \right\}. \quad (4.97)$$

where $\langle \cdot \rangle_c$ indicates an average taken with respect to cumulants rather than moments. This expression encapsulates the full cumulant expansion, where higher-order terms in the interaction vertex V_{ijkl} contribute corrections beyond the mean-field approximation and correlation functions correspond to *connected* Green functions.

The corresponding thermodynamic potential $\Omega[G]$ is

$$\Omega[G] = -\frac{1}{\beta} \ln \det[G^{-1}] - \frac{1}{\beta} \left\langle \exp \left(-\bar{\psi}_i \Sigma_{ij}[G] \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right) - 1 \right\rangle_{c,G}. \quad (4.98)$$

4.7.4 Generating Functional $Z[K]$ for Connected Green Functions

To compute the connected Green functions (cumulants), which include interactions beyond simple moments, we introduce the generating functional $Z[K]$, which couples a source term K_{ij} to the fermionic bilinears $\bar{\psi}_i \psi_j$. The generating functional is given by

$$\begin{aligned} Z[K] &= \int D\bar{\psi} D\psi \exp \left(-\bar{\psi}_i (G_{ij}^{-1} - K_{ij}) \psi_j \right) \\ Z[K] &= \det \left(G^{-1} - K \right). \end{aligned} \quad (4.99)$$

The connected Green functions are obtained by differentiating the logarithm of the generating functional $Z[K]$ with respect to the source term K ,

$$\left\langle \psi_i \bar{\psi}_j \right\rangle_{c,G} = -\frac{\delta}{\delta K_{ij}} \ln \frac{Z[K]}{Z_0} \Big|_{K=0} = G_{ji}, \quad (4.100)$$

and for higher-order connected Green functions (cumulants), we have

$$\begin{aligned} \left\langle \psi_1 \cdots \psi_n \bar{\psi}'_1 \cdots \bar{\psi}'_{n'} \right\rangle_{c,G} &= -\frac{\delta^n}{\delta K^n} \ln \frac{\det[G^{-1} - K]}{\det[G^{-1}]} \Big|_{K=0} \\ &= (-1)^{n+1} (n-1)! G \otimes G \otimes \cdots \otimes G \quad (n \text{ times}). \end{aligned} \quad (4.101)$$

where $\otimes$ is the Kronecker tensor product.

4.7.5 Cumulant Corrections to the Feynman-Jensen Variational Approximation

In the language of cumulants, Jensen's inequality becomes $\langle e^X - 1 \rangle_c \geq \langle X \rangle$ since the moment $M(t)$ and cumulant $K(t)$ generating functions are related by $K(t) = \ln M(t)$. Therefore, applying the 'cumulant' Jensen's inequality, we recover the usual expression,

$$\begin{aligned} &\left\langle \exp \left(-\bar{\psi}_i \Sigma_{ij}[G] \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right) - 1 \right\rangle_{c,G} \\ &= \ln \left\langle \exp \left(-\bar{\psi}_i \Sigma_{ij}[G] \psi_j - \bar{\psi}_i \bar{\psi}_j V_{ijkl} \psi_k \psi_l \right) \right\rangle_G \\ &\leq \ln \exp \left(\Sigma_{ij}[G] \langle \psi_j \bar{\psi}_i \rangle_G - V_{ijkl} \langle \psi_k \psi_l \bar{\psi}_i \bar{\psi}_j \rangle_G \right) \\ &= \Sigma_{ij}[G] \langle \psi_j \bar{\psi}_i \rangle_G - V_{ijkl} \langle \psi_k \psi_l \bar{\psi}_i \bar{\psi}_j \rangle_G, \end{aligned} \quad (4.102)$$

to give,

$$\Omega[G] \leq -\frac{1}{\beta} \ln \det[G^{-1}] - \frac{1}{\beta} \Sigma_{ij}[G] G_{ji} + \frac{1}{\beta} V_{ijkl} (G_{ki} G_{lj} - G_{kj} G_{il}), \quad (4.103)$$

as before in Eq (4.94).

Alternatively, we can expand the exponential in Eq. (4.98) to give,

$$\Omega[G] = -\frac{1}{\beta} \ln \det[G^{-1}] - \frac{1}{\beta} \sum_{n=1}^{\infty} \frac{1}{n!} \left\langle \left[\Sigma_{ij}[G] \psi_j \bar{\psi}_i - V_{ijkl} \psi_k \psi_l \bar{\psi}_i \bar{\psi}_j \right]^n \right\rangle_{c,G}. \quad (4.104)$$

Truncating the summation to the first term reproduces the Feynman-Jensen result and coincides with the Hartree-Fock diagrams for the correspond self energy as before. Higher-order terms then provide perturbative corrections in terms of the mean-field Hartree-Fock self-energy solution in Eq. (4.96).

Unfortunately, this cumulative perturbative expansion does not provide an upper-bound on the thermodynamic potential. Instead, we observe the following inequality from section 4.6 (Eq. (4.81)),

$$\langle e^X \rangle \geq e^{\langle X \rangle} \sum_{n=0}^{2N-1} \frac{1}{n!} \langle (X - \langle X \rangle)^n \rangle \quad (4.105)$$

for $N \in \mathcal{N}$ as a systematic improvement to Jensen's inequality. Then we may write,

$$\begin{aligned} \Omega_N[G] \leq & -\frac{1}{\beta} \ln \det[G^{-1}] - \frac{1}{\beta} \Sigma_{ij}[G] G_{ji} + \frac{1}{\beta} V_{ijkl} (G_{ki} G_{lj} - G_{kj} G_{il}) \\ & - \frac{1}{\beta} \ln \left\{ \sum_{n=0}^{2N-1} \frac{1}{n!} \left\langle \left[\Sigma_{ij} (\psi_j \bar{\psi}_i - G_{ji}) - V_{ijkl} (\psi_k \psi_l \bar{\psi}_i \bar{\psi}_j - G_{ki} G_{lj} + G_{kj} G_{il}) \right]^n \right\rangle_G \right\}, \end{aligned} \quad (4.106)$$

where $N = 2, 3, \dots$ provides higher-order corrections to the thermodynamic potential whilst preserving the varational bound.

CHAPTER 5

COMPUTING RESPONSE FUNCTIONS & POLARON MOBILITY

“This might suggest that the so-called imaginary time is really the real time, and that what we call real time is just a figment of our imaginations. . . a scientific theory is just a mathematical model we make to describe our observations: it exists only in our minds. So it is meaningless to ask: which is real, “real” or “imaginary” time? It is simply a matter of which is the more useful description.”

—Stephen Hawking, *A Brief History of Time*, 1988

In this chapter, I first confirm the accuracy of the FHIP method by comparing the predicted temperature and frequency dependent mobility with Diagrammatic Monte Carlo (DiagMC) calculations by Mishchenko et al. [10]. Next, I generalise the FHIP method to compute the charge-carrier mobility and optical conductivity for more complicated models. This extends FHIP to the multimode Fröhlich polaron, the Holstein small polaron, the many spring-mass extended trial solution, general many-body polarons and for an optimal self-consistent solution that coincides with the optimal free energy solution.

5.1 Numerical Evaluation of the Memory Function

Previous work [17, 18], including my own (see Appendix B), made use of the ‘doubly-oscillatory’ contour-rotated integral for the complex memory function in Eq. (2.203).

The imaginary component of the memory function is (Eqs. (47) in Ref. [17]),

$$\text{Im } \Sigma(\Omega) = \frac{2\alpha\omega_0^2}{3\Omega\sqrt{\pi}} \frac{(\hbar\omega_0\beta)^{\frac{3}{2}}}{\sinh(\hbar\omega_0\beta/2)} \left(\frac{v}{w}\right)^3 \sinh\left(\frac{\hbar\Omega\beta}{2}\right) \int_0^\infty d\tau \frac{\cos(\Omega\tau) \cos(\omega_0\tau)}{\left[\omega_0^2\tau^2 + a^2 - b \cos(v\omega_0\tau)\right]^{\frac{3}{2}}}, \quad (5.1)$$

where $a^2 \equiv (\hbar\omega_0\beta/2)^2 + R\hbar\beta\omega_0 \coth(\hbar\beta\omega_0 v/2)$, $b \equiv R\hbar\beta\omega_0/\sinh(\hbar\beta\omega_0 v/2)$ and $R \equiv (v^2 - w^2)/(w^2 v)$.

The contour integral for the real component of the memory function (see Appendix D for a detailed derivation) is

$$\begin{aligned} \text{Re } \Sigma(\Omega) = & \frac{2\alpha\omega_0^2}{3\Omega\sqrt{\pi}} \frac{(\hbar\omega_0\beta)^{\frac{3}{2}}}{\sinh(\hbar\omega_0\beta/2)} \left(\frac{v}{w}\right)^3 \\ & \times \left\{ \sinh\left(\frac{\hbar\Omega\beta}{2}\right) \int_0^\infty d\tau \frac{\sin(\Omega\tau) \cos(\omega_0\tau)}{\left[\omega_0^2\tau^2 + a^2 - b \cos(v\omega_0\tau)\right]^{\frac{3}{2}}} \right. \\ & \left. - \int_0^{\frac{\hbar\beta}{2}} d\tau \frac{(1 - \cosh(\Omega(\tau - \hbar\beta/2)) \cosh(\omega_0\tau))}{\left[a^2 - \omega_0^2\tau^2 - b \cosh(v\omega_0\tau)\right]^{\frac{3}{2}}} \right\}. \end{aligned} \quad (5.2)$$

The imaginary component of the memory function can be expanded in Bessel functions (originally, the derivation was outlined in Refs. [17, 18]. Still, in Appendix D, I provide a detailed derivation) and the real component in terms of Bessel and Struve functions.

However, I found that the cost of evaluating these expansions became large at low temperatures, requiring arbitrary precision numerics to reach converged solutions slowly. Devreese et al. [18] found an alternative analytic expansion for the real component but similarly found it to have poor convergence for all temperatures, opting to transform the integrand to one with better convergence.

Instead of using any of the contour integrals or power-series expansions, I found that directly numerically integrating Eq. (2.203) using an adaptive Gauss-Kronrod quadrature algorithm leads to faster convergence and controlled errors. Asymptotic limits of these contour integral expansions, especially at low temperatures, may still prove helpful, but are not used here.

5.2 Comparison to Diagrammatic Monte Carlo

Mishchenko et al. [10] recently used Diagrammatic Monte Carlo (DiagMC) calculations to investigate the violation of the so-called “thermal” analogue to the Mott-Ioffe-Regel (MIR) criterion in the Fröhlich polaron model. This “thermal” MIR criterion is perhaps better called the *Planckian bound* [99] under which a quasiparticle is stable to inelastic scattering.

5.2.1 Violation of the Mott-Ioffe-Regel criterion versus Planckian bound

For the quasiparticle to propagate coherently, the inelastic scattering time τ_{inel} must be greater than the “Planckian time” $\tau_{\text{Pl}} = \hbar/k_B T$. For the polaron mobility μ , this requires $\mu \gtrsim \frac{e\hbar}{Mk_B T}$. This Planckian bound can be reformulated into Mishchenko’s [10] “thermal” MIR criterion for the validity of the Boltzmann kinetic equation, $l \gg \lambda$ where l is the mean free path, and λ the de Broglie wavelength, of the charge carrier.

The usual Mott-Ioffe-Regel (MIR) criterion puts bounds on transport coefficients of the Boltzmann equations for quasiparticle-mediated transport, where localised wavepackets are formed from superpositions of single-particle Bloch states. Beyond these bounds, the mean free path of a quasiparticle is of order or smaller than its de Broglie wavelength, so it is no longer possible to form a coherent quasiparticle from superpositions of Bloch states due to the uncertainty in the single-particle state positions.

Violation of the MIR limit is commonly observed in strongly correlated systems at high temperatures. It is often used to suggest that quasiparticle physics does not describe transport in these materials. The “thermal” MIR criterion also depends on the validity of the Boltzmann description. Still, it is subtly different to the usual MIR criterion as clearly explained by Hartnoll and Mackenzie [99, 100] who refer to it instead as a “Planckian bound”. Whereas the MIR criterion discerns the ability to form coherent particles from the superposition of Bloch states, the Planckian bound describes the ability of quasiparticles to survive inelastic many-body scattering.

Despite this, the Feynman variational method, a quasiparticle theory, predicts mobilities outside the Planckian bound, which agree with DiagMC mobility predictions, as shown in the next subsection.

This cautions against using semi-classical mobility theories as the charge-carrier wave-function ansatz to model polar materials.

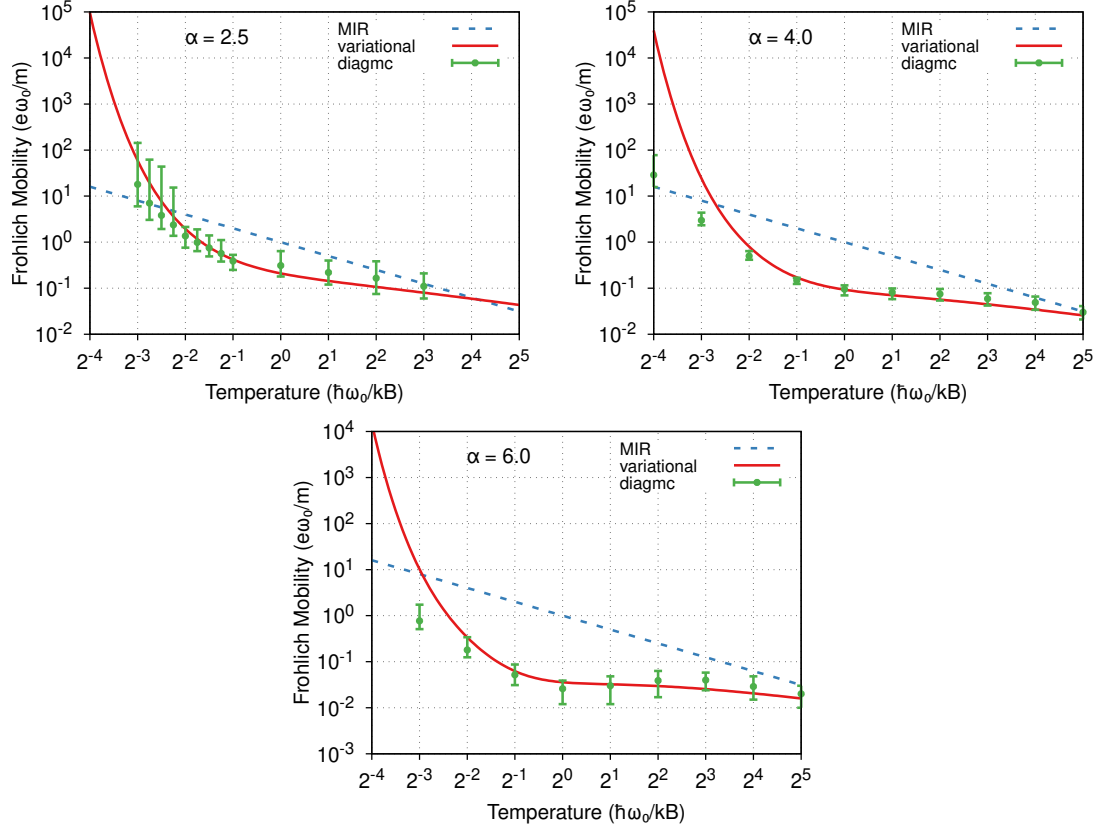


Figure 5.1: Comparison between the FHIP [17] (solid red line) and Mishchenko et al. [10] DiagMC (green dots with error bars) mobility (μ in units $e\omega_0/m_0$) temperature dependence (T in units of $\hbar\omega_0/k_B$) of the polaron mobility for $\alpha = 2.5$ (top-left), 4.0 (top-right) and 6.0 (bottom). The red dotted lines give the Mott-Ioffe-Regel (MIR) threshold.

5.2.2 Numerical Comparison

The anti-adiabatic limit ($k_B T \ll \hbar\omega_0$) corresponds to the weak-coupling limit ($\alpha \ll 1$), where the perturbative theory results for the mobility is (Eq. (5) in [10])

$$\begin{aligned} \mu &= \frac{e}{2M\alpha\omega_0} e^{\hbar\omega_0/k_B T} \\ &= \frac{e}{2m_0\omega_0} \left(\frac{1}{\alpha} - \frac{1}{6} \right) e^{\hbar\omega_0/k_B T}, \quad (k_B T \ll \hbar\omega_0, \quad \alpha \ll 1), \end{aligned} \quad (5.3)$$

where $M = m_0/(1 - \alpha/6)$ is the effective mass renormalisation of the polaron.

In the adiabatic regime ($k_B T \gg \hbar\omega_0$), the mobility is obtained from the kinetic equation as (Eq. (6) in [10])

$$\mu = \frac{4e\sqrt{\hbar}}{3\sqrt{\pi}\alpha M\sqrt{\omega_0 k_B T}}, \quad (k_B T \gg \hbar\omega_0), \quad (5.4)$$

which is valid even when α is not small.

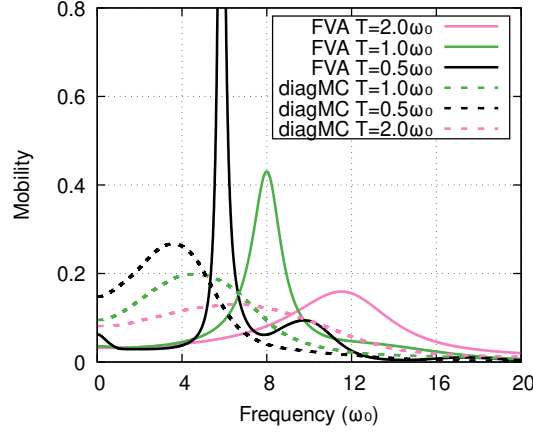


Figure 5.2: Comparison between the FHIP [17] (solid lines) and Mishchenko et al. [10] DiagMC (dashed lines) mobility (μ in units $e\omega_0/m_0$) frequency dependence (Ω in units ω_0) for temperatures $T = 0.5\hbar\omega_0/k_B$ (black), $1.0\hbar\omega_0/k_B$ (green) and $2.0\hbar\omega_0/k_B$ (pink).

Fig. 5.1 compares our numerical results for the polaron mobility (Eq. (2.212)), calculated using `PolaronMobility.jl` [11], with Fig. 2 in Mishchenko et al. [10]. The computational cost of the Feynman variational approach is significantly less than DiagMC, taking mere seconds to minutes on a standard personal computer to produce the results of Fig. 5.1.

The top-left panel shows the polaron mobility at $\alpha = 2.5$. At low temperatures ($k_B T \lesssim \hbar\omega_0/2$), the exponential behaviour matches the low-temperature mobility in Eq. (5.3). As in [10], there appears to be a delay in the onset of the exponential behaviour for $k_B T < \hbar\omega_0$. Likewise, the MIR criterion is violated over the temperature range $0.2 < k_B T/\hbar\omega_0 < 10$. At high temperatures, the FHIP mobility (Eq. (5.7)) has the same $1/\sqrt{T}$ dependence as Eq. (5.4).

In the bottom panel in Fig. 5.1, I compare the temperature dependence of the FHIP polaron mobility with the DiagMC polaron mobility (Fig. 3 [10]) at $\alpha = 6$. The DiagMC polaron mobility exhibits non-monotonic behaviour at $\alpha = 6$, with a clear local minimum around $k_B T = \hbar\omega_0$. Here, we see similar non-monotonic behaviour in the FHIP mobility with a small local minimum around $k_B T = \hbar\omega_0$ too. However, compared to the DiagMC mobility, the local minimum of the FHIP mobility is shallower. Similar to DiagMC, the high-temperature limit is recovered after a maximum at $k_B T/\hbar\omega_0 \sim \alpha$, which shifts with larger α . The minimum too appears to be α -dependent, occurring at $k_B T/\hbar\omega_0 \sim 1$ for $\alpha = 6$ or $k_B T/\hbar\omega_0 \sim 1.5$ for $\alpha = 10$.

In Fig. 5.2, I compare the temperature and frequency dependence of the FHIP polaron mobility with the DiagMC polaron mobility (Fig. 4 in [10]) at $\alpha = 6$ for temperatures $T = 0.5\omega_0, 1.0\omega_0, 2.0\omega_0$. The FHIP mobility, obtained by integrating Eq. (5.7), has similar temperature dependence to the DiagMC mobility but differs in frequency response.

As discussed previously in section 2.3.6, the FHIP mobility shows extra peaks where the first peak is blue-shifted compared to the DiagMC single peak. Devreese et al. [18, 101], showed that these extra FHIP mobility peaks correspond to the polaron quasiparticle's internal relaxed, excited states. These internal states correspond to multiple phonon scattering processes. For $k_B T / \hbar \omega_0 = 0.5$, the first peak around $\Omega / \omega_0 \sim 6$ corresponds to one-phonon processes, the peak at $\Omega / \omega_0 \sim 10$ corresponds to two-phonon processes, and so on. This is more clearly seen by analysing the memory function $\Sigma(\Omega)$ (Eq. (2.203)) at zero temperature, which similarly has peaks at $\Omega / \omega_0 = 1 + n\nu$, where $n = 0, 1, 2, \dots$ and ν is one of the Feynman variational parameters. These peaks in the memory function correspond to the same Frank-Condon states. As the temperature increases, the first few peaks become more prominent and broaden due to an increased effective electron-phonon interaction. Eventually, the excitations can no longer be resolved at high temperatures.

The Feynman variational model of the electron harmonically coupled to a fictitious massive particle (see Section 2.2.3) lacks a dissipative mechanism for the polaron such that the polaron state described by this model does not lose energy and has an infinite lifetime. However, in de Filippis et al. [101], dissipation is included in this model at zero temperature. This attenuates and spreads the harmonic peaks, obscuring the internal polaron transitions and giving closer agreement to the DiagMC mobility at zero temperature. I have not used the de Filippis method in this thesis.

5.3 The Dynamics of Multiple Phonon Modes

In this section, I generalise the Feynman-Hellwarth-Iddings-Platzman [17] (FHIP) approach to polaron mobility to include multiple phonon modes in the Fröhlich model action (Eq (3.10)).

To generalise the frequency-dependent mobility of Eq. (2.211), I follow the same procedure as FHIP but use our generalised polaron action S from Eq. (3.10) and trial action S_0 from Eq. (4.21). The result is a memory function, akin to Eq. (2.203), which is inclusive of multiple (m) phonon branches j ,

$$\Sigma(\Omega) = \sum_{j=1}^m \frac{2\alpha_j \omega_j^2}{3\Omega\sqrt{\pi}} \int_0^\infty dt \left[1 - e^{i\Omega t} \right] \text{Im } S_j(t), \quad (5.5)$$

where

$$S_j(\Omega) = D_{\omega_j}(t)G(t)^{-3/2}. \quad (5.6)$$

Here, $G(t)$ is the polaron Green function $G(it)$ from Eq. (4.24) rotated back to real-time.

The new multiple-phonon frequency-dependent mobility $\mu(\Omega)$ is then obtained from the real and imaginary parts of the generalised Σ using Eq. (5.7). The frequency-dependent mobility $\mu(\Omega)$ is obtained from the impedance using

$$\begin{aligned} \mu(\Omega)^{-1} &= \frac{m_0}{e} \sum_{j=1}^m \omega_j \text{Re} \{z_j(\Omega)\} \\ &= \frac{m_0}{e} \sum_{j=1}^m \omega_j \frac{\Omega^2 - 2\Omega \text{Re } \Sigma_j(\Omega) + |\Sigma_j(\Omega)|^2}{v\Sigma_j(\Omega)}, \end{aligned} \quad (5.7)$$

where $\Sigma_j(\Omega)$ is just the j th component of $\Sigma(\Omega)$.

The limit as the frequency $\Omega \rightarrow 0$ gives the FHIP DC-mobility extended to multiple phonon modes,

$$\mu_{dc}^{-1} = \frac{m_0}{e} \lim_{\Omega \rightarrow 0} \sum_{j=1}^m \omega_j \text{Im } \Sigma_j(\Omega), \quad (5.8)$$

since $\text{Re } \Sigma(\Omega = 0) = 0$.

5.4 The Dynamics of Multiple Fictitious Particles

In this section, I generalise the Feynman-Hellwarth-Iddings-Platzman [17] (FHIP) approach to polaron mobility to the generalised trial action for an electron coupled to multiple (N) fictitious spring masses.

To generalise the frequency-dependent mobility in Eq. (5.12), we follow the same procedure as FHIP but use our generalised polaron trial action S_0 in Eq. (4.21). The result is a memory function akin to FHIP's Σ (Eq. (35) in FHIP [17]), but includes multiple ($2N$) variational parameters v_p and w_p ,

$$\Sigma(\Omega) = \frac{\alpha\omega_0^2}{3\sqrt{\pi}} \int_0^\infty dt \left[1 - e^{i\Omega t} \right] \text{Im } S(t). \quad (5.9)$$

Here,

$$S(t) = D_{\omega_0}(t)[G(t)]^{-3/2}, \quad (5.10)$$

where $G(t)$ is $G(\tau = it)$ from Eq. (4.24) rotated back to real-time,

$$G(t) = it \left(1 - \frac{it}{\hbar\beta} \right) + \sum_{p=1}^N \frac{h_p}{v_p^3} \left(D_{v_p}(0) - D_{v_p}(\tau) - iv_p t \left(1 - \frac{it}{\hbar\beta} \right) \right). \quad (5.11)$$

The new frequency-dependent mobility $\mu(\Omega)$ is then obtained from the real and imaginary parts of the generalised $\Sigma(\Omega)$ using Eq. (5.12).

5.4.1 The Effect of Multiple Fictitious Particles on the Dynamics

Given that the multiple fictitious particle trial model rapidly converges to the optimal bound on the polaron free energy, it is constructive to investigate how the dynamics of the trial system are altered.

Figs. 5.3 and 5.4 show the Fröhlich imaginary memory function and real conductivity of polarons as a function of dimensionless frequency, Ω/ω_0 , for varying electron-phonon coupling strengths, $\alpha = 0.1$ to $\alpha = 7$. The trial action in these calculations incorporates an increasing number of fictitious particles, allowing for a progressively larger set of variational parameters to more accurately describe the polaron's dynamical response.

Effect on the Polaron Memory Function

Fig. 5.3 depicts the Fröhlich imaginary memory function, $\text{Im}\Sigma(\Omega)$, as a function of frequency for different values of α and increasing $N = 1$ to 6, where N represents the number of fictitious particles included in the trial action.

At small coupling, such as $\alpha = 0.1$ (top-left plot), the curves for different values of N rapidly converge, suggesting that several variational parameters suffice to capture the essential physics of the weakly interacting polaron.

As the coupling strength increases (e.g., $\alpha = 1$ to $\alpha = 7$), the behaviour of the imaginary memory function changes, and we observe two notable trends as N increases: (1) the primary peak undergoes a red-shift, meaning the peak position shifts towards lower frequencies, and (2) the higher-order Franck-Condon and multi-phonon peaks become less resolved. The multi-phonon peaks, which correspond to higher-order processes involving the emission and reabsorption of multiple phonons, are less distinct as N increases. This softening of the peaks indicates the trial action spreading the polaron's interaction over a broader range of phonon modes, making the transition between different phonon states smoother. In particular, the reduced resolution of these peaks indicates that with more fictitious particles, the model captures a more complex but less sharply defined structure of the polaron's dynamic behaviour.

Thus, increasing N has two effects: it softens the memory function's features, reflecting a less sharply defined polaron-phonon interaction, and it leads to a redshifting of the spectral features.

Effect on the Polaron Optical Conductivity

Fig. 5.4 presents the real part of the Fröhlich conductivity, $\sigma(\Omega)$, as a function of frequency for varying values of α and N . In the weak-coupling regime ($\alpha = 0.1$, top-left plot), the real conductivity exhibits a single, sharp peak at low frequencies, corresponding to the primary polaron response due to LO phonon absorption. The rapid convergence of the curves for different N indicates that the polaron's dynamics are well-described by a small number of variational parameters in the weak-coupling limit.

As α increases (e.g., $\alpha = 3$, $\alpha = 4$), the peak in the real conductivity broadens and shifts to lower frequencies as N increases. This red shift of the primary peak reflects the growing effective mass of the polaron as more phonons become entangled with the electron, leading to lower energy transitions. The broadening of the peak indicates that the polaron's interaction with the phonon field is becoming more spread out in frequency space, consistent with the softening observed in the memory function.

In the strong coupling regime ($\alpha = 7$, bottom-right plot), the real conductivity shows the emergence of multi-phonon and Franck-Condon peaks at higher frequencies. Still, as N increases, these peaks become less resolved. This reduction in peak resolution can be attributed to the additional fictitious particles smoothing out the abrupt transitions between different phonon emissions and reabsorption processes. Consequently, the previously well-defined Franck-Condon peaks blend into a broader, less distinct structure.

Additionally, we observe a softening of the strongly peaked relaxed-excited-state (RES) peaks as N increases. The RES peaks, typically sharp in the strong-coupling regime due to the polaron's quasi-localisation, become less prominent with increasing N . This softening indicates a more continuous interaction between the electron and the phonon cloud as the polaron becomes less localised with increasing N .

Discussion and Comparison with DiagMC

The redshifting of the primary peaks in the memory function and real conductivity as N increases indicates a softer, more distributed interaction between the electron and phonon cloud. The decreased resolution of the Franck-Condon and multi-phonon peaks reflects the smoother transitions between different phonon states as the trial action better reflects the spectral function of the phonon bath, as suggested by Sels [77] in the case of a general trial spectral function. The softening of the RES peaks further supports the idea that the polaron becomes less localised with more variational parameters, resulting in a broader, less sharply defined interaction with the phonon field.

Despite the improvements, these results still do not fully agree with the polaron conductivity results of de Filippis et al. [101] and Mishchenko et al. [10]. This suggests that this trial model still lacks a sufficient dissipation mechanism for the fictitious particles which mimic the phonons. We might resolve this by using the trial action with a trial Green function (i.e. the $N \rightarrow \infty$ limit), akin to Thornber's [35] self-consistent memory function, or adding damping terms to the oscillators in the trial action.

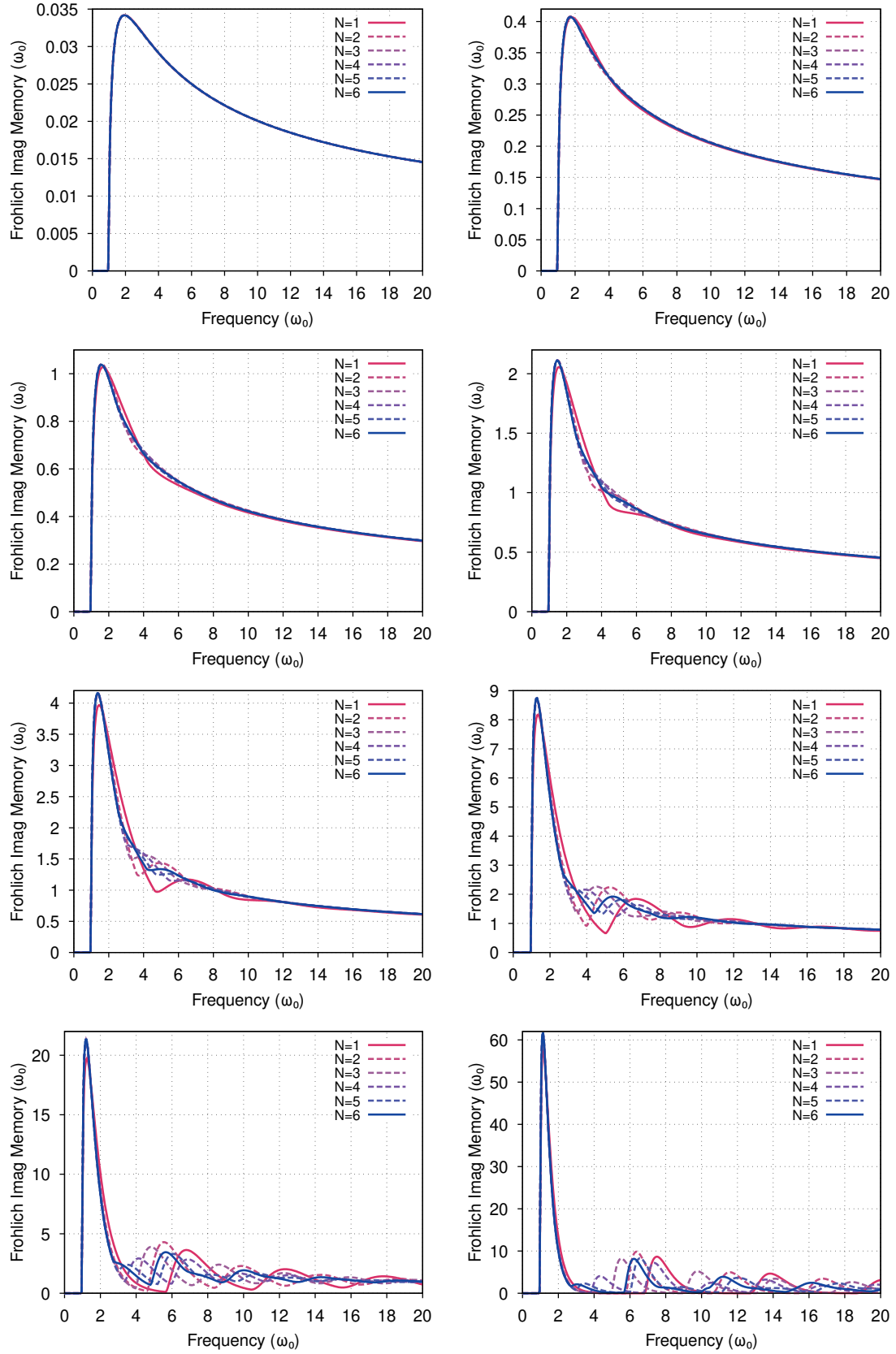


Figure 5.3: Fröhlich Imaginary Memory Function for Polaron Dynamics. The imaginary part of the Fröhlich memory function, $\text{Im}\Sigma(\Omega)$, as a function of dimensionless frequency, Ω/ω_0 , for various electron-phonon coupling strengths ($\alpha = 0.1, 1, 2, 3, 4, 5, 6, 7$) and increasing numbers of fictitious particles in the trial action ($N = 1$ to $N = 6$).

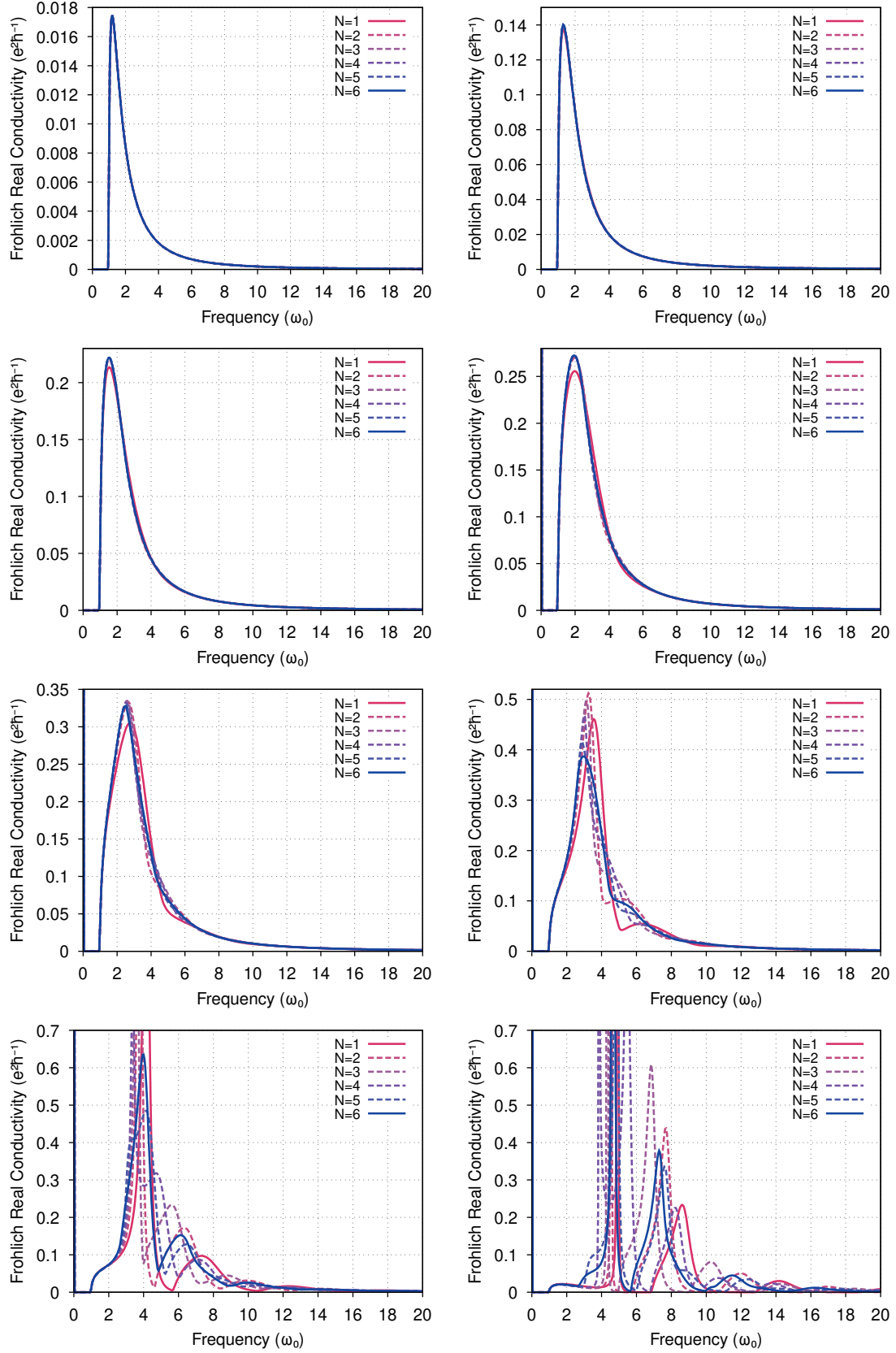


Figure 5.4: Fröhlich Real Conductivity for Polaron Dynamics. The real part of the Fröhlich conductivity, $\sigma(\Omega)$, as a function of dimensionless frequency, Ω/ω_0 , for different electron-phonon coupling strengths ($\alpha = 0.1, 1, 2, 3, 4, 5, 6, 7$) and increasing numbers of fictitious particles in the trial action ($N = 1$ to $N = 6$).

5.5 General Polaron Mobility

The polaron DC mobility may be obtained in the same way as was done for the Fröhlich model from real components of the frequency- and temperature-dependent impedance function

$$\mu_{dc} = \lim_{\Omega \rightarrow 0} \operatorname{Re} \left\{ \frac{1}{z(\Omega)} \right\}, \quad (5.12)$$

where the impedance function is expressed in terms of the memory function $\Sigma(\Omega)$,

$$z(\Omega) = i (\Omega - \Sigma(\Omega)). \quad (5.13)$$

Specifically, we can express the inverse DC mobility directly in terms of the memory function,

$$\mu_{dc}^{-1} = \lim_{\Omega \rightarrow 0} \operatorname{Im} \{ \Sigma(\Omega) \}. \quad (5.14)$$

From the general polaron Hamiltonian and corresponding effective action (see section 3.3), the general memory function can be written as [72]

$$\Sigma(\Omega) = \frac{4}{nm_0\hbar\Omega} \int_0^\infty dt \left(1 - e^{i\Omega t} \right) \operatorname{Im} \left\{ \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 D_{\omega_{\mathbf{q}}}(t) \left\langle e^{i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]} \right\rangle \right\}, \quad (5.15)$$

where n is the dimensionality, m_0 is the electron (or hole) band mass, Ω is frequency of the alternating electric field, t is time, $M_{\mathbf{q}}$ is the electron-phonon coupling matrix element, $\omega_{\mathbf{q}}$ is the phonon frequency, $D_{\omega_{\mathbf{q}}}$ is the phonon Green function, $\mathbf{q}$ is the phonon wavevector/momentum and $\mathbf{r}(t)$ is the electron (or hole) position. We will assume the system is rotationally invariant so that we can neglect any explicit angular dependence when performing the $\mathbf{q}$ integral.

As before, we approximate the electron density-density correlation function with the density-density correlation function of the Feynman polaron trial model,

$$\langle \rho_{\mathbf{q}}(t) \rho_{\mathbf{q}}^*(0) \rangle_0 = e^{-q^2 r_p^2 G(t)}, \quad (5.16)$$

where $G(t)$ is the polaron Green function evaluated in real-time (i.e. substitute $\tau \rightarrow it$ into Eq. (4.13))

$$G(t) = it \left(1 - \frac{it}{\hbar\beta} \right) + \frac{v^2 - w^2}{v^3} \left[D_v(0) - D_v(t) - ivt \left(1 - \frac{it}{\hbar\beta} \right) \right]. \quad (5.17)$$

In n -dimensions, we need to evaluate the reciprocal-space integral (see section 2.2.8),

$$\begin{aligned} I(n) &= V_0 \int \frac{d^n q}{(2\pi)^n} |M_{\mathbf{q}}|^2 q^2 D_{\omega_{\mathbf{q}}}(t) e^{-q^2 r_p^2 G(t)}, \\ &= \frac{V_0 S_{n-1}}{(2\pi)^n} \int_0^R dq q^{n+1} |M_q|^2 D_{\omega_q}(t) e^{-q^2 r_p^2 G(t)}, \end{aligned} \quad (5.18)$$

where V_0 is the unitcell volume and S_{n-1} is the surface volume of an n -ball. To go to the second line we have assumed the system is rotation-invariant.

For a general polaron model, we then have the memory function

$$\Sigma(\Omega) = \frac{4}{nm_0 \hbar \Omega} \frac{V_0 S_{n-1}}{(2\pi)^n} \int_0^\infty dt \left(1 - e^{i\Omega t}\right) \int_0^\Lambda dq |M_q|^2 q^{n+1} \text{Im} \left\{ D_{\omega_q}(t) e^{-q^2 r_p^2 G(t)} \right\}. \quad (5.19)$$

where Λ is an ultraviolet cutoff on the phonon momentum due to the finite lattice spacing. In the zero frequency limit, we get the general polaron DC mobility,

General Polaron DC Mobility

$$\mu_{dc}^{-1} = -\frac{4e^2}{nm_0 \hbar} \frac{V_0 S_{n-1}}{(2\pi)^n} \int_0^\infty dt t \int_0^\Lambda dq q^{n+1} |M_q|^2 \text{Im} \left\{ D_{\omega_q}(t) e^{-q^2 r_p^2 G(t)} \right\}. \quad (5.20)$$

5.5.1 Specialising to the Fröhlich Model

Now equipped with the general polaron variational equations for the free energy and the corresponding memory function, we specialise to the Fröhlich model by substituting

$$|M_{\mathbf{q}}|^2 = \frac{g_F^2(n)}{V_0 q^{n-1}}, \quad \omega_q = \omega_0, \quad \Lambda \rightarrow \infty. \quad (5.21)$$

We evaluate the q -space integral

$$\begin{aligned} I_F(n) &= \frac{g_F^2(n) S_{n-1}}{(2\pi)^n} D_{\omega_0}(t) \int_0^\infty dq q^2 e^{-q^2 r_p^2 G(t)}, \\ &= \frac{g_F^2(n) S_{n-1} \sqrt{\pi}}{(2\pi)^n 4r_p^3} \frac{D_{\omega_0}(t)}{G(t)^{\frac{3}{2}}}, \\ &= \alpha_F \frac{\sqrt{\pi}}{2r_p^3} \frac{(2\sqrt{\pi})^{-n} D_{\omega_0}(t)}{\Gamma\left(\frac{n}{2}\right) G(t)^{\frac{3}{2}}}. \end{aligned} \quad (5.22)$$

The memory function for the Fröhlich model is thereby

$$\Sigma_F(\Omega) = \frac{1}{m_0 \hbar \Omega r_p^3} \frac{\pi \sqrt{2\pi} \alpha_F}{\Gamma\left(\frac{n}{2} + 1\right) (2\sqrt{\pi})^n} \int_0^\infty dt \left(1 - e^{i\Omega t}\right) \frac{D_{\omega_0}(t)}{[G(t)]^{3/2}}. \quad (5.23)$$

Taking the DC frequency limit $\Omega \rightarrow 0$, the inverse Fröhlich DC mobility thus becomes

$$\mu_{dc}^{-1} = -\frac{e^2}{m_0 \hbar r_p^3} \frac{\pi \sqrt{2\pi} \alpha_F}{\Gamma\left(\frac{n}{2} + 1\right) (2\sqrt{\pi})^n} \int_0^\infty dt \frac{t D_{\omega_0}(t)}{[G(t)]^{3/2}}. \quad (5.24)$$

For three dimensions ($n = 3$), these reproduce the FHIP [17] result for the polaron memory function and mobility (Eq. (2.212)).

5.6 The Holstein Model

In this section, I present the theoretical and numerical results, calculated using our `PolaronMobility.jl` code [1], for the polaron mobility and conductivity of the parabolic Holstein model (see Eq. (3.31)).

5.6.1 Parabolic Holstein Polaron Mobility

Starting from the general mobility formula in Eq. (5.12), we can specialise to the parabolic Holstein model by substituting

$$|M_{\mathbf{q}}|^2 = \frac{g_H^2(n)}{V_0}, \quad \omega_{\mathbf{q}} = \omega_0, \quad \Lambda = 2\sqrt{\pi} \left(V_0 \Gamma\left(\frac{n}{2} + 1\right) \right)^{1/n} \equiv \Lambda_n, \quad (5.25)$$

into the general memory function. We then evaluate q -space integral,

$$\begin{aligned} I_H(n) &= \frac{g_H^2(n) S_{n-1}}{(2\pi)^n} D_{\omega_0}(t) \int_0^{\Lambda_n} dq q^{n+1} e^{-q^2 r_p^2 G(t)}, \\ &= \frac{g_H^2(n) S_{n-1}}{2(2\pi)^n r_p^{n+2}} \frac{D_{\omega_0}(t)}{G(t)^{\frac{n}{2}+1}} \left[\Gamma\left(\frac{n}{2} + 1\right) - \Gamma\left(\frac{n}{2} + 1, r_p^2 \Lambda_n^2 G(t)\right) \right], \\ &= \frac{1}{2r_p^2} \frac{n g_H^2(n)}{(2r_p \sqrt{\pi})^n} \frac{D_{\omega_0}(t)}{G(t)^{\frac{n}{2}+1}} \left[1 - \frac{\Gamma\left(\frac{n}{2} + 1, r_p^2 \Lambda_n^2 G(t)\right)}{\Gamma\left(\frac{n}{2} + 1\right)} \right]. \end{aligned} \quad (5.26)$$

The memory function for the parabolic Holstein model is thereby

$$\Sigma_H(\Omega) = \frac{1}{m_0 \hbar \Omega \gamma r_p^{n+2}} \frac{4n\alpha_H}{(2\sqrt{\pi})^n} \int_0^\infty dt \left(1 - e^{i\Omega t} \right) \frac{D_{\omega_0}(t)}{G(t)^{\frac{n}{2}+1}} \left[1 - \frac{\Gamma\left(\frac{n}{2} + 1, r_p^2 \Lambda_n^2 G(t)\right)}{\Gamma\left(\frac{n}{2} + 1\right)} \right], \quad (5.27)$$

where $\gamma = \hbar\omega_0/J$ is the adiabaticity.

Taking the DC frequency limit $\Omega \rightarrow 0$, the inverse parabolic Holstein DC mobility is thus

Holstein DC Polaron Mobility

$$\mu_{dc}^{-1} = \frac{e^2}{m_0 \hbar \gamma r_p^{n+2}} \frac{4n\alpha_H}{(2\sqrt{\pi})^n} \int_0^\infty dt t \frac{D_{\omega_0}(t)}{G(t)^{\frac{n}{2}+1}} \left[1 - \frac{\Gamma\left(\frac{n}{2} + 1, r_p^2 \Lambda_n^2 G(t)\right)}{\Gamma\left(\frac{n}{2} + 1\right)} \right]. \quad (5.28)$$

Numerical Results

In Figs. 5.5, I present the temperature-dependent mobility of the parabolic Holstein polaron in 1D, 2D, and 3D systems, illustrating how mobility varies with electron-phonon coupling strength (α) and temperature. We observe high polaron mobility at weak coupling ($\alpha \approx 0.1$), indicative of ‘*band-like*’ (or ballistic) transport. In this regime, the electron has a large mean-free path as it interacts weakly with the lattice, allowing it to move intramolecularly through coherent Bloch states due to a delocalised wavefunction over the volume of the material. At low temperatures ($T \lesssim 2 \hbar\omega_0/k_B$), phonon scattering is minimal, leading to high mobility. As temperature increases to $T \approx 4 \hbar\omega_0/k_B$, phonon scattering reduces mobility, though the electron largely remains delocalised. the mobility increases again at higher temperatures, $T > 4 \hbar\omega_0/k_B$, indicating the onset of minor scattering-dominated transport (i.e. the thermally-activated ‘hopping’ transport regime).

At intermediate coupling ($\alpha \approx 2$ to 6), we observe a sharper decline in mobility as temperature increases, indicating a transition to ‘*scattering-dominated transport*’. Around temperatures of $T \approx 5 \rightarrow 10 \hbar\omega_0/k_B$, stronger electron-phonon interactions begin to localise the polaron, and phonon scattering becomes more frequent, limiting coherent transport. Mobility is no longer purely band-like, as the polaron’s motion combines coherent and incoherent processes. Dimensionality plays a crucial role, with 2D and 3D systems showing more significant mobility reductions due to stronger localisation effects.

In the strong coupling regime ($\alpha > 8$) and at high temperatures ($T \gtrsim 10 \hbar\omega_0/k_B$), mobility is dominated by ‘*activated hopping*’ (stochastic/thermal transport). In this regime, the polaron has a small mean-free path and is heavily localised by strong electron-phonon interactions, and its movement occurs intermolecularly via thermally activated tunnelling between localised states. At the Debye temperature, $T = \hbar\omega_0/k_B$, the mobility is at a minimum, where localisation effects are more severe. However, at very high temperatures ($T \gtrsim \hbar\omega_0/k_B$), we observe an increase in mobility due to the availability of sufficient thermal energy to assist the hopping process ($\mu \sim T^{\frac{1}{2}}$). The transition between regimes at the Debye temperature is sharper at higher couplings due to the increasing contribution of electron transfer between states *without* phonon participation.

5.6.2 Holstein Memory Function at Zero Temperature

In Fig. 5.6, I present the frequency dependence of the imaginary part of the memory function, $\text{Im}\Sigma(\Omega)$, for the parabolic Holstein model in 1D, 2D, and 3D systems. The imaginary memory function characterises the dissipative processes due to electron-phonon interactions, with peaks indicating resonances where energy dissipation through phonon scattering is maximised.

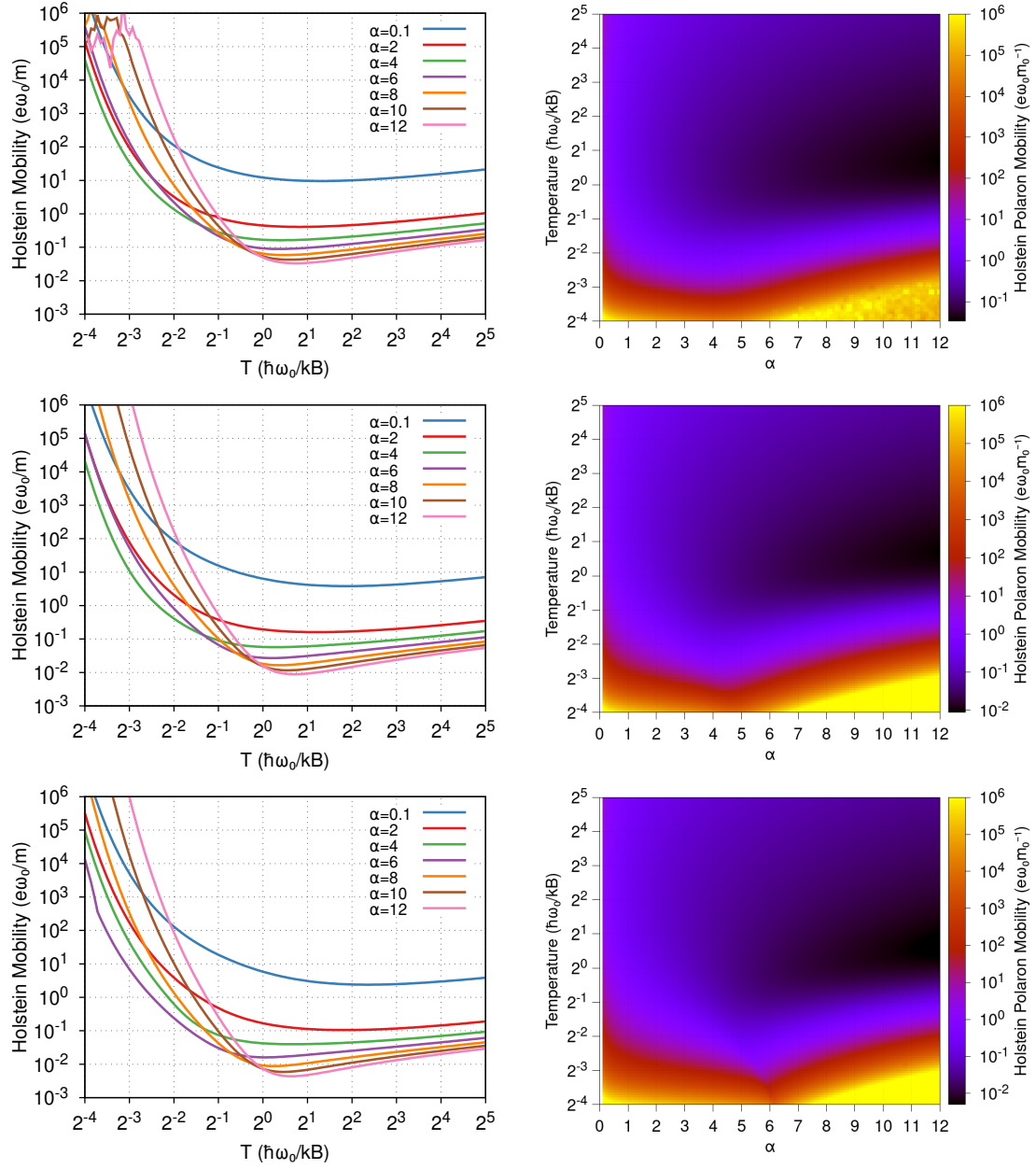


Figure 5.5: Temperature dependence (T , in units of phonon frequency $\hbar\omega_0/k_B$) of the Holstein polaron DC mobility μ in 1D (top) and 2D (middle) and 3D (bottom).

At weak coupling ($\alpha \approx 1$), we observe that the memory function is dominated by low-frequency phonons, which indicates weak scattering and low dissipation. This regime's polaron remains largely delocalised, allowing for band-like transport with minimal phonon interaction. As the coupling strength increases to intermediate values ($\alpha = 2$ to 5), we see the emergence of multiple resonances at higher frequencies. These peaks indicate multi-phonon processes, with more pronounced phonon scattering leading to increased energy dissipation.

In the strong coupling regime ($\alpha > 5$), the resonances become sharper and more widely spaced in 1D and 2D systems, suggesting significant polaron localisation. This localisation restricts the polaron's motion, and transport is now dominated by thermally activated hopping between localised sites. In contrast, in 3D systems, the memory function peaks are broader and more evenly distributed across the frequency spectrum, indicating smoother dissipation and less extreme localisation effects. Higher dimensionality allows for reduced localisation and smoother dissipation across frequencies, resulting in less severe scattering compared to 1D and 2D systems. However, above $\alpha > 2n$, the small polaron localised in 3D too.

5.6.3 Holstein Optical Conductivity at Zero Temperature

In Fig 5.7, we present the frequency dependence of the real part of the optical conductivity $\sigma(\Omega)$ for the Holstein polaron in 1D, 2D, and 3D systems, where the frequency Ω is expressed in units of the phonon frequency ω_0 . The real conductivity characterises the polaron's ability to conduct under an external electromagnetic field, and it is highly sensitive to both the electron-phonon coupling strength α and dimensionality.

At weak coupling ($\alpha \approx 1$), the conductivity is dominated by a single one-phonon peak at low frequencies ($\Omega < 5 \omega_0$), corresponding to the band-like transport regime where the polaron is still fairly delocalised. In this regime, the electron-phonon interaction is weak, and the conductivity is relatively high as the polaron moves coherently. As coupling increases ($\alpha = 2$ to 4), additional peaks appear at higher frequencies. These secondary peaks reflect the enhanced scattering of the polaron by multiple phonons, causing localised resonances that increase the conductivity. At these frequencies, the line plots and heatmaps show that as α increases, the conductivity is characterised by more pronounced multi-phonon peaks. Above $\alpha > 4$, we observe a Relaxed Excited State (RES) that forms around $\Omega \approx 3\omega_0$ and blue-shifts as the coupling increases.

In 2D systems, the peaks in conductivity are more pronounced, and we observe sharper transitions as α increases. At higher values of α , resonances shift toward lower frequencies, and the one-phonon peak is greatly reduced at higher frequencies. This reflects the transition from band-like transport to a scattering-dominated regime, where the polaron's motion is

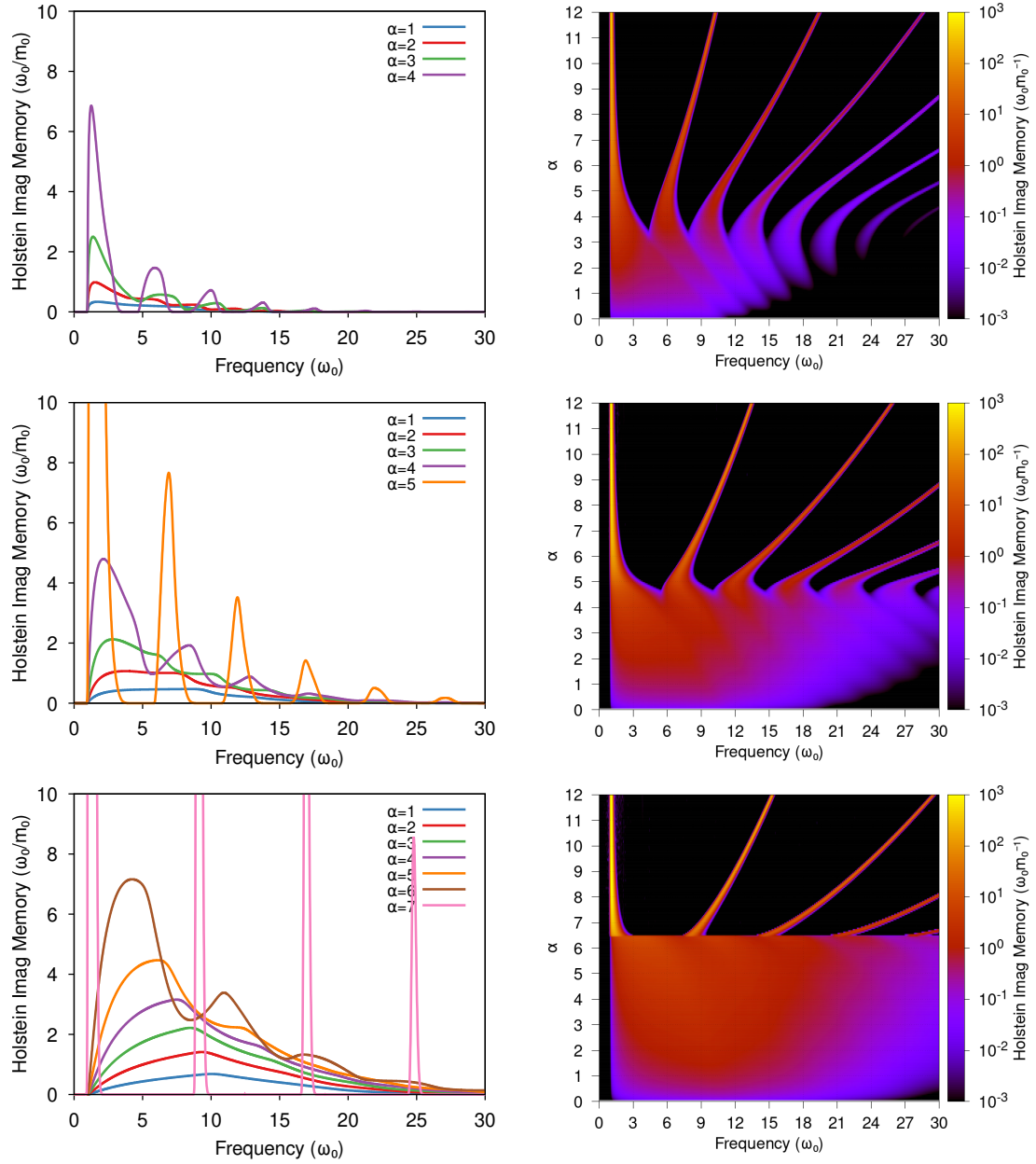


Figure 5.6: Frequency dependence (Ω , in units of the phonon frequency ω_0) of the polaron imaginary memory function $\text{Im } \Sigma(\Omega)$ for the Holstein model in 1D (top), 2D (middle) and 3D (bottom).

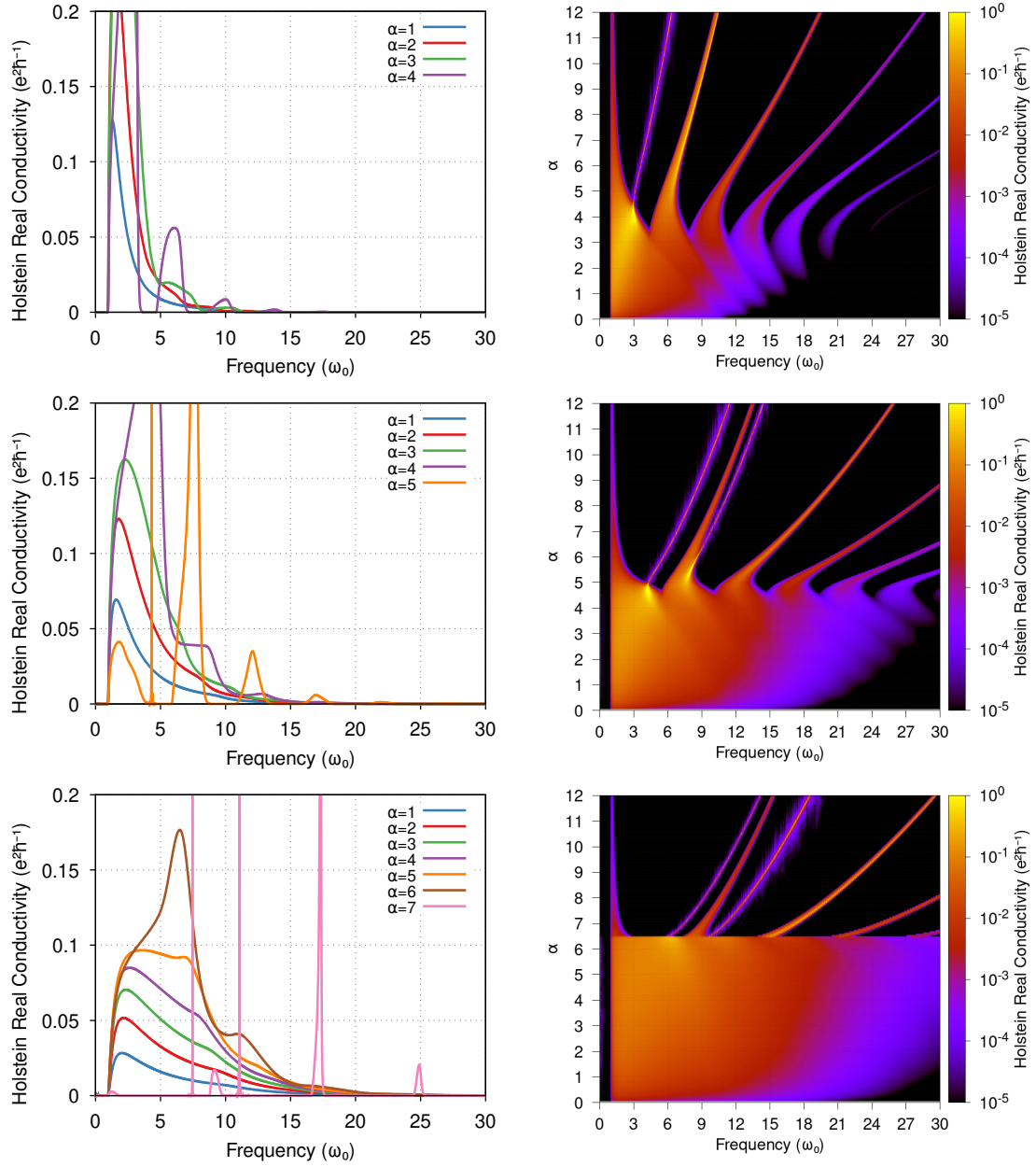


Figure 5.7: Frequency dependence (Ω , in units of the phonon frequency ω_0) of the polaron optical conductivity $\sigma(\Omega)$ for the Holstein model in 1D (top), 2D (middle) and 3D (bottom).

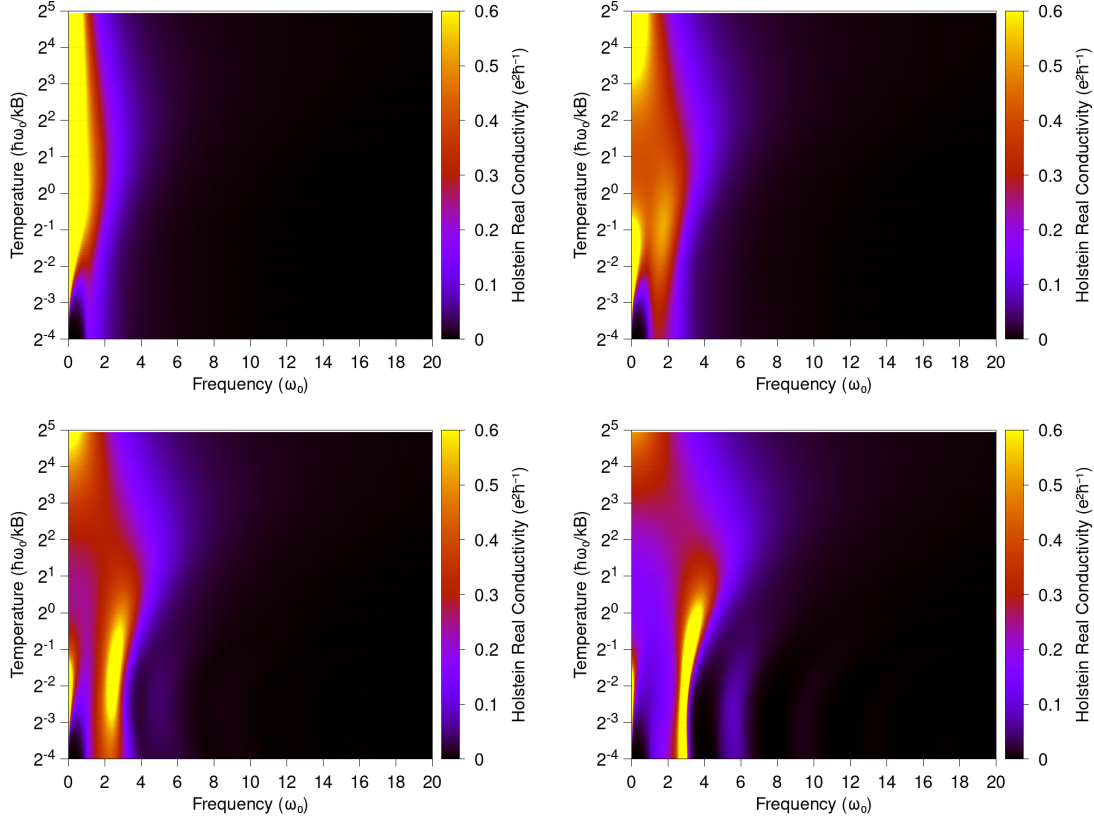


Figure 5.8: Temperature dependence (T , in units of the phonon frequency $\hbar\omega_0/k_B$) of the polaron optical conductivity $\sigma(\Omega)$ for the 1D Holstein model for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (bottom-left) and 4 (bottom-right).

increasingly incoherent and hindered by strong electron-phonon interaction except at key resonant frequencies of the renormalised ‘internal’ phonon states that coupling into the polaron quasi-particle states. We now observe two RES above $\alpha > 5$: around $\Omega \approx 4\omega_0$ and around $\Omega \approx 7\omega_0$. Both blue-shift with increasing coupling.

For 3D systems, we observe that the conductivity peaks are broader and less sharply defined compared to 1D and 2D systems. In the intermediate coupling regime ($\alpha > 5$), the peaks become wider and extend over a broader frequency range. This behaviour indicates less severe localisation in 3D systems than in lower-dimensional systems, where the polaron remains more mobile due to increased spatial freedom. Nonetheless, above $\alpha > 6.5$, the polaron localised, and we see sharp peaks extend over a wider frequency range. The heatmap further demonstrates a smoother conductivity distribution across the frequency spectrum, even as α increases, suggesting that higher dimensions mitigate the effects of strong electron-phonon coupling, allowing for more sustained conductivity over a larger frequency range.

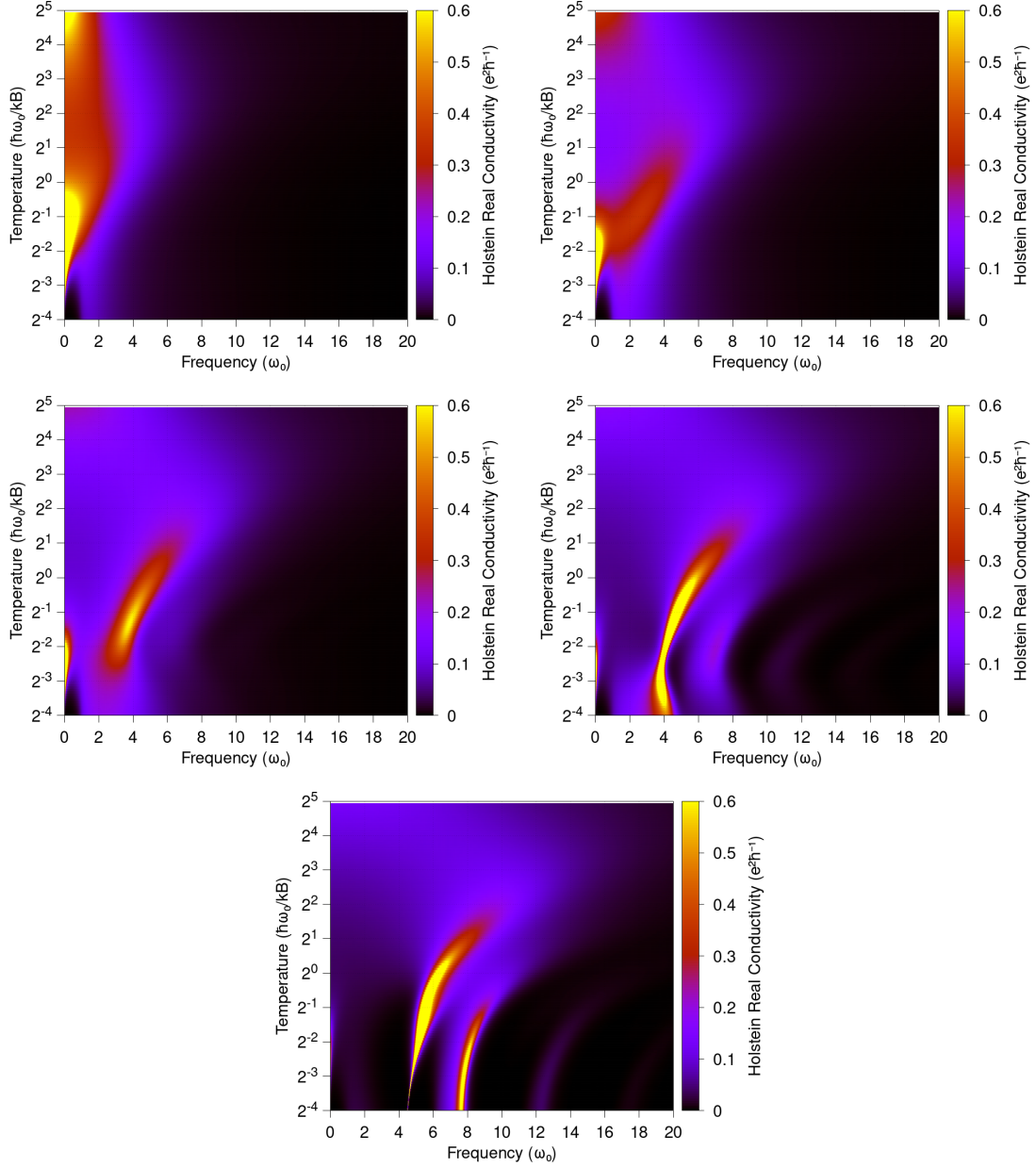


Figure 5.9: Temperature dependence (T , in units of the phonon frequency $\hbar\omega_0/k_B$) of the polaron optical conductivity $\sigma(\Omega)$ for the 2D Holstein model for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (middle-left), 4 (middle-right) and 5 (bottom).

5.6.4 Holstein Optical Conductivity at Finite Temperature

In Figs. 5.8, 5.9 and 5.10, I show the temperature dependence of the real part of the optical conductivity $\sigma(\Omega)$ for the Holstein polaron in 1D, 2D, and 3D systems. The temperature T is expressed in units of the phonon frequency $\hbar\omega_0/k_B$, and the frequency Ω is expressed in units of ω_0 . The coupling strength α varies in each figure, demonstrating the role of electron-phonon interactions at different temperatures and dimensions.

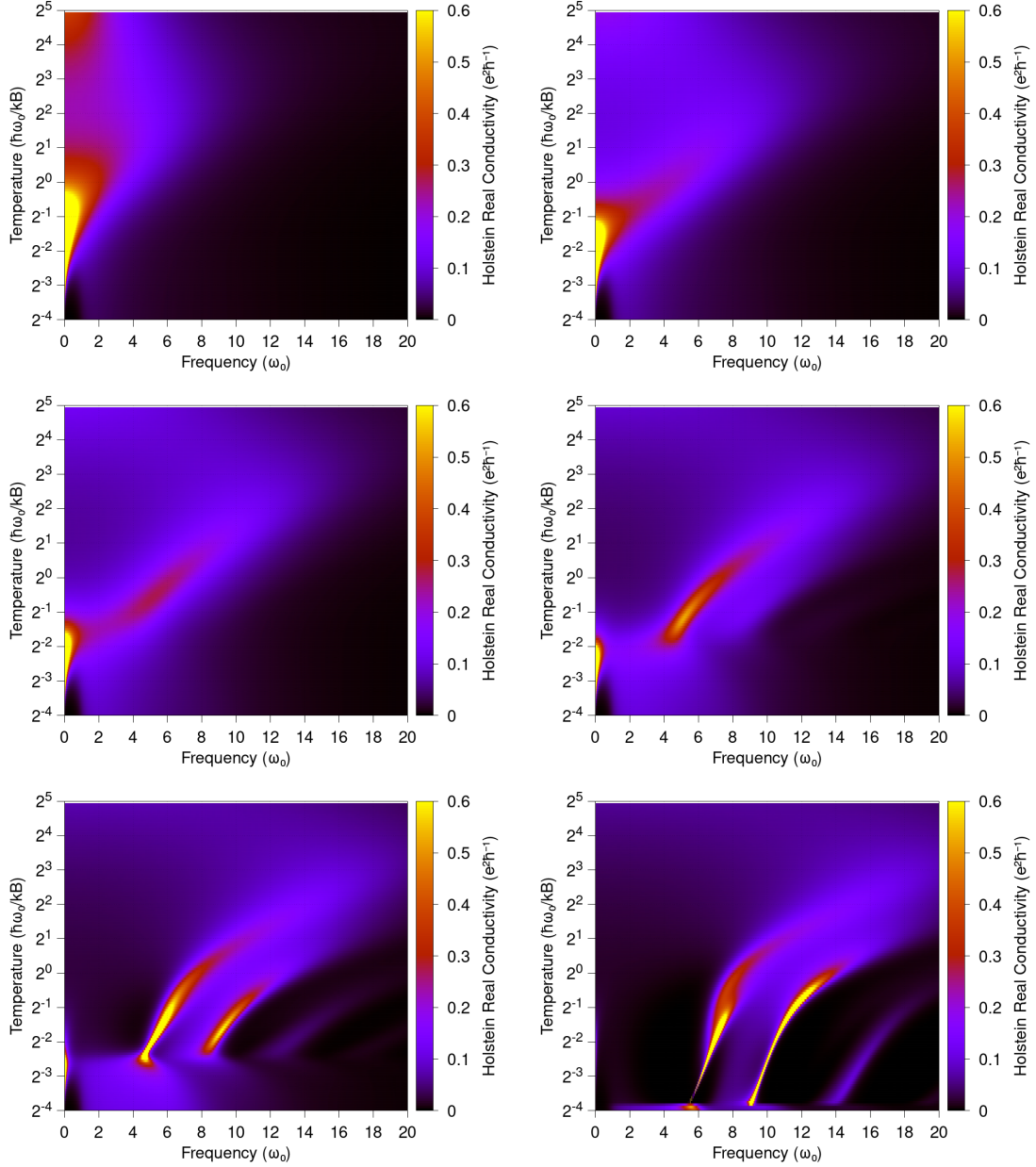


Figure 5.10: Temperature dependence (T , in units of the phonon frequency $\hbar\omega_0/k_B$) of the polaron optical conductivity $\sigma(\Omega)$ for the 3D Holstein model for electron-phonon couplings $\alpha = 1$ (top-left), 2 (top-right), 3 (middle-left), 4 (middle-right), 5 (bottom-left) and 6 (bottom-right).

In the 1D case (Figure 5.8), for weak coupling ($\alpha = 1$), the conductivity is concentrated at low temperatures ($T \approx 2 \hbar\omega_0/k_B$) and low frequencies ($\Omega \approx 2 \rightarrow 4 \omega_0$), indicating band-like transport where the polaron remains relatively mobile. As α increases to 2, 3, and 4, we observe a narrowing of the conductivity spectrum and its confinement to even lower temperatures, which signifies the onset of polaron localisation. The conductivity diminishes sharply at higher temperatures, reflecting the dominance of phonon scattering and reduced mobility as the coupling strength increases at frequencies greater than the phonon frequency, $\Omega > \omega_0$.

We see similar trends in the 2D system (Figure 5.9). At weak coupling ($\alpha = 1$), the optical conductivity remains prominent at low temperatures and moderate frequencies. However, as α increases to 2, 3, 4, and 5, the spectral weight shifts to lower frequencies and higher temperatures. The emergence of a high-temperature peak at higher α values suggests that thermal activation is enabling some polaron mobility, even as strong electron-phonon interactions localise the polaron at lower temperatures.

In the 3D system (Figure 5.10), we observe a broader temperature and frequency range for conductivity compared to the 1D and 2D systems. For $\alpha = 1$, the polaron remains mobile across a wider temperature range, with conductivity peaking at low frequencies. As α increases, the conductivity spreads across higher temperatures, indicating that 3D systems are more resilient to polaron localisation due to the increased spatial freedom. Even at high α values, there is still a noticeable conductivity at higher temperatures, suggesting that 3D systems retain some degree of polaron mobility even in the strong coupling regime.

Physically, the temperature dependence of the optical conductivity can be interpreted as a result of the Boltzmann population (i.e. a density matrix) of thermal phonon states. Phonon activity is minimal at low temperatures; only the lowest-energy modes couple to the electron. As the temperature increases, more phonons are thermally excited, allowing the polaron to interact with a wider range of vibration modes, reflecting the widening of the conductivity spectrum towards higher frequencies.

Higher-dimensional systems (2D and 3D) retain conductivity over a broader temperature range, whereas in 1D systems, conductivity is restricted to a smaller frequency range at low temperatures. With more dimensions, there is an increased phonon density of states, where the electron-phonon interaction is distributed over a larger number of phonon modes, leading to more complex temperature-dependent behaviour.

In all dimensionalities, the coupling α greatly determines the magnitude and frequency range of the polaron response. Strong coupling leads to increasingly sharp peaks over a wider frequency range and the activation of multi-phonon processes, especially at high temperatures.

5.7 The Optimal Self-Consistent Response Function

In section 7 of FHIP [17], they provided suggestions for improving the accuracy of their approach by self-consistently determining the polaron memory function at zero temperature. They observed that in Feynman's 1955 [2] variational principle, we can use a more general trial action that describes an electron coupled to a general linear system, as later derived by others [36, 37, 63, 93] and in section 4.5 of this thesis. However, they also observe that the optimal form of this memory function (which gives the lowest energy in the variational principle) satisfied the same integral equation as the polaron memory function, differing by a Wick-rotation $\tau \rightarrow it$. In 1971 [35] and 1974 [80], Thornber generalised this connection to finite temperatures to relate the exact free energy of the polaron to the sum rule for the exact optical conductivity spectrum integrated over frequency. In 2016 [77], Sels made a similar connection.

Following these approaches, in this section, I try to generalise the Feynman-Hellwarth-Iddings-Platzmann [17] approach to a frequency- and temperature-dependent polaron mobility to obtain a self-consistent approach to polaron transport. This section follows the general self-consistent approach for the polaron free energy derived in section 4.5. It generalises the multiple fictitious particle approach to polaron mobility in section 5.4. The results here are still early in development but are presented to motivate further investigation.

5.7.1 A Self-Consistent Approach to the Polaron Memory Function

Previously, we showed that the the general polaron *memory* function $\Sigma(\Omega)$, satisfies the integral equation (see Eq. (5.15)),

$$\Sigma(\Omega) = \frac{4}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 \int_0^\infty dt \left(e^{i\Omega t} - 1 \right) D_{\omega_{\mathbf{q}}}(t) e^{q^2 r_0^2 [G(t) - G(0)]}, \quad (5.29)$$

where $G(t)$ is the polaron Green function obtained from Feynman's trial model, $M_{\mathbf{q}}$ is the electron-phonon coupling matrix, $D_{\omega_{\mathbf{q}}}$ is the bare phonon Green function, r_0 is the characteristic polaron length and n is the number of dimensions.

Likewise, from Eq. (4.55), we derived the self-consistent polaron self-energy in imaginary time,

$$\Sigma(\tau) = \frac{2}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 (\hbar\beta - \tau) D_{\omega_{\mathbf{q}}}(\tau) e^{q^2 r_0^2 [G(\tau) - G(0)]}, \quad (5.30)$$

where the polaron Green function is given by

$$G(\tau) = \frac{1}{\beta} \sum_{l=-\infty}^{\infty} \frac{e^{i\omega_l \tau}}{G_{0,l}^{-1} - \Sigma_l} \quad (5.31)$$

with $\omega_l = 2\pi l / \hbar\beta$ the even Matsubara frequencies, and $G_{0,l}^{-1}$ and Σ_l the Fourier coefficients for the bare Green function and self-energy respectively. Alternatively, this can be written as the integral equation

$$\int_0^{\hbar\beta} d\tau'' G(\tau - \tau'') \left[G_0^{-1}(\tau' - \tau'') - \Sigma(\tau' - \tau'') \right] = n\delta(\tau - \tau'). \quad (5.32)$$

We observe that just as the polaron Green function enters into these integral equations in a ‘shifted’ form, $G(t) - G(0)$ (where we subtract the zero part), we may identify $\Sigma(\Omega)$ as a ‘shifted’ memory function to define another ‘un-shifted’ memory function $\tilde{\Sigma}(\Omega)$ from

$$\tilde{\Sigma}(\Omega) - \tilde{\Sigma}(0) = \frac{4}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 \int_0^\infty dt \left(e^{i\Omega t} - 1 \right) D_{\omega_{\mathbf{q}}}(t) e^{q^2 r_0^2 [G(t) - G(0)]}. \quad (5.33)$$

Thus,

$$\tilde{\Sigma}(\Omega) = \frac{2}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 \int_{-\infty}^\infty dt e^{i\Omega t} D_{\omega_{\mathbf{q}}}(t) e^{q^2 r_0^2 [G(t) - G(0)]} \quad (5.34)$$

where we use the fact that the integrand is even to change the limits of the integral. We see that this is just the Fourier transform of the real-time memory function,

$$\tilde{\Sigma}(t) = \frac{2}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 D_{\omega_{\mathbf{q}}}(t) e^{q^2 r_0^2 [G(t) - G(0)]}. \quad (5.35)$$

Now, we remember that the self-energy is β -periodic, $\Sigma(\hbar\beta - \tau) = \Sigma(\tau)$ for $\tau \in [0, \hbar\beta]$ (Eq. (4.29)). Since the bare phonon Green function and the polaron Green function are also β -periodic, we can equivalently express the self-energy as

$$\Sigma(\tau) = \frac{2}{n} \sum_{\mathbf{q}} |M_{\mathbf{q}}|^2 q^2 r_0^2 D_{\omega_{\mathbf{q}}}(\tau) e^{q^2 r_0^2 [G(\tau) - G(0)]}. \quad (5.36)$$

We see that the self-energy and the ‘un-shifted’ memory function are seemingly related by a Wick-rotation $\tau \rightarrow it$

$$\Sigma(\tau \rightarrow it) \stackrel{?}{=} \tilde{\Sigma}(t). \quad (5.37)$$

Therefore, the optimal memory function may coincide with the Wick-rotated optimal self-energy function that minimises the general variational principle for the polaron free energy (Eq. (4.31)).

Although I do not provide further derivations here, we might speculate that the higher-order cumulants corrections beyond the Feynman-Jensen approximation coincide with higher-order self-energy diagrams, which may be identified with higher-order terms in the FHIP approach related via a Wick-rotation. Further work in this area could lead to a general, systematically improvable, variational principle for the polaron self-energy from

which the frequency-dependent polaron mobility and conductivity can be evaluated from an *analytic* Wick-rotation (i.e. an analytic continuation). The power of this approach is that this analytic continuation does not need to be done numerically. Instead, we would solve for the optimal trial self-energy function using the variational principle and then determine the memory function through the relation between the polaron Green function and the optimal trial self-energy. More investigation is required to determine if this method is numerically viable.

Finally, although not presented in this thesis, this derivation lays the groundwork for many-body systems using the self-energy determined from the coherent state path integral variational principle in section 4.7.

CHAPTER 6

APPLICATION TO REAL SEMICONDUCTORS

“One shouldn’t work on semiconductors, that is a filthy mess; who knows whether any semiconductors exist.”

—Wolfgang Pauli, *Letter to Peierls, 1931*

In this chapter, I apply the Feynman variational approach to calculate the polaronic properties of real semiconductors. Using the multimode extension to the Fröhlich polaron, I evaluate the polaron energy, mass, mobility and optical conductivity of bulk Methylammonium Lead Iodide Perovskite using material data from Brivio et al. [20] and compare the results to the single effective mode method from Eq. (3.7). I use the parabolic Holstein polaron theory to calculate bulk rubrene crystals’ polaron energy, mass, mobility and optical conductivity using material data obtained from Ordejon et al. [22]. I use the anisotropic band extension to calculate the Zero-Point Renormalisation (ZPR) and polaron size with weak coupling perturbation results for dozens of II-VI, III-V and oxide semiconductor materials to characterise the validity of the continuum approximation in the Fröhlich model and the use of the perturbation approximation. The data for these materials was taken from Guster et al. [8]. Finally, I do a high-throughput analysis of 1258 materials from the Materials Project [13] used in the Liège Dataset [14]. Here, I compare my ZPR results with those obtained from perturbation theory [23] and further calculate these materials’ polaron mass and mobility.

Material	ϵ_∞	ϵ_0	ϵ_I	ω_0	m_b
MAPbI ₃ -e	$4.5 \epsilon_0$	$19.4 \epsilon_0$	$14.9 \epsilon_0$	1.62 THz	$0.12 m_e$
MAPbI ₃ -h	$4.5 \epsilon_0$	$19.4 \epsilon_0$	$14.9 \epsilon_0$	1.62 THz	$0.15 m_e$

Table 6.1: Parameters of the Feynman polaron model (single effective phonon mode) are used in this work. Relative high frequency (ϵ_∞), static (ϵ_0) and ionic (ϵ_I) dielectric constants are given in units of the permittivity of free space (ϵ_0). Frequency (ω_{LO}) is in units of $\text{THz}2\pi$. Effective mass (m_b) is in units of the bare electron mass m_e . These data are as similar to Frost [60], except there the effective frequency was calculated using the method of Hellwarth and Biaggio [21] which gave $\omega_0 = 2.25 \text{ THz}$.

6.1 Methyllummonium Lead Halide Perovskites

Having extended the Feynman theory with explicit phonon modes in the *model* action, I now try and answer what improvement this makes by looking at a particular case.

Lead halide perovskites are relatively new semiconductors of considerable technical interest due to their solution processibility. Due to their unusual mix of light effective mass and strong dielectric electron-phonon coupling, they host strongly interacting large polarons. Recently, it has become possible to measure the coherent charge-carrier dynamics upon photo-excitation using Terahertz spectroscopy, which shows rich transient vibrational features [102].

Therefore, I use this system to represent the more complex systems that could be modelled with our extended theory. Applied to the 15 optical solid-state phonon modes in MAPbI₃, I show that my explicit mode method predicts slightly higher mobility for temperatures 0 K to 400 K, with as much as 100% increase at low temperature $T \approx 1 \text{ K}$ to 1% increase at $T = 300 \text{ K}$. At $T = 300 \text{ K}$ I predict electron and hole mobilities of 145.36 and $125.67 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. This is to be compared to previous predictions of $133 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $94 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for one effective phonon mode of frequency 2.25 THz evaluated using Hellwarth and Biaggio's [21] 'B scheme' (see Eqs. (2.262)) by Frost [60] and I [4]. Compared to my new method for calculating the effective phonon mode using Eq. (3.7), I find the effective mode mobilities of $143.69 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $124.20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively, which are in better agreement with the multimode case.

More importantly, my multimode theory recovers considerable structure in the complex conductivity and impedance functions, not seen in the single effective mode theory, as individual phonon modes are activated. The effective and explicit methods show the same temperature and frequency dependence towards higher temperatures - the quantum details are washed out.

In what follows, I take the MAPbI₃ material parameters as shown in Table 6.1.

Phonon Frequency	Infrared Activity	ϵ_j	Coupling α_j
4.02 THz	$0.0817 e^2 u^{-1}$	$0.300 \epsilon_0$	0.0340
3.89 THz	$0.00631 e^2 u^{-1}$	$0.0247 \epsilon_0$	0.00285
3.53 THz	$0.0535 e^2 u^{-1}$	$0.254 \epsilon_0$	0.0308
2.76 THz	$0.0213 e^2 u^{-1}$	$0.166 \epsilon_0$	0.0228
2.44 THz	$0.232 e^2 u^{-1}$	$2.31 \epsilon_0$	0.336
2.25 THz	$0.262 e^2 u^{-1}$	$3.07 \epsilon_0$	0.465
2.08 THz	$0.234 e^2 u^{-1}$	$3.20 \epsilon_0$	0.505
2.03 THz	$0.0623 e^2 u^{-1}$	$0.893 \epsilon_0$	0.142
1.57 THz	$0.0367 e^2 u^{-1}$	$0.886 \epsilon_0$	0.161
1.02 THz	$0.0126 e^2 u^{-1}$	$0.721 \epsilon_0$	0.162
1.00 THz	$0.00682 e^2 u^{-1}$	$0.402 \epsilon_0$	0.0912
0.997 THz	$0.0104 e^2 u^{-1}$	$0.618 \epsilon_0$	0.141
0.920 THz	$0.011 e^2 u^{-1}$	$0.767 \epsilon_0$	0.182
0.801 THz	$0.00168 e^2 u^{-1}$	$0.156 \epsilon_0$	0.0395
0.574 THz	$0.00646 e^2 u^{-1}$	$1.16 \epsilon_0$	0.349

Table 6.2: Infrared activity (units $e^2 u^{-1}$ with $u \sim 1.66 \times 10^{-24}$ kg the atomic mass unit) and frequency (units THz) of phonon modes in MAPbI₃ as calculated by Brivio et al. [20]. Also the calculated ionic dielectric contribution ϵ_j (units of the vacuum permittivity ϵ_0) and Fröhlich alpha α_j of the j th phonon mode.

Material	α	ν	w	E	M	R
MAPbI ₃ -e	2.663	5.45 THz 2π	4.25 THz 2π	−18.6 meV	+0.643	123 Å
MAPbI ₃ -h	2.978	5.55 THz 2π	4.16 THz 2π	−20.9 meV	+0.775	109 Å
MAPbI ₃ -e	2.663	5.84 THz 2π	4.64 THz 2π	−19.6 meV	+0.585	122 Å
MAPbI ₃ -h	2.978	5.92 THz 2π	4.54 THz 2π	−22.0 meV	+0.701	108 Å

Table 6.3: Athermal 0 K results. Dielectric electron-phonon coupling (α), Feynman athermal variational parameters (ν and w , THz) and polaron binding energy (E), polaron effective mass (M , m_0) and polaron radius (R , Å) for an effective phonon mode (top rows) and for multiple explicit phonon modes from Table 6.2 (bottom rows). The lattice constant for MAPbI₃ in its cubic phase at 330 K is $a = 6.391$ Å

Material	ν	w	F	M	R	μ
MAPbI ₃ -e	44.3 THz 2π	38.2 THz 2π	−63.1 meV	+0.348	23.0 Å	144 cm ² V ^{−1} s ^{−1}
MAPbI ₃ -h	44.8 THz 2π	37.9 THz 2π	−70.8 meV	+0.400	20.6 Å	124 cm ² V ^{−1} s ^{−1}
MAPbI ₃ -e	44.4 THz 2π	38.3 THz 2π	−63.2 meV	+0.347	23.0 Å	145 cm ² V ^{−1} s ^{−1}
MAPbI ₃ -h	44.9 THz 2π	38.0 THz 2π	−70.8 meV	+0.399	20.6 Å	126 cm ² V ^{−1} s ^{−1}

Table 6.4: 300 K Results. Feynman thermal variational parameters (ν and w , THz), polaron free energy (F , meV), dc mobility (μ , cm²V^{−1}s^{−1}), polaron effective mass (M , m_0) and polaron radius (R , Å) for an effective phonon mode (top rows) and for multiple explicit phonon modes from Table 6.2 (bottom rows).

This work was first published in Martin and Frost [4], where we used the Hellwarth B-scheme (Eq. (2.262)) to calculate the effective phonon frequency. Instead, in this section, I use Eq. (3.7) to give an effective phonon frequency of $\omega_0 = 1.62$ THz from the phonon mode frequencies and infrared activities in Table 6.2.

6.1.1 MAPI Polaron Free energy

I compare the polaron free energy and variational parameters evaluated by my explicit multiple phonon mode theory to one effective phonon mode of frequency $\omega_0 = 1.62$ THz.

Using Eq. (3.5), I calculated the partial Fröhlich alpha α_j parameters for each of the 15 phonon branches in MAPbI₃, which are given in Table 6.2. For MAPbI₃-e the partial Fröhlich alphas sum to $\alpha = 2.66$ and for MAPbI₃-h they sum to $\alpha = 2.98$. These 15 partial alphas α_j and corresponding phonon frequencies ω_j were then used in the variational principle for the multiple phonon-dependent free energy in Eq. (4.2). From Eq. (4.2), we variationally evaluated a corresponding v and w parameter.

Using the effective phonon frequency $\omega_0 = 1.62$ THz, I obtained a Fröhlich alpha for MAPbI₃-e of $\alpha = 2.663$ and MAPbI₃-h of $\alpha = 2.978$, which agree with the multimode results.

In Fig. 6.1, I show, in the top-left plot, the polaron free energy comparison. The explicit multiple phonon mode approach predicts a larger (more negative) free energy at all temperatures, with a maximum difference of 8.1% at $T = 17$ K. Both approaches predict the same polaron free energy at larger temperatures. See Table 6.3 for my athermal results, where I find new multiple-mode estimates for the polaron binding energy E (at 0 K) for MAPbI₃-e as $E = -19.6$ meV and MAPbI₃-h as $E = -22.0$ meV. Also see Table 6.4 for my thermal results at $T = 300$ K, where I find new multiple-mode estimates for the polaron free energy F for MAPbI₃-e at 300 K as $F = -63.2$ meV and MAPbI₃-h as $F = -70.8$ meV. These are to be compared to our previous results in [60], and the single effective mode results, which are also provided in the top rows of Tables (6.3, 6.4).

In the top-right plot of Fig. 6.1, I show the comparison in polaron variational parameters v and w . Both the multimode and effective mode approaches produce very similar results, with the multimode variational parameters being slightly larger in value than the effective mode variational parameters at all temperatures. Towards higher temperatures, the two methods agree.

6.1.2 MAPI DC Polaron Mobility

I calculate the zero-frequency (direct current, DC) electron-polaron mobility μ in MAPbI₃ using the effective phonon mode and explicit multiple phonon mode approaches. Both

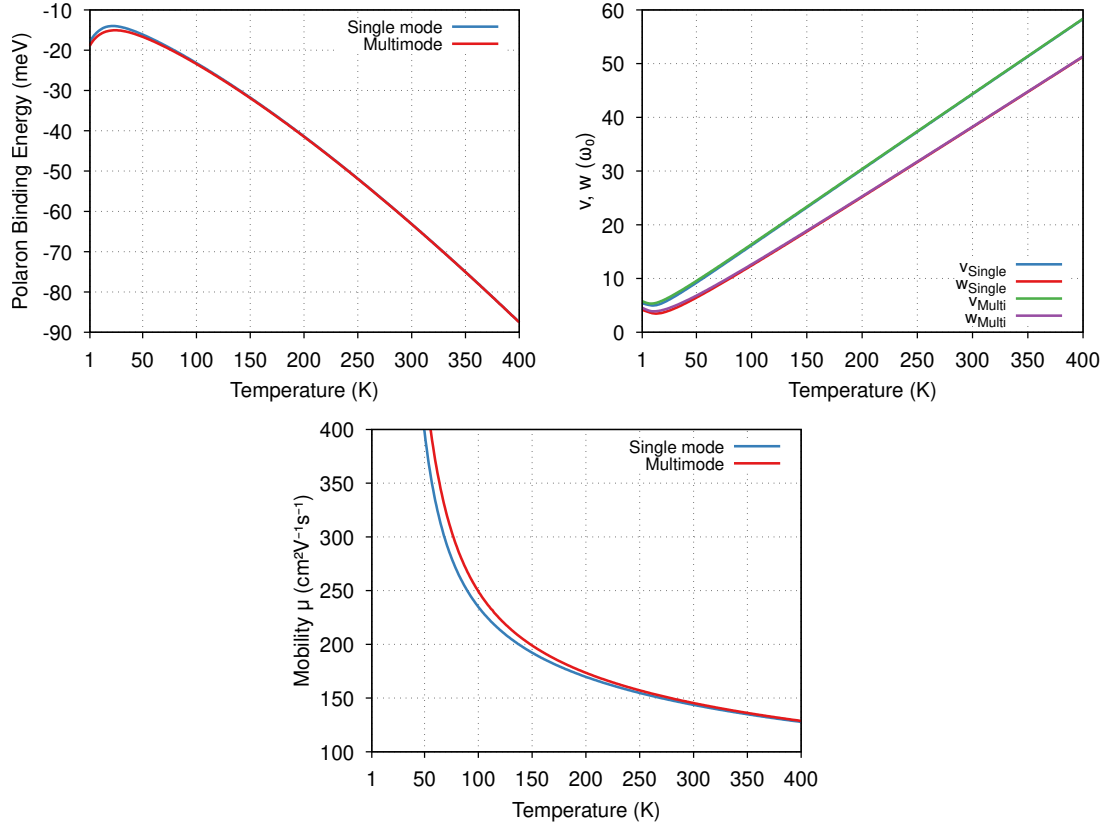


Figure 6.1: Top-left: Comparison of the polaron free energy as a function of temperature for MAPbI_3 , using the single effective phonon mode approach (blue) and the explicit multiple phonon mode approach (red). Top-right: Comparison of the two polaron variational parameters, v and w , for MAPbI_3 , with the single effective phonon mode approach (blue) and the explicit multiple phonon mode approach (red). Bottom: Comparison of the temperature-dependent mobility predicted for MAPbI_3 , using the single effective phonon mode approach (blue) and the explicit multiple phonon mode approach (red).

approaches have the same relationship between the mobility and the memory function (Eqs. (2.203, 2.212)), but the effective mode approach uses the memory function $\Sigma(\Omega)$ from Eq. (2.203) (the FHIP [17] memory function, Eq. (35) *ibid.*), whereas the multiple phonon mode approach uses our $\Sigma_{\text{multi}}(\Omega)$ from Eqn. (5.9) (with a sum over the phonon modes).

The bottom panel of Fig. 6.1 presents the temperature dependence of polaron mobility. Contrary to expectations, the multimode approach (red) consistently predicts higher mobility than the single-mode approach (blue) across all temperatures. This suggests that the more accurate treatment of phonon modes in the multimode model may reduce scattering effects or result in more efficient charge transport. One possible reason is that the multimode approach allows the electron to couple more effectively to the different phonon modes, distributing the interaction across multiple modes and reducing the overall scattering rates.

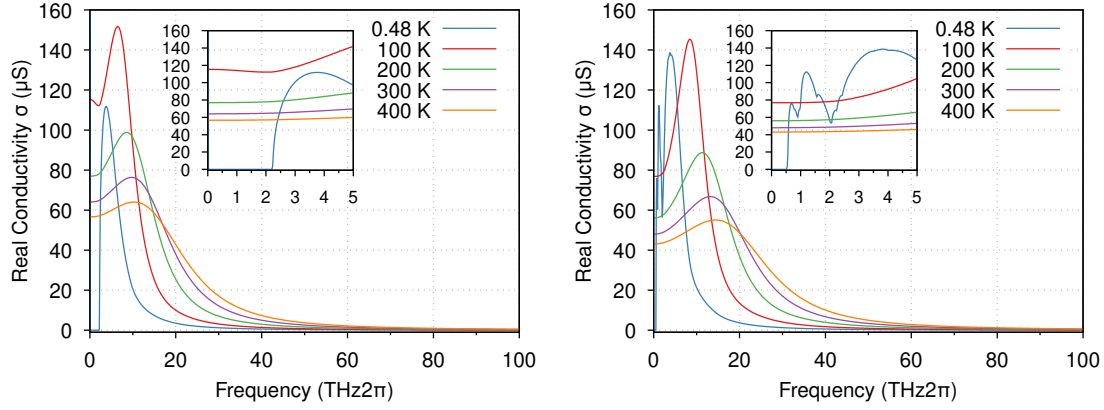


Figure 6.2: Frequency dependence of the single effective mode (left) and explicit multimode (right) the real complex conductivity for MAPbI_3 , for temperatures $T = 0.48 \text{ K}$, 100 K , 200 K , 300 K and 400 K . The insets show the low-frequency dependence more to highlight the additional structure in the multimode results.

In contrast, the single-mode approach confines the interaction to a single phonon mode, which may overestimate the scattering effects and consequently predict lower mobility. This highlights the importance of considering multiple phonon interactions when modelling polaron transport, especially in materials with complex phonon spectra like MAPbI_3 .

However, we cannot neglect that the prediction of higher mobility from the multimode method may be specific to MAPbI_3 , and other semiconductors should be investigated.

6.1.3 MAPI Polaron Optical Conductivity

I calculate the complex impedance $z_{\text{multi}}(\Omega)$ for the polaron in MAPbI_3 using Eq. (2.211), where the only difference between the effective mode and multiple mode approaches is in the form of the memory function $\Sigma_{\text{multi}}(\Omega)$ as described for the polaron mobility above. The complex conductivity $\sigma_{\text{multi}}(\Omega)$ is the reciprocal of the complex impedance, $\sigma_{\text{multi}}(\Omega) = 1/z_{\text{multi}}(\Omega)$.

In Figs. 6.2 and 6.3, I analyse the frequency and temperature dependence of the real and imaginary components of the optical conductivity $\sigma(\Omega)$ for methylammonium lead iodide (MAPbI_3) perovskites.

In Fig. 6.2, I show the real part of the conductivity of MAPbI_3 as a function of frequency for various temperatures, ranging from 0.48 K to 400 K . For a single mode (left panel), we observe that the conductivity is dominated by a low-frequency peak, which diminishes as temperature increases, shifting to higher frequencies. As temperature rises, phonon scattering becomes more significant, broadening the conductivity peak and reducing its magnitude, especially at lower frequencies. A similar trend is observed in the multimode case (right panel), though additional structures and fine details appear at low frequencies,

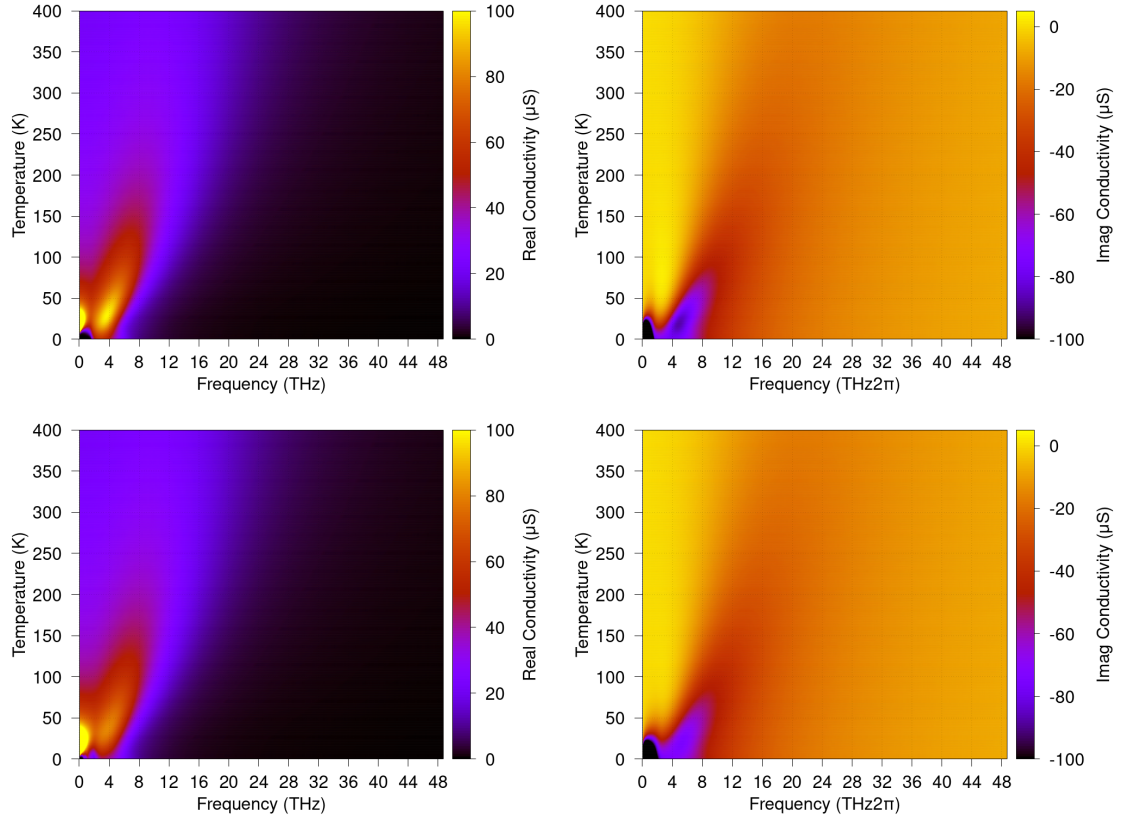


Figure 6.3: Temperature and frequency dependence of the real (left) and imaginary (right) components of the complex conductivity for MAPbI_3 , comparing two theoretical models for phonon interactions. The top row represents the single effective phonon mode approach, while the bottom row includes all explicit phonon branches.

particularly noticeable in the insets. This highlights the presence of multiple phonon modes that contribute to the scattering and complex frequency response. The additional structure is generated by the convolution of the 15 different phonon peaks, each starting at their respective frequency shown in Table 6.2.

In Fig. 6.3, I provide a temperature-frequency contour plot of both the real (left) and imaginary (right) components of the conductivity of MAPbI_3 . The single-mode approach (top row) shows a strong peak in real conductivity at low temperatures and frequencies, which rapidly diminishes as temperature increases beyond 100 K. The imaginary part, meanwhile, indicates a smooth decline with temperature, becoming more negative as frequency increases. For the multimode case (bottom row), the real conductivity shows more nuanced behaviour at low temperatures (although hard to make out at this scale), with more dispersed conductivity across a wider range of frequencies due to the involvement of multiple phonon modes. The imaginary part in the multimode case reflects trends similar to single mode. The single-mode and multimode approaches produce similar polaron conductivities for most temperatures and frequencies; they only differ significantly at low temperatures and frequencies $\Omega < 5$ THz where the explicit phonons modes can

be resolved. For most temperatures, the single-mode conductivity is only slightly larger than that of the multimode approach, and both approaches give the same results at large temperatures and frequencies.

6.1.4 Modelling Terahertz Spectroscopy Photoconductivity Dynamics in Metal-Halide Perovskites

Recently, our collaborators used ultrafast visible pump-infrared push-terahertz probe spectroscopy to measure the real-time photo-conductivity of methyl-ammonium lead iodide in [103]. I provided my multiple phonon mode mobility, applied to the 15 modes of MAPbI₃ in Table 6.2, to model the complex conductivity and compare the results to the photo-conductivity measurements.

Fig. 6.4 presents key results from a frequency-resolved pump-push-probe (PPP) experiment in the terahertz (THz) range. The two-dimensional map in panel (a) illustrates the evolution of the THz probe intensity as a function of both frequency and push-probe delay, with the pump-push delay set to 10 ps. Two clear resonances at approximately 1.25 and 2.25 THz are visible in the map, corresponding to strong carrier-phonon coupling, specifically with phonon modes associated with the Pb-I bond vibrations in the material. These phonons are essential to the system's polaron dynamics, as indicated by the significant reduction in absorption around these frequencies when the “push” arrives, indicating resonance in the charge carriers.

In panel (b), the THz photoconductivity spectra decompose the real ($\Delta\sigma_{\text{Re}}$) and imaginary ($\Delta\sigma_{\text{Im}}$) components of the complex conductivity at various times relative to the arrival of the push. The data show that before the push (blue line), the photoconductivity peaks at the resonant frequencies of 1.25 and 2.25 THz are dominant. As the push arrives (black line), there is a substantial reduction in both real and imaginary components, particularly at these frequencies. After the push (green line), the conductivity begins to recover. Still, the phonon-coupled peaks remain, reflecting the non-Drude-like behaviour associated with polaronic effects rather than free carriers. This suggests that the carriers behave not simply as free charges but are coupled to the phonon modes, leading to a complex photoconductivity response and implies a polaron quasi-particle state.

Panel (c) shows the THz probe signal's recovery time (τ) across different frequencies. The recovery time is frequency-dependent, with the slowest recovery occurring at the two resonant frequencies (1.25 and 2.25 THz). This suggests that carrier relaxation is coupled to specific phonon modes, as these frequencies influence the recovery time. This behaviour suggests that these phonon modes are directly heated when the push excites the carriers, and their energy dissipation takes longer. The strong coupling between carriers

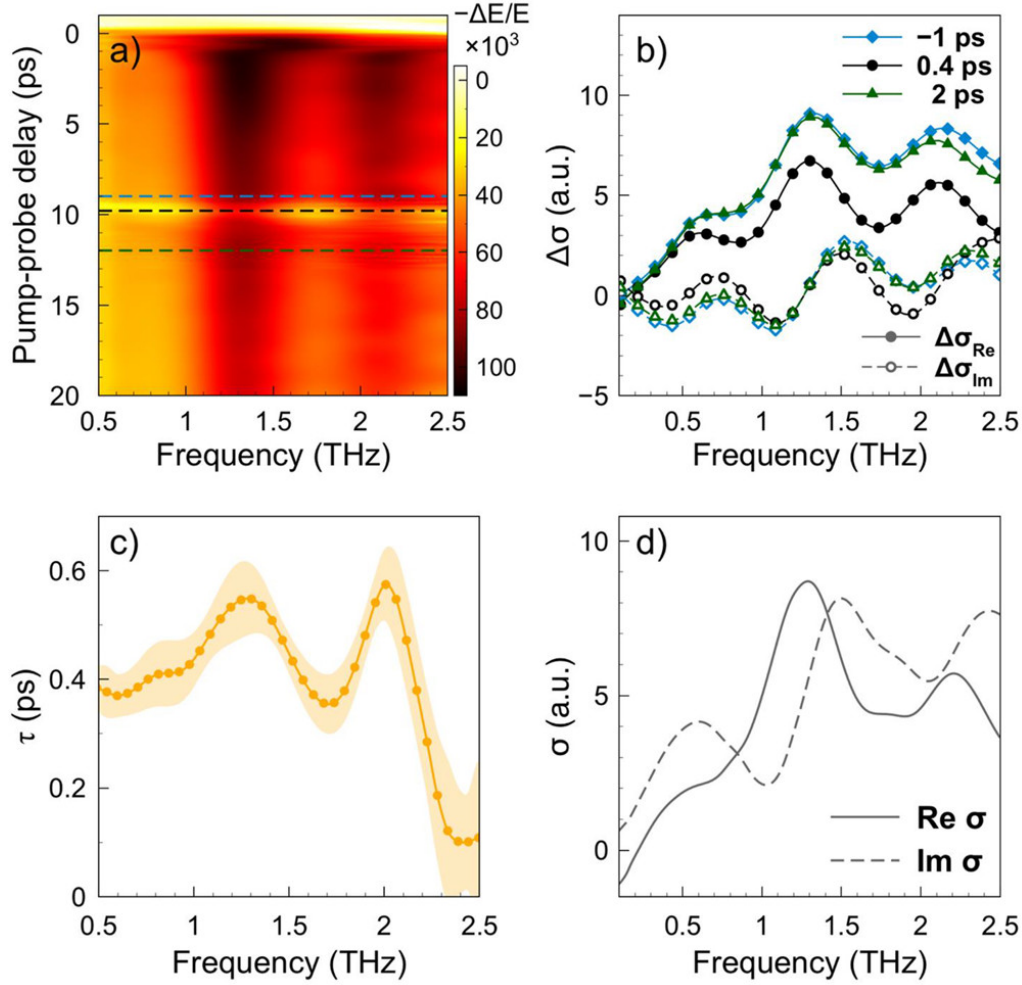


Figure 6.4: Reproduced without permission from ref. [103]. (a) Two-dimensional probe frequency vs. push-probe delay intensity map from a pump-push-THz probe experiment, with the pump-push delay set to 10 ps. (b) THz photoconductivity spectra showing the real and imaginary components of the complex conductivity ($\Delta\sigma = \Delta\sigma_{\text{Re}} + \Delta\sigma_{\text{Im}}$) before, during, and after the push. (c) Probe recovery time at different frequencies. (d) Simulated frequency-resolved conductivity using the FHIP polaron mobility theory, showing agreement with experimental peaks at 1.25 and 2.25 THz, corresponding to carrier-phonon coupling.

and phonons likely prolongs the recovery time at these frequencies, as the energy stored in these modes must dissipate before the carriers can fully relax back to equilibrium.

Panel (d) shows the simulated real and imaginary parts of the frequency-resolved conductivity calculated using my multimode approach. The simulation captures the experimental behaviour well, with peaks at 1.25 and 2.25 THz, corresponding to the primary phonon modes involved in the carrier-phonon coupling. This simulation supports the argument that polaron-renormalised carrier interactions with phonon modes drive the observed response. The best fit to the data is achieved using a zero-temperature mobility theory, suggesting that the subpicosecond timescale of the THz measurements corresponds to a prethermal regime, where the polaron response is not yet fully equilibrated with the lattice. To improve the

result, we would need to generalised the FHIP method to non-equilibrium systems. This has already been derived by Feynman and Thornber [33], where they found an effective electron temperature separate from the lattice which may account for the discrepancy found. Lastly, the FHIP approach only account for a single electron. In reality, there are a many electrons described by a density distribution/carrier density which would change the dissipative properties of the system.

In summary, the experimental and theoretical data collectively demonstrate the significant role of carrier-phonon coupling in determining the frequency-dependent photoconductivity. The observed peaks in both the experimental and simulated data point to specific phonon modes (around 1.25 and 2.25 THz) that strongly interact with the carriers, affecting both the conductivity and the relaxation dynamics of the system. These more accurate methods enable the prediction and optimisation of multimodal polar semiconductors and a more accurate comparison to experiment by describing the richer device physics and phonon dynamics revealed by THz mobility measurements.

g (meV)	ω_0 (THz)	J (meV)	a (Å)	γ	m_b (m_e)	λ^2	α
106.8	5.768	134.0	14.06	0.178	0.144	19.75	0.586

Table 6.5: 3D rubrene Bulk crystal data derived from [22]. Here g is the Holstein hole-phonon coupling element, ω_0 is the single-mode effective phonon frequency, J is the electron transfer/hopping integral, a is the geometric-meaned crystal lattice constant, γ is the Holstein adiabaticity unitless parameter, m_b is the effective hole band-mass, $\lambda^2 = (g/\hbar\omega_0)^2$ is the unitless squared hole-phonon coupling element and $\alpha = \lambda^2\gamma/6$ is the 3D unitless Holstein electron-phonon parameter.

6.2 Rubrene Organic Crystals

The charge-carrier state is often considered a small polaron in organic electronic materials. This is frequently modelled with semi-classical transfer rate theories as a classical object hopping from site to site. The matrix elements that parameterise these rate equations can be calculated within certain approximations using electronic structure calculations. Still, defining the sites where the charge carriers are localised is challenging (and often an input to the simulation and calculations).

One of the prototypical materials studied frequently to investigate electron-phonon coupling is rubrene (5,6,11,12-tetraphenyltetracene), which has one of the highest carrier mobilities that can reach a few tens of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for holes [79]. This is a good test for applying my new variational Holstein polaron model to predict the charge-carrier mobility. We take parameters for rubrene from Ordejon et al. [22], who derived intermolecular Peierls (off-site) and intramolecular Holstein (on-site) contributions by fitting the generalise Holstein-Peierls model with careful Density Functional Theory (DFT) calculations performed using SIESTA [104]. I use their Holstein parameters coupling, which I reproduce in Table 6.5. For simplicity, we consider a single effective phonon frequency, though the technique presented here could be extended to multiple phonon modes, as we have demonstrated for the Fröhlich Hamiltonian [4].

6.2.1 Rubrene Athermal Polaron Properties

Table 6.6, I show the results for thermal ($T = 0$ K) parabolic Holstein and Fröhlich polarons for rubrene. Here, I have used the same value for the Holstein and Fröhlich dimensionless coupling parameter, α , to facilitate direct comparison between the results. This is further justified by Fig 4.1 where in 3D, we see that the weak-to-strong coupling transition occurs around $\alpha \approx 6$ for both polaron models.

	v_0 (THz)	w_0 (THz)	M_0 (m_e)	R_0 (Å)	F_0 (meV)
Holstein	21.01	7.258	0.146	121.3	-6.867
Fröhlich	17.66	16.88	0.149	304.2	-5.842

Table 6.6: Ground-state polaron properties for a rubrene Bulk crystal calculated using the variational Holstein and Fröhlich models.

	v (THz)	w (THz)	M (m_e)	R (Å)	F (meV)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Holstein	77.22	74.37	0.155	34.28	-18.10	47.72
Fröhlich	43.56	41.15	0.151	99.10	-10.95	92.59

Table 6.7: Room temperature (300 K) polaron properties for a rubrene Bulk crystal calculated using the variational Holstein and Fröhlich models.

6.2.2 Rubrene Thermal Polaron Properties

In Table 6.7, I give the result for $T = 300$ K, including the finite temperature DC mobility, which I calculate to be $\mu_{\text{rubrene}}^{(H)} = 47.72 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the parabolic Holstein polaron and $\mu_{\text{rubrene}}^{(F)} = 92.59 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the Fröhlich polaron. The Holstein model is closer to experiment, whereas the Fröhlich model overestimates the experimental value.

In Fig. 6.5, I present the rubrene polaron's temperature-dependent properties: free energy (top-left) and mobility (bottom). I provide the optimal variational parameters v and w for temperatures $T = 1$ K to 400 K (top-right).

In the top-right panel, I show the optimal variational parameters v and w (THz) as functions of temperature. These parameters characterise the polaron state, with v_H , v_F , w_H , and w_F representing the variational solutions for the Holstein and Fröhlich models, respectively. Both parameters exhibit a non-monotonic dependence on temperature, with minima occurring around 50 K for the Fröhlich model and 120 K for the parabolic Holstein model, suggesting a crossover in the polaron's structural configuration at lower temperatures. At high temperatures, both v and w increase steadily for both models, with the Fröhlich model yielding slightly larger values.

In the bottom figure, I show the temperature dependence of the polaron charge-carrier mobility. Both models show similar band-like mobility at low temperatures $T < 130$ K. Above this temperature, the parabolic Holstein polaron mobility descends far more quickly than the mobility of the Fröhlich polaron and reaches $\mu = 47.72 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at $T = 300$ K, whereas the Fröhlich mobility only drops to $\mu = 92.59 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. At higher temperatures, the Fröhlich polaron mobility will continue to decrease at a rate proportional to $\mu \sim T^{-1/2}$, whereas the Holstein polaron mobility reaches a minimum of $\mu \approx 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ near $T \approx 1555$ K, which corresponds to the energy of the transfer integral

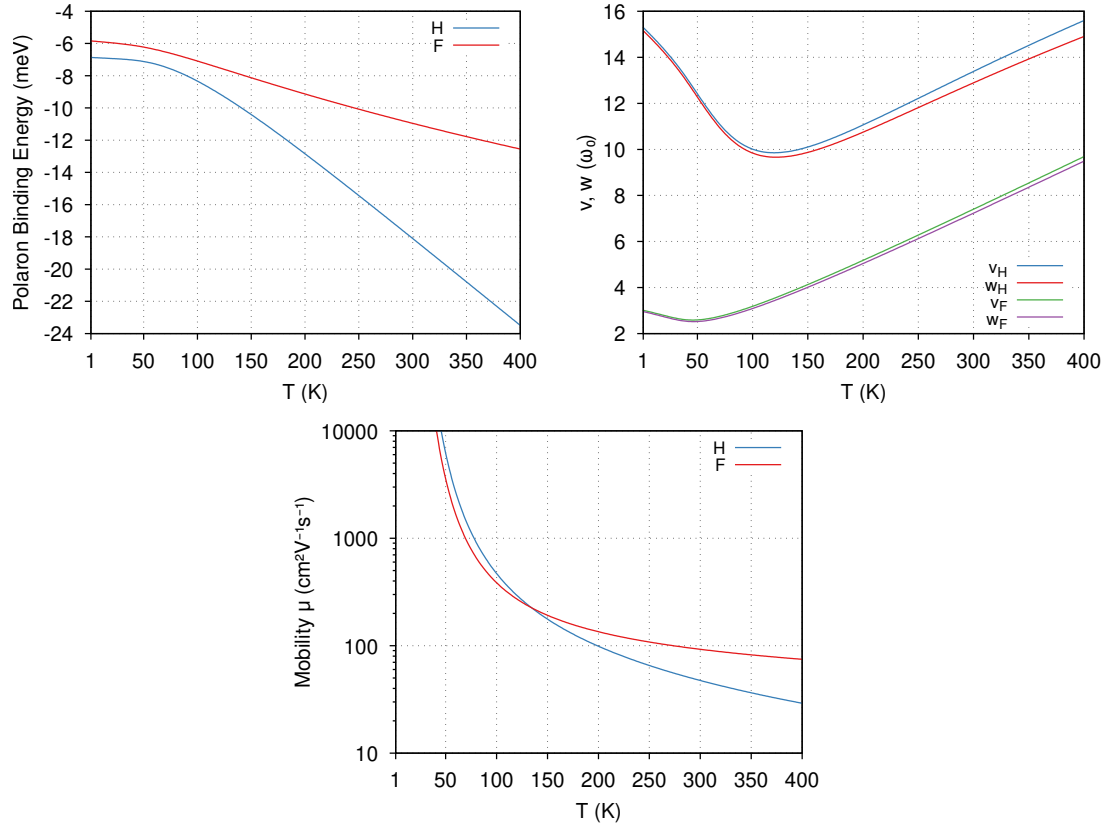


Figure 6.5: Polaron properties predicted from the variational parabolic Holstein and Fröhlich models for a bulk 3D rubrene organic crystal. Top-left: The polaron free energy F (meV) in rubrene as a function of temperature (K). Top-right: Optimal variational parameters v and w (THz) as a function of temperature (K). Bottom: The DC polaron mobility $\mu(T)$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) as a function of temperature T (K) calculated along the high-mobility direction ‘ b ’ of the rubrene crystal

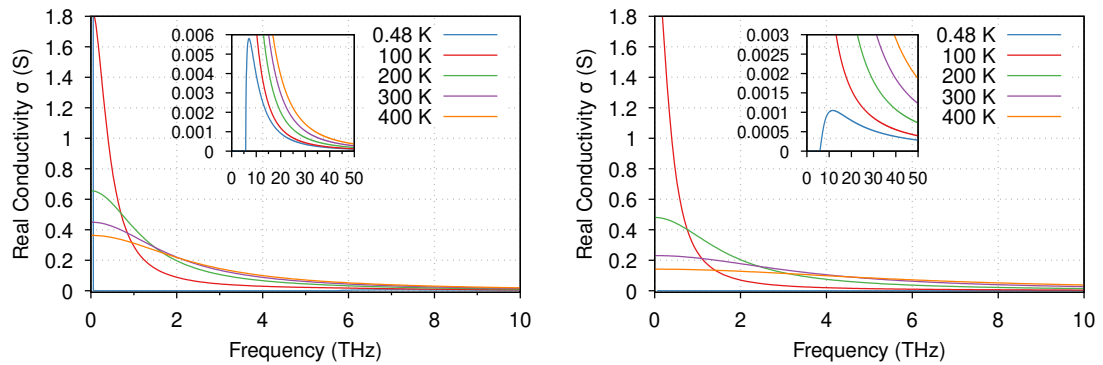


Figure 6.6: Frequency dependence of the polaron complex conductivity (in units of S cm^{-1}) predicted by the variational parabolic Holstein (left) and Fröhlich (right) models for a bulk 3D rubrene organic crystal, for temperatures $T = 0.48$ K, 100 K, 200 K, 300 K and 400 K.

$J = 134$ meV. Above this temperature, the Holstein polaron mobility will increase at a rate proportional to $\mu \sim T^{1/2}$.

6.2.3 Rubrene Complex Conductivity

In Fig. 6.6, I show the frequency dependence of the real part of the polaron complex conductivity $\sigma(\Omega)$ (in S) for the 3D rubrene organic crystal, as predicted by the variational parabolic Holstein (left) and Fröhlich (right) models, at various temperatures ranging from 0.48 K to 400 K.

The left subplot of Fig. 6.6 displays the real component of the Fröhlich model's conductivity across a range of temperatures: 0.48 K, 100 K, 200 K, 300 K, and 400 K. At the lowest temperature (0.48 K), the real conductivity shows a significant one-phonon peak at low frequencies starting at the phonon frequency $\Omega = \omega_0 = 5.768$ THz, which rapidly decreases with increasing frequency. As temperature rises, the peak becomes less pronounced and is no longer visible, indicating a reduction in the polaronic response due to thermally excited phonons that generate an extra Drude-like background response. The inset in the top-left subplot provides a closer view of the high-frequency behaviour, emphasising the one-phonon peak and the gradual decline in real conductivity across all temperatures.

6.2.4 Improving the Variational Approach for Organic Crystals

In this section, we have applied the variational approach to the Holstein model to the case of rubrene, resulting in a reasonable prediction for the room-temperature mobility of $47.72 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

However, this method overlooks some relevant physical aspects of rubrene, most notably the intermolecular (Peierls) electron-phonon interactions and the highly anisotropic nature of the band structure. Rubrene crystal is a quasi-2D material, and since the polaron properties are strongly dependent on dimensionality, proper consideration of the crystal structure is needed. Moreover, the intermolecular 'Peierls' phonon modes significantly affect the charge carrier, perhaps more so than the intramolecular Holstein modes.

Therefore, to improve this model, a first step would be to account for the Peierls electron-phonon coupling. A simple approximation would be calculating the corresponding Peierls dimensionless coupling parameter akin to alpha α_P and adding it to the Holstein alpha α_H in the parabolic Holstein method. Alternatively, we could also attempt to extend the variational path integral method to the Peierls electron-phonon coupling matrix,

$$M_{\mathbf{k},\mathbf{q}} = \frac{4i}{\sqrt{N}} g_P \omega_{\mathbf{q}} \sin\left(\frac{qr_0}{2}\right) \cos\left(kr_0 + \frac{qr_0}{2}\right). \quad (6.1)$$

The difficulty is that this electron-phonon matrix depends on the electron momentum $\mathbf{k}$, so it is unclear how to proceed following the usual approach to deriving the path integral for which a variational principle can be developed.

Assuming instead that the $\mathbf{k}$ -dependence is small, $M_{\mathbf{k},\mathbf{q}} \sim M_{0,\mathbf{q}}$, we may proceed in the same way as we did for the Holstein model by making the parabolic band approximation and substituting the Peierls electron-phonon matrix into our variational principle. If we approximate $M_{\mathbf{k},\mathbf{q}} \sim M_{0,0} \sim g_P$ as a constant, then we end up with an additional constant coupling in addition to the Holstein electron-phonon coupling $g = g_H + g_P$.

Alternatively, suppose we expand the Peierls electron-phonon matrix to quadratic order in $\mathbf{k}$. In that case, we find that by the symmetry of the $\mathbf{k}$ -sum, the linear (odd) term must vanish so that we would end up with only the k^2 term. This would enter the model as a time-dependent transfer integral J since $J \rightarrow J(q)$. Taking the effective mass approximation and deriving the path integral, we end up with a time-dependent mass term that also depends on the phonon wavevector $\mathbf{q}$.

Finally, we could use the variational principle for the Holstein-Peierls model derived from the coherent state path integral. I believe this is the best and most fruitful approach to further apply the variational principle to organic crystals like rubrene.

Overall, there is plenty of scope to develop the variational principle further. This thesis will not present further work in this direction, but hopefully, these suggestions will direct further developments.

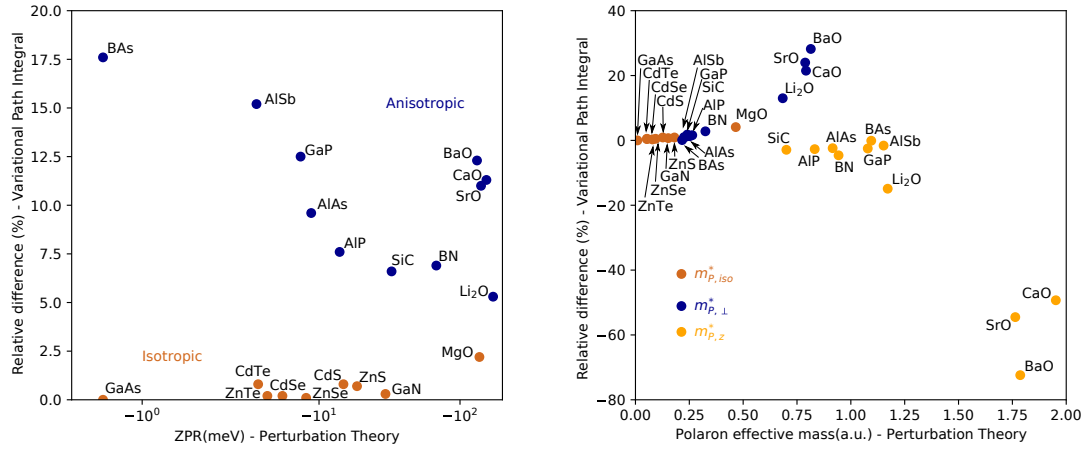


Figure 6.7: Figures reproduced without permission from [8]. (left): The relative differences between the ground-state energy of the polaron determined using perturbation theory (which fully accounts for any anisotropy) and the Feynman variational approach (using my approximate treatment of anisotropy). (right): The relative difference between the effective masses was determined using perturbation theory and the Feynman variational approach (again, only approximately accounting for anisotropy). $m_{P,iso}^*$ is the isotropic effective mass, $m_{P,\perp}^*$ and $m_{P,z}^*$ are the in-plane and out-of-plane polaron effective masses.

6.3 Cubic & Anisotropic Materials

In 2021, Guster et al. [8], collaborators and I investigated the polaron effective mass, radius and ground-state energy that arise from a generalised Fröhlich Hamiltonian that incorporates degenerate bands with anisotropy and multiple phonon branches. These polaron properties are calculated for 20 cubic materials (including II-VI compounds: CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe; III-V compounds: AlAs, AlSb, AlP, BaS, BN, GaAs, GaN, GaP; oxides: BaO, CaO, Li₂O, MgO, SrO; and SiC) using the lowest order of perturbation theory, and the strong coupling limit.

In the non-degenerate case, I provide a naïve extension of Feynman’s path integral approach to include anisotropic effective band masses, which is used as a point of comparison with the full perturbative treatment for characterising the polaron in the weak-coupling limit (see section IIb in [8]). From Figure 6.7 (left), we see that the variational approach gives a lower estimate for the ground state compared to the perturbative result for both isotropic (up to 2.5% lower) and anisotropic (up to 17.5% lower) materials. In Figure 6.7 (right), we have the relative difference in polaron effective mass between the two approaches. The most significant difference is found in materials that, within the Fröhlich approach, are found in [8] to be at the continuum limit breakdown where the discrete nature of the lattice cannot be ignored. These materials include BaO, CaO, SrO and, to a lesser extent, Li₂O. In both the anisotropic and isotropic cases, the relative difference increases with polaron

effective mass, and the in-plane and out-of-plane effective mass differences seem to diverge. This sudden increase in the relative difference is associated with a breakdown limit around $\alpha = 6$ in the perturbative approach for determining the polaron effective mass.

This section outlines my contribution to the collaborative work in Guster et al. [8]. I used my anisotropic band mass version of the Feynman path integral variational method to investigate polaron properties across 20 cubic materials, accounting for anisotropy and multiple phonon branches. Comparing this approach with perturbation theory, the variational method generally provided lower estimates for the ground-state energy, with differences up to 17.5% for anisotropic materials. This is particularly notable in materials where the continuum approximation breaks down, such as BaO, CaO, and SrO, where the discrete lattice effects become significant—additionally, the two approaches' relative differences in polaron effective mass increase with larger polaron renormalised masses. For anisotropic materials, the in-plane and out-of-plane masses begin to diverge. These findings highlight the utility of the Feynman path integral method in capturing nuances of polaron behaviour that perturbative methods may miss, particularly in the presence of anisotropy and near the breakdown limits of perturbative approximations.

6.4 High-Throughput Material Classification

In this section, I analyse a comprehensive dataset of 1258 materials from de Melo et al. [23] using the FVA. I extend this approach to address scenarios involving multiple phonon modes in electron-phonon coupling, analogous to Miglio et al.'s Fröhlich model generalisation [64]. I examine these materials to illustrate the distribution of ground-state energies and the errors introduced by perturbation theories. Additionally, I calculate the room-temperature FHIP mobilities for all these materials and discuss trends that may offer design clues for future potential high-mobility materials.

6.4.1 Polaron Zero-Point-Renormalisation Energy

In Fig. 6.8, I present the relationship between polaron energy E (in meV) and the electron-phonon coupling constant α for various materials, as computed using Feynman's variational path integral theory.

The left panel shows the polaron energy as a function of α , where α spans a wide range from weak to strong coupling. Different materials are coloured in green, orange or blue depending on if they contain group 15 (pnictogens), 16 (chalcogenides), or 17 (halogens) elements, respectively. Other materials are coloured purple. If a material contains a halogen and a chalcogenide or pnictogens, the halogen takes precedence and is coloured blue.

The polaron energy exhibits a clear increasing trend with α , spanning multiple orders of magnitude, from sub-meV to over 10^5 meV as α increases. The huge ZPR values (i.e. > 3 eV) can be observed in materials whose electronic structures present large effective masses (flat bands) of $m_b > 10 m_e$ in at least one direction.

At low values of α (less than 1), the energy is relatively small and shows slow growth. However, as α crosses 1 and approaches 10, the energy increases more rapidly, indicating stronger electron-phonon interactions and enhanced polaron binding. Beyond $\alpha \approx 6$, a significant rise in polaron energy occurs, reflecting the transition into the strong coupling regime when perturbation theory breaks down. We mention that some of these ZPR values at strong coupling are unphysically large (much greater than 3 eV). These unphysical ZPR values may indicate a breakdown in the fundamental assumptions of the Fröhlich model, such as parabolicity and isotropy of the electronic bands, or the validity of the continuum and large polaron hypotheses.

The right panel compares the percentage energy difference between Feynman's variational approach and the weak-coupling perturbation theory. The difference is minimal for low α (below 1), remaining below 0.01%, indicating strong agreement between the two ap-

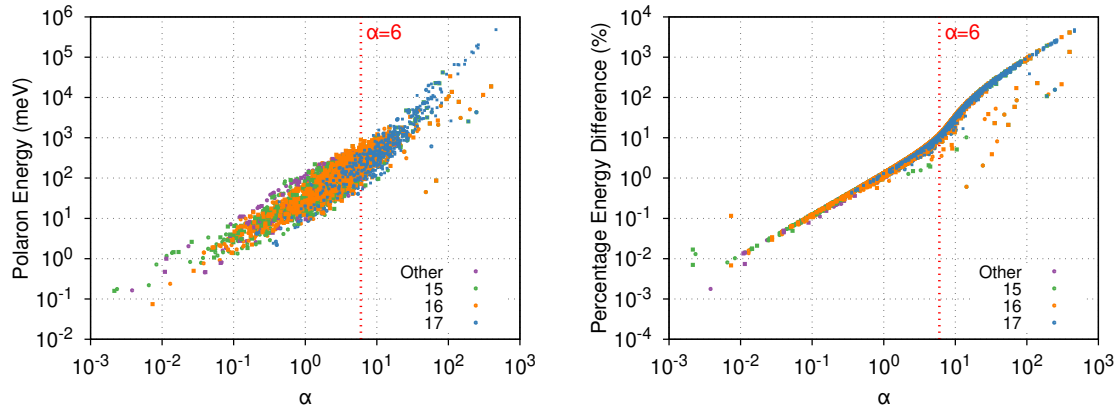


Figure 6.8: The left panel shows the polaron energy in E (meV) as a function of the electron-phonon coupling constant α , calculated using Feynman’s variational path integral theory for 1258 materials from the Liège dataset [14]. Materials containing group 15, 16, or 17 elements are highlighted. Squares indicate holes, while circles indicate electrons. The right panel compares the percentage energy difference between the weak-coupling perturbation theory and the Feynman result, showing increasing deviations at higher α , particularly beyond $\alpha = 6$, indicating the breakdown of perturbation theory in the strong-coupling regime.

proaches. The deviation grows as α increases, especially beyond $\alpha = 6$, where the percentage energy difference rises sharply. This highlights the breakdown of perturbation theory in the strong-coupling regime, as perturbative methods become increasingly inaccurate for higher α . The FVA, being non-perturbative, provides more accurate predictions in these strong-coupling scenarios.

Thus, this further demonstrates the reliability of Feynman’s variational path integral method across the full range of electron-phonon coupling strengths compared to perturbative methods, particularly in the strong coupling regime, where weak perturbation theory fails. For example, in the intermediate coupling regime ($1 \leq \alpha \leq 6$), we see errors between 1% and 10% compared to the FVA’s more accurate results. The sharp increase in energy difference beyond $\alpha = 6$ illustrates the limitations of perturbation theory as α grows larger. However, we must question the validity of the Fröhlich model itself at these strong couplings in light of the *huge* polaron renormalisation energies that are predicted.

6.4.2 Polaron Effective Mass

In Fig. 6.9, I show the coupling dependence of the polaron effective mass, M , in units of m_e (Eq. (2.130)). The left panel shows the polaron mass at zero temperature (0 K), while the right panel presents the polaron mass at room temperature (300 K). The critical coupling value of $\alpha = 6$ (red dashed line) marks the transition between weak and strong coupling regimes.

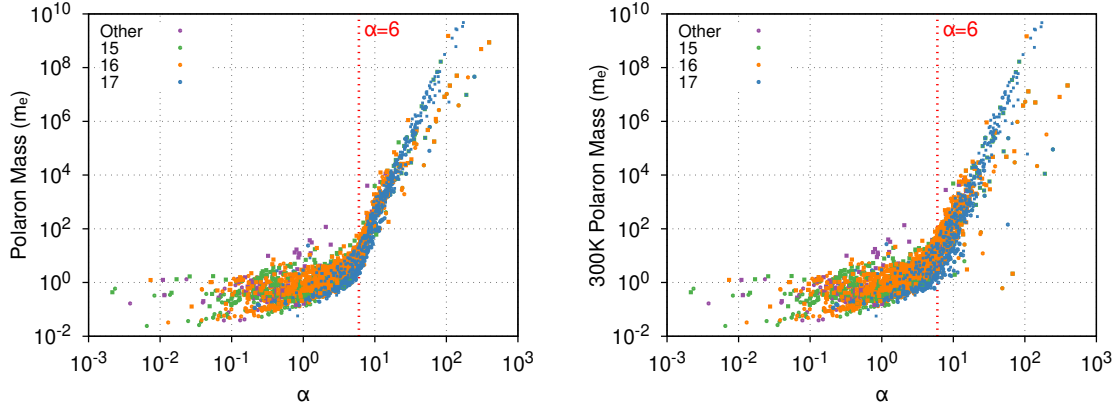


Figure 6.9: Polaron effective mass as a function of the electron-phonon coupling constant α for 1258 materials from the Liège dataset [14]. Materials containing group 15, 16, or 17 elements are highlighted. Squares indicate holes, while circles indicate electrons. The left panel shows the effective polaron mass at zero temperature, while the right panel displays the results at room temperature (300 K). The critical value of $\alpha = 6$ (red dashed line) marks the transition from weak to strong coupling.

In the left panel, at low values of α (below 1), the polaron mass is close to the electron mass, and the variation is small. However, as α increases towards 10, we observe a sharp increase in the polaron mass, indicating the onset of stronger electron-phonon interactions, which cause the polaron to become heavier. Beyond $\alpha = 6$, a dramatic increase in polaron mass is evident. This suggests a transition to the strong coupling regime, where the polaron becomes highly localised due to strong coupling to the lattice. However, these effective masses are huge ($M > 5m_e$) and likely unphysical as they would correspond to very flat bands, and many of these materials will not be semiconductors.

The right panel shows the polaron mass at room temperature (300 K), with a similar trend. For low α , the mass remains close to the electron mass, but as α increases beyond 1, the mass grows rapidly. At room temperature, however, there is more scatter in the data compared to the 0 K case, which may reflect some temperature-induced effects on polaron behaviour. Nonetheless, the overall trend of increasing mass with higher α remains evident, especially beyond $\alpha = 6$, where the strong coupling regime leads to highly localised, heavy polarons. However, as mentioned, this is likely unphysical.

6.4.3 Room Temperature Polaron Mobility

In Fig. 6.10 and Fig. 6.11, we illustrate the relationship between polaron mobility μ and the electron-phonon coupling constant α .

In Fig. 6.10, the left panel shows the mobility using a single effective phonon mode based on Eq. (3.7), while the right panel accounts for all phonon branches in the material. The polaron mobility decreases as α increases in both cases, spanning several orders of

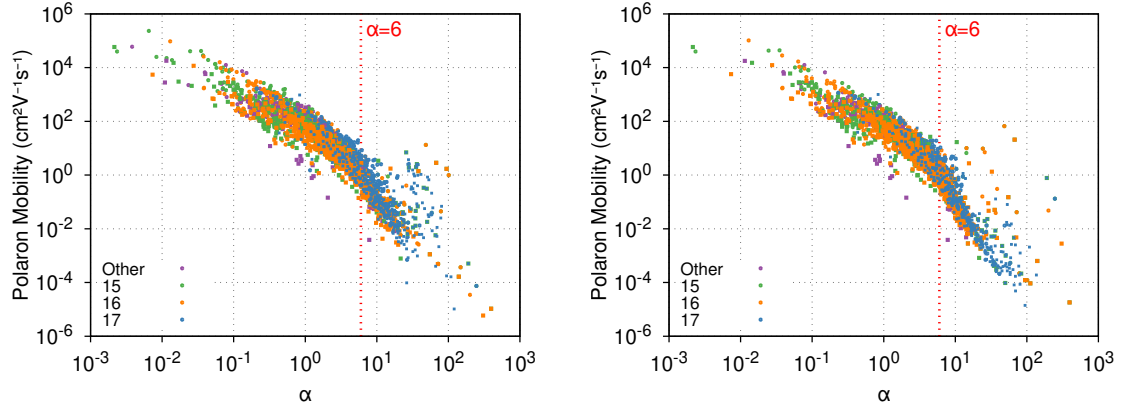


Figure 6.10: Polaron mobility as a function of the electron-phonon coupling constant α at room temperature for 1258 materials from the Liège dataset [14]. Materials containing group 15, 16, or 17 elements are highlighted. Squares indicate holes, while circles indicate electrons. The left plot shows mobility results using a single effective phonon mode based on our effective mode scheme in Eq. (3.7), while the right plot accounts for all phonon branches in the material. The red vertical line marks $\alpha = 6$, indicating a critical transition between weak and strong coupling regimes.

magnitude from 10^6 to less than $10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Polarons are highly mobile below $\alpha = 1$, reflecting weak electron-phonon interactions. The mobility drops rapidly beyond the critical point $\alpha = 6$, where polarons become highly localised due to strong coupling. Accounting for multiple phonon branches (right panel) results in a different distribution of mobility values, suggesting additional scattering mechanisms.

Fig. 6.11 shows the polaron mobility against α (x -axis) and band mass m_b (colour axis) in the top panels, and swaps the α and m_b axes in the bottom panels. Only a single effective phonon mode is used in the left panels, while all phonon branches are included in the right panels. As seen previously, the mobility decreases with increasing α , especially beyond $\alpha = 6$. A key observation in the bottom panels is the inverse relationship between mobility and band mass, with larger band masses associated with lower mobility. However, some materials show unrealistically large band masses, exceeding $5m_e$, which may suggest numerical artefacts or an overestimation in the perturbative model used to generate the data for these particular materials.

Much of the observed variation in mobility, especially between the single effective mode and explicit multimode mobilities, is due to the diverse range of phonon mode frequencies and the number of phonon bands across these materials.

Interestingly, some materials show unusually large mobilities despite being in the strong coupling regime. For some, due to their large effective masses, we can rule them out as unphysical. However, some materials remain with reasonable polaron masses. This phenomenon was noted by Ōsaka in 1961 [32], who explained that when the coupling becomes very strong, the phonon's wavelength contributing to polaron scattering decreases

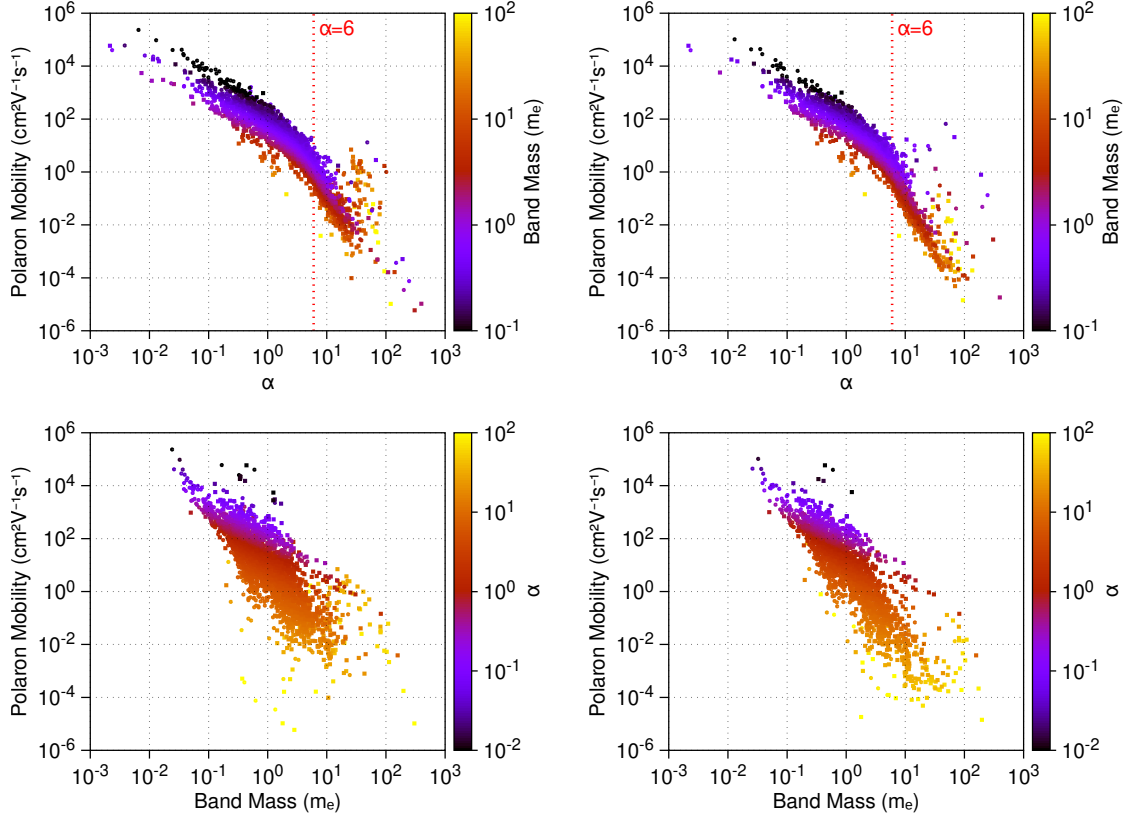


Figure 6.11: Polaron mobility at room temperature as a function of the electron-phonon coupling constant α and effective band mass m_e for 1258 materials from the Liège dataset [14]. The top panels show the α dependence on the x -axis and the m_b dependence on the colour axis. The bottom panels swaps these axes. The left column uses a single effective phonon mode from Eq. (3.7), while the right column accounts for all phonon branches explicitly. A critical point at $\alpha = 6$ (red dashed line) marks the transition to the strong coupling regime, where mobility decreases sharply, especially for materials with larger band masses.

more steeply than the polaron's localisation length. As a result, the polaron becomes less sensitive to phonon scattering, leading to an increase in mobility. This occurs because the effective wavelength of the phonons, proportional to $1/\alpha^2$, decreases faster than the localisation length of the polaron, proportional to $1/\alpha$. While this explanation assumes that the polaron mobility is influenced by scattering due to the phonon cloud surrounding the polaron, Ōsaka also pointed out that the scattering of the electronic part of the polaron primarily determines the mobility tied to the electronic current. Therefore, some uncertainty remains regarding the exact behaviour of the mobility at high α , suggesting the need for further investigation.

In Tables 6.8 and 6.9, I identify materials with polaron mobility $\mu > 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ whilst also having a polaron effective mass $M \leq 5m_e$ and strong electron-phonon coupling $\alpha > 6$.

MP ID	Formula	α	m_0 (m_e)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
mp-12885	BaAl ₂ Sb ₂ O ₇	6.435	1.273	1.656
mp-12992	BaTiO ₃	6.418	0.7447	8.321
mp-27369	RbGeCl ₃	6.708	1.066	1.919
mp-27385	KTiCl ₄	6.456	0.6291	4.044
mp-28243	RbLiCl ₂	8.732	0.4329	4.115
mp-30056	CsCaBr ₃	6.203	0.3228	10.60
mp-4047	Cs ₂ SiF ₆	6.730	0.5018	3.223
mp-5280	In ₂ Ge ₂ O ₇	25.82	0.2371	7.106
mp-552663	LiScAs ₂ O ₇	14.37	0.5889	10.08
mp-569149	K ₂ TeCl ₆	7.298	0.5263	3.895
mp-643243	Cs ₂ H ₆ Pt	7.000	1.102	1.937
mp-6929	Ca ₂ As ₂ O ₇	24.33	0.5232	9.603
mp-7017	NaNbN ₂	14.31	0.6609	6.631
mp-7232	Cs ₂ HgO ₂	6.782	0.9362	1.851
mp-7467	RbCuO ₂	6.093	1.989	1.027
mp-754212	BaSr ₂ I ₆	10.19	0.6502	4.064
mp-754596	RbGaO ₂	7.142	0.3114	5.451
mp-7684	Tl ₃ AsSe ₃	48.47	0.2159	66.16
mp-989547	Rb ₂ NaInCl ₆	7.180	0.4171	4.533
mp-998198	RbCaBr ₃	8.944	0.3537	4.881
mp-998297	CsSrBr ₃	9.428	0.3563	4.774

Table 6.8: List of materials from the Materials Project [12] and Liège [23] databases, for which the *conduction*-band polaron mobility exceeds $\mu > 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the electron-phonon coupling is strong $\alpha > 6$ and the renormalised polaron mass is $M < 5 m_e$.

MP ID	Formula	α	m_0 (m_e)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
mp-12992	BaTiO ₃	9.076	1.476	1.910
mp-13548	Cs ₂ Pt	6.536	2.223	1.648
mp-23017	CsCu ₂ Br ₃	12.85	1.695	1.143
mp-23405	Cs ₂ TeBr ₆	6.586	1.717	1.680
mp-29751	CsMgI ₃	7.271	0.8719	3.237
mp-540703	Cs ₂ S	6.415	1.675	1.082
mp-541037	CsCuO	7.597	1.341	1.269
mp-570324	Rb ₂ TeBr ₆	6.983	1.693	1.438
mp-573763	Cs ₂ Te	6.076	1.206	2.891
mp-5986	BaTiO ₃	6.829	1.476	2.522
mp-7017	NaNbN ₂	10.48	0.4465	16.92
mp-7684	Tl ₃ AsSe ₃	67.58	0.4276	20.88
mp-9794	Rb ₂ GeSe ₃	6.823	1.600	1.742
mp-996944	Cs ₂ TlInBr ₆	9.173	0.7671	2.258
mp-998599	KCaBr ₃	6.240	1.176	1.535

Table 6.9: List of materials from the Materials Project [12] and Liège [23] databases, for which the *valence*-band polaron mobility exceeds $\mu > 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the electron-phonon coupling is strong $\alpha > 6$ and the renormalised polaron mass is $M < 5 m_e$.

CHAPTER 7

CONCLUSION & OUTLOOK

In this thesis, I have extended the theoretical framework of polaron physics by developing and generalising the Feynman variational path integral method to more accurately model real semiconductors. Building upon Feynman’s pioneering work on the variational path integral approximation (FVA) [2], the research presented here has systematically addressed several key limitations by enhancing the theoretical structure to include multiple phonon modes, phonon dispersions, and anisotropic electronic band structures. These advances improve the understanding of polaron formation and transport, contributing practical computational tools capable of predicting polaronic properties in a wide range of technologically significant materials, including semiconductors and organic crystals.

A key practical outcome of this research is the co-development of the `PolaronMobility.jl` computational package, implemented in the Julia programming language. This package encapsulates the advanced path integral techniques developed throughout this thesis and facilitates high-throughput computational screening of materials for their polaronic properties. The utility of the computational framework was demonstrated through detailed case studies on materials such as methylammonium lead halide perovskites and rubrene organic crystals. These case studies revealed the importance of accounting for material-specific characteristics, such as multiple phonon branches, phonon mode dispersion and effective mass anisotropy, in predicting polaronic behaviour. Furthermore, these studies illustrate how the path integral approach can provide insights into material performance, particularly for optoelectronic applications like photovoltaic cells.

7.0.1 Improving the Model Action

One principal contribution is generalising the FVA model action to incorporate multiple phonon modes. This development is significant, as many real materials possess multiple

longitudinal optical (LO) phonon branches, rendering the standard single-mode Fröhlich model inadequate for capturing the full spectrum of electron-phonon interactions.

Additionally, I derived the path integral corresponding to the Holstein model and identified the challenges associated with applying Feynman’s variational method in this context. These challenges arise from the non-quadratic nature of the electron kinetic action and the constrained electronic paths characteristic of lattice models. I presented a series of approximations that maintain the lattice description of the phonons while transforming the problem into one that is tractable using a parabolic-band Hamiltonian. This allowed me to apply the variational method successfully, and I subsequently derived the polaronic properties of the organic semiconductor rubrene, a material of particular interest. My analysis yielded key properties such as the polaron binding energy, size, effective mass, and dynamical properties, including charge-carrier mobility and complex conductivity. A comparison of these results with those obtained from the original Fröhlich large-polaron model demonstrated that the new variational Holstein model produces more realistic predictions for rubrene, especially in the case of room-temperature mobility, as evidenced in Tables 6.6 and 6.7.

The extended formalism introduced in this thesis advances the model action further by using coherent-state path integrals (CSPI) and techniques from quantum field theory, enabling the treatment of a more comprehensive range of Hamiltonians, such as the full (without making a parabolic-band approximation) Holstein and Peierls Hamiltonian for small polarons. These improved model actions further enhance the accuracy of polaron transport models across weak, intermediate, and strong electron-phonon coupling regimes, offering a significant improvement in predicting material-specific polaron properties.

7.0.2 Improving the Trial Action and Variational Principle

A second core advance presented in this thesis is improving the trial action within the variational framework. While innovative, Feynman’s original spring-mass harmonic trial model was limited in its capacity to model real materials with more complex phonon spectra. By introducing a more flexible trial action in which the electron is coupled to multiple fictitious particles, we systematically improved the variational approximation of critical polaronic properties such as self-energy, effective mass, and charge-carrier mobility. Rigorous comparisons with state-of-the-art Diagrammatic Monte Carlo (DiagMC) simulations validate the accuracy of this approach, particularly in predicting the temperature-dependent mobility at varying coupling strengths. Combined with higher-order cumulant corrections, this generalised trial model may allow for a more nuanced description of electron-phonon coupling, thereby providing better approximations for polarons’ static and dynamic properties.

7.0.3 Improved Calculation of Polaron Response Functions

One fascinating insight from this research (discussed in section 5.7.1) is the connection I identified between the optimal self-energy (or, similarly, the spectral function) derived from the Feynman variational method and the memory function used in FHIP theory to describe dynamical properties such as complex conductivity and charge-carrier mobility. This connection can be understood via a Wick rotation since the memory function is analytic across a semi-infinite strip in the complex plane. Furthermore, comparisons between the free energy inequality derived in this work and the expression for the Luttinger-Ward function suggest that the memory and spectral functions are analogous to the non-local one-particle self-energy functions in real or imaginary time, respectively. This interpretation positions the Feynman variational method as a potential approximation to the Luttinger-Ward-like functional, in which one variationally or self-consistently optimises the trial self-energy or quasi-particle Green function.

This analogy is particularly compelling when considering the possibility of generalising the Feynman variational method to many-body Hamiltonians or grand canonical systems with a variable number of particles. By leveraging many-body Green function techniques, extending this method to study systems with more complex interactions may be possible. In this context, I speculate that the Feynman variational method may be seen as a variational approximation analogous to how exchange-correlation functionals are handled in Density Functional Theory (DFT), where one self-consistently solves for the optimal electron density to minimise the ground-state energy, since the Luttinger-Ward (or similarly the Kadanoff-Baym) theorem generalises DFT from density functions to many-body Green functions.

A logical next step would be to implement numerically the variational principle for coherent-state path integrals. Such an extension could move beyond the parabolic-band approximation, thereby allowing the treatment of more complex band structures and addressing discrepancies, such as those observed between the predicted polaron binding energy at higher coupling in the parabolic Holstein variational model and results from Diagrammatic Monte Carlo methods.

7.0.4 Application to Real Semiconductors

This thesis highlights the high-throughput analysis of 1,258 materials of the Materials Project [13] and Liege [14] databases. Fundamental polaronic properties—including the zero-point renormalisation energy (ZPR), effective mass, and room-temperature mobility—were systematically calculated using the extended path integral formalism. This study managed to identify some materials with significant polaron mobility for potential use in

devices. This offers a valuable resource for the computational discovery and design of materials optimised for high mobility and low charge trapping.

7.0.5 Summary and Perspective

The ultimate vision of my PhD was to develop a highly accurate, potentially *ab initio*, variational method capable of predicting real, complex materials' thermodynamic and dynamical properties. This approach could then be applied across broad classes of materials, identifying trends and guiding materials design and discovery. Compared to other methods, such as Monte Carlo approaches (e.g., Path Integral or Diagrammatic Monte Carlo) or self-consistent methods (e.g., self-consistent GW theory or Dynamical Mean-Field Theory), the variational path integral method offers significant advantages: the efficiency and well-defined variational bound make it an attractive option for studying various quantum systems. Unlike Monte Carlo methods, it provides controlled errors and is computationally tractable due to the convex nature of the path integrand, allowing for optimised solutions.

However, it is important to acknowledge certain limitations of the variational method. My multiple fictitious particle trial action analysis demonstrated that the system's higher frequency dynamics can be susceptible to the derived ground-state properties. This issue, also investigated by Sels [77] and Thornber [80], stems from the limited physics captured by the trial system, which remains quadratic in its variables. A quadratic action typically corresponds to a non-interacting system, limiting its ability to represent interacting particles accurately. A clearer understanding of which diagrams are retained in the Feynman variational method—likely akin to those kept in cumulant Green function methods—could improve the method's accuracy. Ultimately, adding higher-order cumulant corrections to the Feynman-Jensen inequality would further refine this approximation, incorporating additional infinite sets of diagrams and improving the method's predictive power, albeit at the cost of increased computational complexity and the loss of the variational bound.

An exciting avenue for overcoming these challenges lies in integrating machine learning with the variational method. The Feynman-Jensen inequality can be interpreted as mapping an intractable probability distribution onto a simpler Gaussian distribution in an infinite-dimensional function space—a process that resembles variational inference in machine learning. By employing normalising flows or diffusion methods, it may be possible to minimise the Kullback-Leibler divergence between the trial model's likelihood and the true distribution, offering a new pathway for improving the method. Using deep neural networks to solve for the optimal trial self-energy function would circumvent the need for self-consistently solving complex functional equations. While the practical application of

this idea remains speculative at this stage, the potential for combining machine learning and path integrals presents a compelling direction for future research.

In conclusion, this work has extended the scope of the Feynman variational path integral method, enabling its application to more realistic materials and providing a more nuanced understanding of polaronic systems. This dissertation lays the groundwork for future studies of organic semiconductors and other technologically significant materials by deriving a variational parabolic-band Holstein model and its successful application to rubrene. The theoretical and computational tools developed herein provide an efficient and flexible framework for predicting polaronic properties and open the door to further innovations in theory and application, including nonequilibrium dynamics, machine learning-enhanced methods, and studying many-body quantum systems.

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APPENDIX A

THE PATH INTEGRAL FORMULATION OF QUANTUM MECHANICS

The path integral formulation of quantum mechanics, introduced by Richard Feynman [1], offers a versatile framework for understanding quantum physics. Unlike the traditional operator-based approach, which uses wavefunctions and operators to describe quantum states and their evolution, the path integral formulation conceptualises quantum mechanics as a sum of all possible trajectories a particle can take between two space-time points. Each path contributes an amplitude weighted by the exponential of the action associated with that path, thereby providing a direct link between quantum and classical mechanics.

In this appendix, we derive the path integral formulation and demonstrate its application to several exactly solvable systems: the free particle, the harmonic oscillator, and the forced harmonic oscillator.

Derivation of the Path Integral Formulation

We first need to derive the propagator, which describes the probability amplitude for a particle to transition from one state to another over a specified time interval.

Propagator and Transition Amplitude

The propagator $K(x_f, t_f; x_i, t_i)$ is defined as the amplitude for a particle to propagate from position x_i at time t_i to position x_f at time t_f . Mathematically, it is expressed as:

$$K(x_f, t_f; x_i, t_i) = \langle x_f | e^{-iH(t_f-t_i)/\hbar} | x_i \rangle, \quad (\text{A.1})$$

where H is the Hamiltonian operator of the system, and $|x_i\rangle$ and $|x_f\rangle$ are position eigenstates corresponding to positions x_i and x_f , respectively. The propagator serves as the kernel of the evolution operator in the position basis, enabling the calculation of the wavefunction at any later time given its initial state.

Time-Slicing and Path Integration

To derive the path integral representation of the propagator, we employ the *time-slicing* method [1]. This involves partitioning the time interval $T = t_f - t_i$ into N infinitesimal segments of duration $\epsilon = T/N$. We insert a complete set of position eigenstates between each time slice, effectively decomposing the propagator into a product of short-time propagators.

Starting with the expression for the propagator:

$$K(x_f, t_f; x_i, t_i) = \langle x_f | e^{-iHT/\hbar} | x_i \rangle, \quad (\text{A.2})$$

we insert $N - 1$ complete sets of position eigenstates:

$$K(x_f, t_f; x_i, t_i) = \int \prod_{j=1}^{N-1} dx_j \prod_{j=1}^N \langle x_{j+1} | e^{-iH\epsilon/\hbar} | x_j \rangle, \quad (\text{A.3})$$

where $x_0 = x_i$ and $x_N = x_f$.

Assuming the Hamiltonian H is of the form $H = \frac{p^2}{2m} + V(x)$, and employing the *Trotter product formula* [84], we approximate each short-time propagator $\langle x_{j+1} | e^{-iH\epsilon/\hbar} | x_j \rangle$ as:

$$\langle x_{j+1} | e^{-iH\epsilon/\hbar} | x_j \rangle \approx \left(\frac{m}{2\pi i \hbar \epsilon} \right)^{1/2} \exp \left[\frac{i\epsilon}{\hbar} \left(\frac{m(x_{j+1} - x_j)^2}{2\epsilon^2} - V \left(\frac{x_{j+1} + x_j}{2} \right) \right) \right]. \quad (\text{A.4})$$

Taking the limit $N \rightarrow \infty$ (and hence $\epsilon \rightarrow 0$), the product of these short-time propagators becomes an integral over all possible intermediate positions x_j , leading to the *path integral* expression for the propagator:

$$K(x_f, t_f; x_i, t_i) = \int Dx(t) \exp \left(\frac{i}{\hbar} S[x(t)] \right). \quad (\text{A.5})$$

Here, $Dx(t)$ denotes the functional measure encompassing all possible paths $x(t)$ that satisfy the boundary conditions $x(t_i) = x_i$ and $x(t_f) = x_f$, and $S[x(t)]$ is the action defined by:

$$S[x(t)] = \int_{t_i}^{t_f} dt \left(\frac{1}{2} m [\dot{x}(t)]^2 - V(x(t)) \right). \quad (\text{A.6})$$

Action and Classical Paths

Within the path integral formulation, each path $x(t)$ contributes an amplitude $e^{iS[x(t)]/\hbar}$ to the propagator. Notably, in the classical limit where $\hbar \rightarrow 0$, the contributions from paths that deviate significantly from the classical trajectory interfere destructively, leaving the classical path $x_{\text{cl}}(t)$ — the path that extremises the action — as the dominant contributor.

To systematically evaluate the path integral, especially for actions that are quadratic in $x(t)$, we decompose the path $x(t)$ into the classical path $x_{\text{cl}}(t)$ and a fluctuation $\eta(t)$ around it:

$$x(t) = x_{\text{cl}}(t) + \eta(t), \quad (\text{A.7})$$

where $\eta(t_i) = \eta(t_f) = 0$. Substituting this decomposition into the action allows us to separate the classical contribution from the quantum fluctuations, simplifying evaluating the path integral.

Application to Specific Systems

With the general framework established, we now apply the path integral formulation to various systems, demonstrating the process of determining classical paths and evaluating the corresponding path integrals.

Free Particle

Consider a free particle for which the potential $V(x) = 0$. The action simplifies to:

$$S[x(t)] = \frac{m}{2} \int_0^T dt [\dot{x}(t)]^2, \quad (\text{A.8})$$

where $T = t_f - t_i$.

Determining the Classical Path

The classical path $x_{\text{cl}}(t)$ extremises the action. For the free particle, the Euler-Lagrange equation derived from the action is:

$$\frac{\delta S}{\delta x(t)} = m\ddot{x}_{\text{cl}}(t) = 0. \quad (\text{A.9})$$

Integrating twice, we obtain:

$$x_{\text{cl}}(t) = x_i + \frac{x_f - x_i}{T}(t - t_i). \quad (\text{A.10})$$

This linear trajectory corresponds to a constant velocity motion from x_i at t_i to x_f at t_f .

Evaluating the Path Integral

Expressing the path $x(t)$ as $x(t) = x_{\text{cl}}(t) + \eta(t)$, with $\eta(t_i) = \eta(t_f) = 0$, the action becomes:

$$S[x(t)] = S[x_{\text{cl}}] + \frac{m}{2} \int_0^T dt [\dot{\eta}(t)]^2. \quad (\text{A.11})$$

Since the fluctuations $\eta(t)$ do not alter the classical path, the path integral factorises into:

$$K(x_f, T; x_i, 0) = e^{\frac{i}{\hbar} S[x_{\text{cl}}]} \int D\eta(t) e^{\frac{i}{\hbar} \frac{m}{2} \int_0^T dt [\dot{\eta}(t)]^2}. \quad (\text{A.12})$$

The integral over $\eta(t)$ is a Gaussian functional integral, which for the free particle evaluates to:

$$\int D\eta(t) e^{\frac{i}{\hbar} \frac{m}{2} \int_0^T dt [\dot{\eta}(t)]^2} = \left(\frac{m}{2\pi i \hbar T} \right)^{1/2}. \quad (\text{A.13})$$

Resulting Propagator

Substituting the classical action $S[x_{\text{cl}}] = \frac{m(x_f - x_i)^2}{2T}$ into the expression for the propagator, we obtain:

$$K(x_f, T; x_i, 0) = \left(\frac{m}{2\pi i \hbar T} \right)^{1/2} \exp \left[\frac{im(x_f - x_i)^2}{2\hbar T} \right]. \quad (\text{A.14})$$

This result is consistent with the well-known propagator for a free particle derived via operator methods.

Harmonic Oscillator

Next, we consider the harmonic oscillator with the potential,

$$V(x(t)) = \frac{1}{2} m \omega^2 [x(t)]^2, \quad (\text{A.15})$$

where ω is the angular frequency.

Determining the Classical Path

The Euler-Lagrange equation for the harmonic oscillator is:

$$\frac{\delta S}{\delta x(t)} = m \ddot{x}_{\text{cl}}(t) + m \omega^2 x_{\text{cl}}(t) = 0. \quad (\text{A.16})$$

The general solution to this homogeneous differential equation is:

$$x_{\text{cl}}(t) = A \cos(\omega t) + B \sin(\omega t). \quad (\text{A.17})$$

Applying the boundary conditions $x_{\text{cl}}(0) = x_i$ and $x_{\text{cl}}(T) = x_f$, we determine the constants A and B :

$$x_{\text{cl}}(0) = A = x_i \quad (\text{A.18})$$

$$x_{\text{cl}}(T) = x_i \cos(\omega T) + B \sin(\omega T) = x_f \quad \Rightarrow \quad B = \frac{x_f - x_i \cos(\omega T)}{\sin(\omega T)}. \quad (\text{A.19})$$

Thus, the classical path is:

$$x_{\text{cl}}(t) = x_i \cos(\omega t) + \frac{x_f - x_i \cos(\omega T)}{\sin(\omega T)} \sin(\omega t). \quad (\text{A.20})$$

This trajectory represents the oscillator's motion between the two boundary points over the time interval T .

Evaluating the Path Integral

Expressing the path as $x(t) = x_{\text{cl}}(t) + \eta(t)$, where $\eta(t)$ satisfies $\eta(0) = \eta(T) = 0$, the action decomposes into:

$$S[x(t)] = S[x_{\text{cl}}] + \frac{m}{2} \int_0^T dt [\dot{\eta}(t)]^2 - \frac{1}{2} m \omega^2 \int_0^T dt [\eta(t)]^2. \quad (\text{A.21})$$

The path integral thus becomes:

$$K(x_f, T; x_i, 0) = e^{\frac{i}{\hbar} S[x_{\text{cl}}]} \int D\eta(t) e^{\frac{i}{\hbar} \left(\frac{m}{2} \int_0^T dt [\dot{\eta}(t)]^2 - \frac{1}{2} m \omega^2 \int_0^T dt [\eta(t)]^2 \right)} \quad (\text{A.22})$$

The integral over $\eta(t)$ is again Gaussian, now with a quadratic form that includes kinetic and potential terms. Evaluating this Gaussian functional integral yields:

$$\int D\eta(t) e^{\frac{i}{\hbar} \left(\frac{m}{2} \int_0^T dt \dot{\eta}^2(t) - \frac{1}{2} m \omega^2 \int_0^T dt \eta^2(t) \right)} = \left(\frac{m\omega}{2\pi i \hbar \sin(\omega T)} \right)^{1/2} \quad (\text{A.23})$$

Propagator for the Harmonic Oscillator

Substituting the classical action and the result of the Gaussian integral into the expression for the propagator, we obtain:

$$K(x_f, T; x_i, 0) = \sqrt{\frac{m\omega}{2\pi i\hbar \sin(\omega T)}} \exp \left[\frac{im\omega}{2\hbar \sin(\omega T)} \left((x_i^2 + x_f^2) \cos(\omega T) - 2x_i x_f \right) \right]. \quad (\text{A.24})$$

This exact propagator describes the quantum dynamics of the harmonic oscillator and reduces to the free particle propagator in the limit $\omega \rightarrow 0$.

Forced Harmonic Oscillator

Introducing an external time-dependent force $f(t)$ modifies the potential to include a linear term, resulting,

$$V(x(t)) = \frac{1}{2}m\omega^2[x(t)]^2 - f(t)x(t). \quad (\text{A.25})$$

The classical action is defined as,

$$S[x(t)] = \int_{t_i}^{t_f} dt \left(\frac{m}{2}[\dot{x}(t)]^2 - \frac{m\omega^2}{2}[x(t)]^2 + f(t)x(t) \right). \quad (\text{A.26})$$

The presence of the external force modifies the Euler-Lagrange equation for the classical path,

$$\frac{\delta S}{\delta x(t)} = m\ddot{x}_{cl}(t) + m\omega^2 x_{cl}(t) = f(t). \quad (\text{A.27})$$

We can use this equation of motion to simplify the action evaluated on the classical path. We begin by rewriting the kinetic term using integration by parts:

$$\begin{aligned} \int_{t_i}^{t_f} [\dot{x}(t)]^2 dt &= [x(t)\dot{x}(t)]_{t_i}^{t_f} - \int_{t_i}^{t_f} dt x(t)\ddot{x}(t) \\ &= [x_{cl}(t)\dot{x}_{cl}(t)]_{t_i}^{t_f} + \omega^2 \int_{t_i}^{t_f} dt [x_{cl}(t)]^2 - \frac{1}{m} \int_{t_i}^{t_f} f(t)x_{cl}(t) dt, \end{aligned} \quad (\text{A.28})$$

where in the second line we have substituted the classical equation of motion. Thus, by substituting this kinetic term, the action evaluated on the classical path is,

$$S[x_{cl}(t)] = \frac{m}{2} [x_{cl}(t)\dot{x}_{cl}(t)]_{t_i}^{t_f} + \frac{1}{2} \int_{t_i}^{t_f} dt f(t)x_{cl}(t). \quad (\text{A.29})$$

The Green function solution for the forced harmonic oscillator is,

$$x_{cl}(t) = A \sin(\omega[t - t_i]) + B \sin(\omega[t_f - t]) + \frac{1}{m\omega} \int_{t_i}^t f(t') \sin(\omega[t - t']) dt'. \quad (\text{A.30})$$

The velocity is then,

$$\dot{x}_{cl}(t) = \omega \left[A \cos(\omega[t - t_i]) - B \cos(\omega[t_f - t]) + \frac{1}{m\omega} \int_{t_i}^t f(t') \cos(\omega[t - t']) dt' \right]. \quad (\text{A.31})$$

Defining,

$$\begin{aligned} X_S &\equiv \frac{1}{m\omega} \int_{t_i}^{t_f} dt' f(t') \sin(\omega[t_f - t']), \\ X_C &\equiv \frac{1}{m\omega} \int_{t_i}^{t_f} dt' f(t') \cos(\omega[t_f - t']), \end{aligned} \quad (\text{A.32})$$

gives the initial and final values,

$$\begin{aligned} x_i &= B \sin \omega T, & x_f &= A \sin(\omega T) + X_S, \\ \dot{x}_{cl}(t_i) &= \omega[A - B \cos(\omega T)], & \dot{x}_{cl}(t_f) &= \omega[A \cos(\omega T) - B + X_C]. \end{aligned} \quad (\text{A.33})$$

Solving for A and B :

$$B = \frac{x_i}{\sin(\omega T)}, \quad A = \frac{x_f - X_S}{\sin(\omega T)}. \quad (\text{A.34})$$

From the above,

$$\begin{aligned} [x_{cl}(t)\dot{x}_{cl}(t)]_{t_i}^{t_f} &= x_f \omega[A \cos(\omega T) - B + X_C] - x_i \omega[A - B \cos(\omega T)] \\ &= \omega A(x_f \cos(\omega T) - x_i) + \omega B(-x_f + x_i \cos(\omega T)) + \omega x_f X_C \\ &= \frac{\omega}{\sin(\omega T)} \left[(x_f^2 + x_i^2) \cos \omega T - 2x_i x_f + x_f(X_C \sin(\omega T) - X_S \cos(\omega T)) + x_i X_S \right]. \end{aligned} \quad (\text{A.35})$$

Using the trigonometric identity $\sin(A - B) = \sin A \cos B - \cos A \sin B$, we find

$$X_C \sin(\omega T) - X_S \cos(\omega T) = \frac{1}{m\omega} \int_{t_i}^{t_f} f(t') \sin(\omega[t' - t_i]) dt'. \quad (\text{A.36})$$

Thus, for the kinetic part of the action we have,

$$\begin{aligned} \frac{m}{2} [x_{cl}(t)\dot{x}_{cl}(t)]_{t_i}^{t_f} &= \frac{m\omega}{2 \sin(\omega T)} \left[(x_f^2 + x_i^2) \cos(\omega T) - 2x_i x_f \right. \\ &\quad + \frac{2x_f}{m\omega} \int_{t_i}^{t_f} f(t') \sin(\omega[t' - t_i]) dt' \\ &\quad \left. + \frac{2x_i}{m\omega} \int_{t_i}^{t_f} f(t') \sin(\omega[t_f - t']) dt' \right]. \end{aligned} \quad (\text{A.37})$$

For the potential part of the action we have,

$$\begin{aligned}
\frac{1}{2} \int_{t_i}^{t_f} dt f(t) x_{cl}(t) &= \frac{1}{2} \left[A \int_{t_i}^{t_f} dt f(t) \sin(\omega[t - t_i]) + B \int_{t_i}^{t_f} f(t) \sin(\omega[t_f - t]) \right. \\
&\quad \left. + \frac{1}{m\omega} \int_{t_i}^{t_f} dt \int_{t_i}^t dt' f(t) f(t') \sin(\omega[t - t']) \right] \\
&= \frac{1}{2 \sin(\omega T)} \left[x_f \int_{t_i}^{t_f} dt f(t) \sin(\omega[t - t_i]) + x_i \int_{t_i}^{t_f} f(t) \sin(\omega[t_f - t]) \right. \\
&\quad - \frac{1}{m\omega} \int_{t_i}^{t_f} dt \int_{t_i}^{t_f} dt' f(t) f(t') \sin(\omega[t_f - t]) \sin(\omega[t' - t_i]) \\
&\quad \left. + \frac{\sin(\omega T)}{m\omega} \int_{t_i}^{t_f} dt \int_{t_i}^t dt' f(t) f(t') \sin(\omega[t - t']) \right]
\end{aligned} \tag{A.38}$$

Bringing the kinetic and potential parts together, we arrive at the action evaluated on the classical path,

$$\begin{aligned}
S[x_{cl}(t)] &= \frac{m\omega}{2 \sin(\omega T)} \left[(x_f^2 + x_i^2) \cos(\omega T) - 2x_f x_i \right. \\
&\quad + \frac{2x_f}{m\omega} \int_{t_i}^{t_f} dt f(t) \sin \omega(t - t_i) \\
&\quad + \frac{2x_i}{m\omega} \int_{t_i}^{t_f} dt f(t) \sin \omega(t_f - t) \\
&\quad \left. - \frac{2}{m^2 \omega^2} \int_{t_i}^{t_f} dt \int_{t_i}^t dt' f(t) f(t') \sin(\omega[t_f - t]) \sin(\omega[t' - t_i]) \right].
\end{aligned} \tag{A.39}$$

Thus, since any terms linear in the fluctuations $\eta(t)$ disappear, we have the kernel for the forced harmonic oscillator,

$$\begin{aligned}
K(x_f, T; x_i, 0) &= \sqrt{\frac{m\omega}{2\pi i \hbar \sin(\omega T)}} \\
&\quad \times \exp \left\{ \frac{im\omega}{2\hbar \sin(\omega T)} \left[(x_f^2 + x_i^2) \cos(\omega T) - 2x_i x_f \right. \right. \\
&\quad + \frac{2x_f}{m\omega} \int_0^T f(t) \sin(\omega t) dt \\
&\quad + \frac{2x_i}{m\omega} \int_0^T f(t) \sin \omega(T - t) dt \\
&\quad \left. \left. - \frac{2}{m^2 \omega^2} \int_0^T dt \int_0^t dt' f(t) f(t') \sin(\omega[T - t]) \sin(\omega t') \right] \right\}.
\end{aligned} \tag{A.40}$$

APPENDIX B

FEYNMAN-VERNON INFLUENCE FUNCTIONALS

The influence functional is a central concept in studying open quantum systems, particularly in the Feynman-Vernon formalism [16]. When a quantum system interacts with an external environment, often called a “bath,” the system no longer evolves unitarily due to the influence of the environmental degrees of freedom. Instead, it becomes necessary to describe the reduced dynamics of the system by tracing out the environmental degrees of freedom. The influence functional encapsulates the environmental effects on the system and provides a powerful tool to analyse dissipation and decoherence phenomena within the path integral formulation of quantum mechanics.

In this appendix, we will first review the general derivation of the influence functional in the case of linear system-environment coupling. We will then extend this formalism to the case of non-linear coupling, where the interaction between the system and environment is mediated by a non-linear functional of the system’s coordinates. We will discuss the form of the bath kernel (or correlation function) and its role in system dynamics. Finally, we will present a detailed example where the system couples to a harmonic bath via an exponential interaction of the form $g[x] = M_k e^{ikx}$, with k representing the wavevector of the environmental modes and M_k the system-bath coupling element. This type of system-bath coupling arises in the polaron model [17].

Path Integral Formulation for the Combined System

Consider a quantum system S interacting with an environment (bath) E . The total Hamiltonian for the combined system is given by

$$\hat{H}_{\text{tot}} = \hat{H}_S + \hat{H}_E + \hat{H}_{\text{int}}, \quad (\text{B.1})$$

where $\hat{H}_S$ is the Hamiltonian of the system, $\hat{H}_E$ is the Hamiltonian of the environment, and $\hat{H}_{\text{int}}$ describes the interaction between the system and the environment. The environment is typically modelled as a collection of harmonic oscillators with masses m_α and frequencies ω_α , such that the environment Hamiltonian can be written as

$$\hat{H}_E = \sum_{\alpha} \left(\frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} m_{\alpha} \omega_{\alpha}^2 y_{\alpha}^2 \right), \quad (\text{B.2})$$

where p_{α} and y_{α} are the momentum and position operators for the α -th oscillator, respectively.

The interaction Hamiltonian $\hat{H}_{\text{int}}$ typically couples the system coordinate $x(t)$ to the environmental oscillators. In the simplest case of linear coupling, the interaction Hamiltonian is given by

$$\hat{H}_{\text{int}} = \sum_{\alpha} c_{\alpha} x(t) y_{\alpha}, \quad (\text{B.3})$$

where c_{α} is the coupling constant between the system and the α -th oscillator. This form of coupling implies that the system's coordinate $x(t)$ interacts linearly with the positions of the environmental oscillators $y_{\alpha}(t)$.

The full density operator for the combined system $\hat{\rho}_{\text{tot}}(t)$ is given by the Liouville-von-Neumann equation,

$$i\hbar \frac{d\hat{\rho}_{\text{tot}}(t)}{dt} = [\hat{H}_{\text{tot}}(t), \hat{\rho}_{\text{tot}}(t)], \quad (\text{B.4})$$

where the brackets denote a commutator.

For a time-independent Hamiltonian, $\hat{H}_{\text{tot}}$, the solution to the von Neumann equation is,

$$\hat{\rho}_{\text{tot}}(t) = e^{-i\hat{H}_{\text{tot}}t/\hbar} \hat{\rho}_{\text{tot}}(0) e^{i\hat{H}_{\text{tot}}t/\hbar}. \quad (\text{B.5})$$

More generally, the solution is

$$\hat{\rho}_{\text{tot}}(t) = \hat{U}_{\text{tot}}(t) \hat{\rho}_{\text{tot}}(0) \hat{U}_{\text{tot}}^{\dagger}(t), \quad (\text{B.6})$$

where $\hat{U}_{\text{tot}}(t)$ is the unitary wavefunction propagator over some time interval.

We can use a representation of the density operator in spatial coordinates of our combined system and environment,

$$\begin{aligned} \langle x_f, y_f | \hat{\rho}_{\text{tot}}(t) | y'_f, x'_f \rangle &= \int dx_i dx'_i dy_i dy'_i \langle x_f, y_f | \hat{U}_{\text{tot}}(t) | y_i, x_i \rangle \langle x_i, y_i | \hat{\rho}_{\text{tot}}(0) | y'_i, x'_i \rangle \\ &\times \langle x'_i, y'_i | \hat{U}_{\text{tot}}^{\dagger}(t) | y'_f, x'_f \rangle, \end{aligned} \quad (\text{B.7})$$

where x_i and y_i are the initial spatial coordinates for the system and environment at time $t = 0$, x_f and y_f are the initial spatial coordinates for the system and environment at time t , and $\hat{\rho}_{\text{tot}}(0)$ is the initial density operator at $t = 0$.

Initially, if we assume that the system and environment are decoupled so that the total density matrix can be written as a product of the system's and the environment's initial states, $\rho_{\text{tot}}(0) = \rho_S(0) \otimes \rho_E$, where $\rho_E = e^{-\beta \hat{H}_E}$. The time evolution of the total system is given by the unitary evolution operator $\hat{U}_{\text{tot}}(t)$, and the reduced density matrix of the system is obtained by tracing out the environmental degrees of freedom:

$$\hat{\rho}_S(t) = \text{Tr}_E \left(\hat{U}_{\text{tot}}(t) \hat{\rho}_{\text{tot}}(0) \hat{U}_{\text{tot}}^\dagger(t) \right). \quad (\text{B.8})$$

In the path integral formulation, the evolution of the total system is represented as a double path integral over the system and environment coordinates. Let $x(t)$ and $y(t)$ be the paths corresponding to the system and environment. A propagator matrix element for the full system can be written as a path integral,

$$\langle x_f, y_f | \hat{U}_{\text{tot}}(t) | x_i, y_i \rangle = \int_{x(0)=x_i}^{x(t)=x_f} Dx(s) \int_{y(0)=y_i}^{y(t)=y_f} Dy(s) e^{\frac{i}{\hbar} S_{\text{tot}}[x(s), y(s)]}, \quad (\text{B.9})$$

where $S_{\text{tot}}[x, y]$ is the total action of the system plus environment, given by

$$S_{\text{tot}}[x, y] = S_S[x] + S_E[y] + S_{\text{int}}[x, y]. \quad (\text{B.10})$$

Here, $S_S[x]$ is the action of the system, $S_E[y]$ is the action of the environment, and $S_{\text{int}}[x, y]$ describes the interaction between the system and environment.

To obtain the reduced dynamics of the system, we trace over the environmental degrees of freedom, which corresponds to integrating out the $y(t)$ paths. The reduced density matrix of the system becomes

$$\begin{aligned} \langle x_f | \hat{\rho}_{\text{tot}}(t) | x'_f \rangle &= \int dy_f dy'_f dx_i dx'_i dy_i dy'_i \langle x_f, y_f | \hat{U}_{\text{tot}}(t) | y_i, x_i \rangle \langle x_i, y_i | \hat{\rho}_{\text{tot}}(0) | y'_i, x'_i \rangle \\ &\quad \times \langle x'_i, y'_i | \hat{U}_{\text{tot}}^\dagger(t) | y'_f, x'_f \rangle \\ &= \int dy dx_i dx'_i dy_i dy'_i \int_{x_i}^{x_f} Dx \int_{y_i}^y Dy \int_{x'_i}^{x'_f} Dx' \int_{y'_i}^{y'(t)=y} Dy' \\ &\quad \times \exp \left\{ \frac{i}{\hbar} (S_{\text{tot}}[x, y] - S_{\text{tot}}[x', y']) \right\} \langle x_i, y_i | \hat{\rho}_{\text{tot}}(0) | y'_i, x'_i \rangle \\ &= \int dx_i dx'_i \langle x_i | \hat{\rho}_S(0) | x'_i \rangle \int_{x_i}^{x_f} Dx \int_{x'_i}^{x'_f} Dx' e^{\frac{i}{\hbar} (S[x] - S[x'])} \mathcal{F}[x, x']. \end{aligned} \quad (\text{B.11})$$

This procedure leads to the emergence of the influence functional, which encodes the effect of the environment on the system,

$$\mathcal{F}[x, x'] = \int dy dy_i dy'_i \langle y_i | \hat{\rho}_E | y'_i \rangle \int_{y_i}^y Dy \int_{y'_i}^{y'} Dy' e^{\frac{i}{\hbar}(S_E[y] + S_E[y'] + S_{\text{int}}[x, y] - S_{\text{int}}[x', y'])}. \quad (\text{B.12})$$

The influence functional describes how the environment influences the system through the interaction term. In general, $\mathcal{F}[x, x']$ is complex, with its real part describing dissipation and its imaginary part corresponding to decoherence.

Linear Coupling to the Bath

In many physically relevant situations, the influence functional formalism can lead to a closed-form expression for the system's reduced density matrix, particularly when the total system-environment interaction results in a Gaussian path integral in terms of the system's coordinate $x(t)$. These cases are particularly tractable because Gaussian integrals can be evaluated exactly, allowing us to obtain explicit expressions for the system's reduced dynamics.

In this section, we derive a closed-form influence functional for a system described by a quadratic action and linearly coupled to a harmonic bath. Specifically, we will assume that the system's dynamics are governed by the standard kinetic term $\frac{m}{2}\dot{x}^2(t)$ and a potential term $\frac{m\omega^2}{2}x^2(t)$, and that the system is linearly coupled to the bath of harmonic oscillators.

The Total Action for the System and Environment

We begin by considering the action for a system S interacting linearly with an environment E consisting a collection of harmonic oscillators with masses m_α , frequencies ω_α , and coordinates $y_\alpha(t')$. The action of the bath is

$$S_E[y] = \sum_{\alpha} \int_0^t dt' \left(\frac{m_{\alpha}}{2} \dot{y}_{\alpha}^2(t') - \frac{m_{\alpha}\omega_{\alpha}^2}{2} y_{\alpha}^2(t') \right). \quad (\text{B.13})$$

The system is linearly coupled to the environment through the interaction Hamiltonian

$$\hat{H}_{\text{int}} = \sum_{\alpha} c_{\alpha} x(t') y_{\alpha}(t'), \quad (\text{B.14})$$

where c_α are the coupling constants between the system and the α -th oscillator in the bath. The corresponding interaction action is given by

$$S_{\text{int}}[x, y] = \sum_{\alpha} \int_0^t dt' c_{\alpha} x(t') y_{\alpha}(t'). \quad (\text{B.15})$$

Thus, the total action for the system and environment is

$$S_{\text{tot}}[x, y] = S_S[x] + S_E[y] + S_{\text{int}}[x, y]. \quad (\text{B.16})$$

The Influence Functional

The effect of the environment on the system is encoded in the *influence functional*, which is obtained by integrating over the bath variables $y_{\alpha}(t')$. This integral is Gaussian in the bath variables $y_{\alpha}(t')$, allowing us to evaluate it exactly. The result is

$$\mathcal{F}[x, x'] = \exp \left(-\frac{1}{\hbar} \int_0^t dt' \int_0^t dt'' (x(t') - x'(t')) (K(t' - t'')x(t'') - K^*(t' - t'')x'(t'')) \right), \quad (\text{B.17})$$

where $K(t)$ is the *bath correlation function*, given by

$$K(t) = \sum_{\alpha} \frac{\hbar c_{\alpha}^2}{2m_{\alpha}\omega_{\alpha}^2} \left[\coth \left(\frac{\hbar\beta\omega_{\alpha}}{2} \right) \cos(\omega_{\alpha}t) - i \sin(\omega_{\alpha}t) \right]. \quad (\text{B.18})$$

This correlation function describes the environment's memory effects and governs how the system's evolution is influenced by its past interactions with the bath.

Nonlinear Coupling to the Bath

The above formulation assumes linear coupling between the system and the environment. However, many physical systems' coupling between the system and the environment is non-linear. This occurs when the interaction Hamiltonian is not a simple product of the system coordinate $x(t)$ and the environment coordinate $y_{\alpha}(t)$, but instead depends on a more complicated functional of the system's path.

Let us now consider the more general case where the interaction Hamiltonian takes the form

$$\hat{H}_{\text{int}} = \sum_{\alpha} g_{\alpha}[x(t)] y_{\alpha}, \quad (\text{B.19})$$

where $g_{\alpha}[x(t)]$ is an arbitrary functional of the system's path. This could represent, for example, higher-order terms in $x(t)$ or periodic functions of $x(t)$. The total action for the

system and bath is now

$$S_{\text{tot}}[x, y] = S_S[x] + \sum_{\alpha} \int_0^t dt' \left(\frac{m_{\alpha}}{2} \dot{y}_{\alpha}^2(t') - \frac{m_{\alpha} \omega_{\alpha}^2}{2} y_{\alpha}^2(t') \right) + \sum_{\alpha} \int_0^t dt' g_{\alpha}[x(t')] y_{\alpha}(t'). \quad (\text{B.20})$$

As before, the reduced density matrix for the system is obtained by tracing out the environmental degrees of freedom, which requires integrating over the $y_{\alpha}(t)$ paths. Since the environment consists of harmonic oscillators, the path integral over the y_{α} 's is still Gaussian, even with the non-linear coupling $g_{\alpha}[x(t)]$. Performing the Gaussian integral yields the influence functional,

$$\begin{aligned} \mathcal{F}[x, x'] = \exp & \left(-\frac{1}{\hbar} \sum_{\alpha} \int_0^t dt' \int_0^t dt'' (g_{\alpha}[x(t')] - g_{\alpha}[x'(t')]) \right. \\ & \left. \times (K_{\alpha}(t' - t'') g_{\alpha}^*[x(t'')] - K_{\alpha}^*(t' - t'') g_{\alpha}^*[x'(t'')]) \right), \end{aligned} \quad (\text{B.21})$$

where $K_{\alpha}(t)$ is,

$$K_{\alpha}(t) = \frac{\hbar}{2m_{\alpha}\omega_{\alpha}} \left(\coth\left(\frac{\hbar\beta\omega_{\alpha}}{2}\right) \cos(\omega_{\alpha}t) - i \sin(\omega_{\alpha}t) \right) \quad (\text{B.22})$$

This influence functional captures the nonlinear interaction between the system and the bath. In particular, the nonlinear functional $g[x(t)]$ introduces more complex dependencies on the system's path, resulting in nonlinear dissipation and decoherence effects.

Example: Exponential Coupling to a Harmonic Bath

A relevant example of non-linear coupling arises when the interaction is of the form $g[x] = M_k e^{ikx}$, as in the polaron model [17], where k is the wavevector of the bath modes and M_k is the system-bath coupling element. This form of coupling is encountered in systems where the environment consists of phonons or photons, and the system interacts with these modes via a periodic function of its position.

The interaction Hamiltonian for this case is given by

$$\hat{H}_{\text{int}} = \sum_k M_k e^{ikx(t)} y_k(t), \quad (\text{B.23})$$

where $y_k(t)$ represents the position of the k -th environmental mode. The total action is

$$S_{\text{tot}}[x, y] = S_S[x] + \sum_k \int_0^t dt' \left(\frac{m_k}{2} \dot{y}_k^2(t') - \frac{m_k \omega_k^2}{2} y_k^2(t') \right) + \sum_k \int_0^t dt' M_k e^{ikx(t')} y_k(t'). \quad (\text{B.24})$$

The influence functional of this system is

$$\begin{aligned} \mathcal{F}[x, x'] = \exp & \left(-\frac{1}{\hbar} \int_0^t dt' \int_0^t dt'' \sum_k |M_k|^2 \left(e^{ikx(t')} - e^{ikx'(t')} \right) \right. \\ & \left. \times \left(K_k(t' - t'') e^{-ikx(t'')} - K_k^*(t' - t'') e^{-ikx'(t'')} \right) \right), \end{aligned} \quad (\text{B.25})$$

where $K_k(t' - t'')$ is the environmental correlation function, which for a harmonic oscillator bath at zero temperature is given by

$$K_k(t' - t'') = \frac{\hbar}{2m_k \omega_k} \left[n_{\omega_k} e^{i\omega_k(t' - t'')} + (n_{\omega_k} + 1) e^{-i\omega_k(t' - t'')} \right], \quad (\text{B.26})$$

where $n_{\omega} = (1 + e^{\hbar\beta\omega})^{-1}$ is the Bose-Einstein distribution.

This influence functional describes the complex interaction between the system and a bath of harmonic oscillators, with a non-linear coupling that depends on the exponential of the system's position. Due to the environmental correlation function's non-locality in time, the non-linear dependence on the system's path leads to more complex dissipation, decoherence, and non-Markovian memory effects. This is the type of influence functional encountered in the polaron problem [17].

Bath Correlation Function and Spectral Density

The kernel function $K(t - t')$ encodes the bath's memory effects, describing how the system's past interactions with the environment influence its current state. It can be split into real and imaginary components:

$$K(t - t') = K_R(t - t') + iK_I(t - t'). \quad (\text{B.27})$$

The real part $K_R(t - t')$ describes noise (fluctuations introduced by the bath), while the imaginary part $K_I(t - t')$ describes dissipative effects (energy loss to the bath).

The kernel function is directly related to the bath spectral function $J(\omega)$, characterising the bath modes and their coupling to the system. The bath spectral function is defined as:

$$J(\omega) = \sum_i \frac{c_i^2}{2m_i\omega_i} \delta(\omega - \omega_i). \quad (\text{B.28})$$

The imaginary part of the kernel function $K_I(t - t')$ can be expressed as:

$$K_I(t - t') = -\frac{1}{\pi} \int_0^\infty d\omega J(\omega) \sin(\omega(t - t')). \quad (\text{B.29})$$

This describes the dissipative memory effects of the bath, with $K_I(t - t')$ capturing how the system's past influences its present due to the bath's dynamics. The real part of the kernel function $K_R(t - t')$ is given by:

$$K_R(t - t') = \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \cos(\omega(t - t')) \coth\left(\frac{\beta\omega}{2}\right), \quad (\text{B.30})$$

where $\beta = \frac{1}{k_B T}$ is the inverse temperature. The term $\coth\left(\frac{\beta\omega}{2}\right)$ ensures that both quantum fluctuations (at zero temperature) and thermal fluctuations (at finite temperature) are included in the description of the noise. For non-linear system-bath coupling, higher-order terms lead to non-Gaussian noise in the system's dynamics, which can manifest as skewed fluctuation distributions or enhanced correlations between system variables.

Memory Effects and Markovian vs Non-Markovian Dynamics

The nature of the memory effects introduced by the bath depends on the form of the kernel function $K(t - t')$. In Markovian dynamics, the system's future evolution depends only on its current state, and the bath has no memory of past interactions. This corresponds to a local kernel function, where $K(t - t')$ is sharply peaked around $t = t'$, leading to local dissipation and white noise (noise without temporal correlations).

In contrast, non-Markovian dynamics arise when the bath retains a long memory of its interactions with the system. This corresponds to a kernel function with significant support over a broad time range, meaning that the system's past state influences its future evolution more complexly. Non-Markovian dynamics can lead to coloured noise (temporally correlated noise) and non-local dissipation.

For non-linear couplings, non-Markovian memory effects are often more pronounced. The feedback from the environment, coupled with non-linearity in the interaction, can lead to strong correlations between the system's state at different times. Such effects are particularly relevant in systems with structured environments, such as in low-temperature baths or environments where the bath modes are strongly correlated.

The Fluctuation-Dissipation Theorem

The fluctuation-dissipation theorem establishes a fundamental connection between energy dissipation into the bath and the fluctuations (or noise) the bath induces in the system. This relationship holds for systems in thermal equilibrium and provides a way to connect the system's response to external perturbations with the thermal noise it experiences.

For linear couplings, the fluctuation-dissipation theorem can be written as:

$$\text{Im}G^R(\omega) = \frac{\pi}{2}J(\omega) \coth\left(\frac{\beta\omega}{2}\right), \quad (\text{B.31})$$

where $G^R(\omega)$ is the retarded Green function of the system, and $J(\omega)$ is the bath spectral function. This relation shows that the imaginary part of the Green function, which describes the noise introduced by the bath, is related to the bath's dissipation through the spectral function. The $\coth\left(\frac{\beta\omega}{2}\right)$ factor ensures that both quantum and thermal fluctuations are accounted for.

For non-linear couplings, the fluctuation-dissipation theorem becomes more complex. The non-linear interaction alters the relationship between dissipation and fluctuations, leading to non-Gaussian noise and more intricate dissipation behaviour. The theorem may still apply in such cases, but higher-order corrections to the noise and dissipation terms must be considered.

APPENDIX C

COHERENT STATES

The coherent state path integral is a fundamental tool in quantum mechanics and quantum field theory. It offers an alternative formulation that is particularly advantageous for systems with bosonic or fermionic degrees of freedom. This appendix provides an in-depth description of the coherent state path integral, starting with the foundational aspects of coherent states, demonstrating some of their properties, and providing explicit derivations and applications to various quantum systems.

Coherent States

Coherent states are specific quantum states closely resembling classical states, possessing properties that bridge the quantum and classical regimes. In bosonic systems, particularly the harmonic oscillator, coherent states are defined as eigenstates of the annihilation operator. Consider the harmonic oscillator with annihilation ($\hat{a}$) and creation ($\hat{a}^\dagger$) operators satisfying the commutation relation $[\hat{a}, \hat{a}^\dagger] = 1$. A bosonic coherent state $|z\rangle$ is defined by the eigenvalue equation:

$$\hat{a}|z\rangle = z|z\rangle, \quad (\text{C.1})$$

where z is a complex number. These states can be expressed in the Fock (number) basis as:

$$|z\rangle = e^{-|z|^2/2} \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}} |n\rangle. \quad (\text{C.2})$$

Coherent states exhibit several notable properties. Firstly, they are eigenstates of the annihilation operator, which uniquely characterises them within the Hilbert space of the harmonic oscillator. Secondly, they minimise the Heisenberg uncertainty relation, achieving the lowest possible uncertainty product $\Delta x \Delta p = \frac{\hbar}{2}$, thus embodying the “most classical” quantum states. Furthermore, coherent states can be generated by applying the

displacement operator $\hat{D}(z) = e^{z\hat{a}^\dagger - \bar{z}\hat{a}}$ to the vacuum state $|0\rangle$, yielding $|z\rangle = \hat{D}(z)|0\rangle$. Under time evolution governed by the harmonic oscillator Hamiltonian $\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2})$, coherent states evolve in time while retaining their coherent nature:

$$|z(t)\rangle = e^{-i\hat{H}t/\hbar}|z\rangle = |ze^{-i\omega t}\rangle. \quad (\text{C.3})$$

Importantly, coherent states form an overcomplete basis for the Hilbert space, meaning they span the space but are not linearly independent. This overcompleteness is harnessed in the path integral formulation by resolving the identity. For bosonic coherent states, the resolution of identity is given by:

$$\int \frac{d^2z}{\pi} e^{-\bar{z}z} |z\rangle\langle z| = \hat{I}, \quad (\text{C.4})$$

where $d^2z = d(\text{Re } z) d(\text{Im } z)$, and $\hat{I}$ is the identity operator. The overlap between two coherent states $|z\rangle$ and $|z'\rangle$ is given by:

$$\langle z'|z\rangle = e^{\bar{z}'z}. \quad (\text{C.5})$$

This non-orthogonality is a direct consequence of the overcompleteness of the coherent state basis.

In fermionic systems, coherent states are constructed using Grassmann numbers, which are anticommuting variables. Consider fermionic annihilation ($\hat{\psi}$) and creation ($\hat{\psi}^\dagger$) operators satisfying the anticommutation relations $\{\hat{\psi}, \hat{\psi}^\dagger\} = 1$ and $\{\hat{\psi}, \hat{\psi}\} = \{\hat{\psi}^\dagger, \hat{\psi}^\dagger\} = 0$. A fermionic coherent state $|\theta\rangle$ is defined by:

$$\hat{\psi}|\theta\rangle = \theta|\theta\rangle, \quad (\text{C.6})$$

where θ is a Grassmann number. The resolution of identity for fermionic coherent states involves integration over Grassmann variables and is given by:

$$\int d\bar{\theta}d\theta e^{-\bar{\theta}\theta} |\theta\rangle\langle\theta| = \hat{I}. \quad (\text{C.7})$$

The overlap between two fermionic coherent states $|\theta\rangle$ and $|\theta'\rangle$ is:

$$\langle\theta'|\theta\rangle = e^{\bar{\theta}'\theta}. \quad (\text{C.8})$$

The sign in the exponent reflects the anticommuting nature of Grassmann variables, distinguishing fermionic overlaps from their bosonic counterparts.

Coherent State Path Integral

The path integral formulation of quantum mechanics, pioneered by Richard Feynman [1], represents quantum amplitudes as integrals over all possible paths that a system can take between initial and final states, weighted by the exponential of the action. While the standard formulation often employs position or momentum eigenstates, the coherent state path integral leverages the overcomplete basis of coherent states, proving particularly useful for systems involving creation and annihilation operators.

In bosonic systems, the coherent state path integral expresses the transition amplitude between an initial coherent state $|z_i\rangle$ and a final coherent state $|z_f\rangle$ over a time interval T as:

$$\langle z_f | e^{-i\hat{H}T} | z_i \rangle = \int D\bar{z}Dz e^{iS[\bar{z},z]}. \quad (\text{C.9})$$

Here, $D\bar{z}Dz$ denotes the path integral measure over the complex functions $z(t)$ and $\bar{z}(t)$, and $S[\bar{z}, z]$ is the action expressed in terms of these coherent state variables.

For fermionic systems, the coherent state path integral similarly expresses the transition amplitude between fermionic coherent states $|\theta_i\rangle$ and $|\theta_f\rangle$ as:

$$\langle \theta_f | e^{-i\hat{H}T} | \theta_i \rangle = \int D\bar{\theta}D\theta e^{iS[\bar{\theta},\theta]}. \quad (\text{C.10})$$

In this case, $D\bar{\theta}D\theta$ represents the path integral measure over Grassmann-valued functions $\theta(t)$ and $\bar{\theta}(t)$, and the action $S[\bar{\theta}, \theta]$ incorporates the Grassmann variables and their time derivatives.

Derivation of the Coherent State Path Integral

Bosonic Case

To derive the coherent state path integral for bosonic systems, we begin by considering the transition amplitude between two coherent states $|z_i\rangle$ and $|z_f\rangle$ over a time T , given by $\langle z_f | e^{-i\hat{H}T} | z_i \rangle$. The first step involves discretising the time interval T into N small slices of duration $\epsilon = T/N$. Between each pair of time slices, we insert a resolution of the identity in terms of coherent states, exploiting their overcompleteness:

$$\langle z_f | e^{-i\hat{H}T} | z_i \rangle = \lim_{N \rightarrow \infty} \int \prod_{k=1}^{N-1} \frac{d^2 z_k}{\pi} \prod_{k=1}^N \langle z_k | e^{-i\hat{H}\epsilon} | z_{k-1} \rangle. \quad (\text{C.11})$$

Here, $z_0 = z_i$ and $z_N = z_f$. For each small time slice, the matrix element $\langle z_k | e^{-i\hat{H}\epsilon} | z_{k-1} \rangle$ is approximated by expanding the exponential to first order in ϵ :

$$\langle z_k | e^{-i\hat{H}\epsilon} | z_{k-1} \rangle \approx \langle z_k | z_{k-1} \rangle \left(1 - i\epsilon \frac{\langle z_k | \hat{H} | z_{k-1} \rangle}{\langle z_k | z_{k-1} \rangle} \right). \quad (\text{C.12})$$

Using the overlap of coherent states:

$$\langle z_k | z_{k-1} \rangle = e^{-\frac{1}{2}(|z_k|^2 + |z_{k-1}|^2 - 2\bar{z}_k z_{k-1})} \quad (\text{C.13})$$

and recognising that the expectation value of the Hamiltonian in coherent states is $H(\bar{z}, z) = \langle z | \hat{H} | z \rangle$, we can express the matrix element as:

$$\langle z_k | e^{-i\hat{H}\epsilon} | z_{k-1} \rangle \approx \langle z_k | z_{k-1} \rangle e^{-i\epsilon H(\bar{z}_k, z_{k-1})}. \quad (\text{C.14})$$

In the continuum limit as $N \rightarrow \infty$, the product of overlaps and exponentials yields the path integral expression:

$$\langle z_f | e^{-i\hat{H}T} | z_i \rangle = \int D\bar{z} D z \exp \left(i \int_0^T dt (i\bar{z}(t)\dot{z}(t) - H(\bar{z}(t), z(t))) \right). \quad (\text{C.15})$$

The term $i\bar{z}\dot{z}$ arises from the logarithm of the coherent state overlaps and represents the kinetic part of the action, often referred to as the Berry phase or geometric phase.

Fermionic Case

For fermionic systems, the derivation of the coherent state path integral follows a similar discretisation approach, but with the incorporation of Grassmann variables to account for the anticommuting nature of fermions. Consider the transition amplitude $\langle \theta_f | e^{-i\hat{H}T} | \theta_i \rangle$. The time interval T is divided into N small slices of duration $\epsilon = T/N$, and resolutions of the identity in terms of fermionic coherent states $|\theta_k\rangle$ are inserted between each time slice:

$$\langle \theta_f | e^{-i\hat{H}T} | \theta_i \rangle = \lim_{N \rightarrow \infty} \int \prod_{k=1}^{N-1} d\bar{\theta}_k d\theta_k \prod_{k=1}^N \langle \theta_k | e^{-i\hat{H}\epsilon} | \theta_{k-1} \rangle. \quad (\text{C.16})$$

For each small time slice, the matrix element $\langle \theta_k | e^{-i\hat{H}\epsilon} | \theta_{k-1} \rangle$ is approximated by:

$$\langle \theta_k | e^{-i\hat{H}\epsilon} | \theta_{k-1} \rangle \approx \langle \theta_k | \theta_{k-1} \rangle e^{-i\epsilon H(\bar{\theta}_k, \theta_{k-1})}. \quad (\text{C.17})$$

The overlap of fermionic coherent states is:

$$\langle \theta_k | \theta_{k-1} \rangle = e^{\bar{\theta}_k \theta_{k-1}}. \quad (\text{C.18})$$

Taking the continuum limit, the path integral expression for fermionic systems becomes:

$$\langle \theta_f | e^{-i\hat{H}T} | \theta_i \rangle = \int D\bar{\theta} D\theta \exp \left(i \int_0^T dt \left(i\bar{\theta}(t)\dot{\theta}(t) - H(\bar{\theta}(t), \theta(t)) \right) \right). \quad (\text{C.19})$$

APPENDIX D

MEMORY FUNCTION EXPANSIONS

Contour integration of the memory function

Following Devreese et al. [18] I derived infinite-power-series expansions of the real and imaginary components of Eq. (2.203) (or Eq. (35) in FHIP [17]) in terms of Bessel and Struve special functions, and hypergeometric functions.

The practical computational implementation of these expansions was made difficult by the high precision required for the special functions to converge. A partially working implementation was developed using arbitrary precision numerics. Still, it was discovered that direct numeric integration of Eq. (2.203) could achieve the same result with less computation time and less complex code.

We start by changing the contour of the memory function as done in FHIP [17]. The memory function for the polaron is defined to linear order [72] as $\Sigma(\Omega) = \chi(\Omega)/\Omega$, where,

$$\chi(\Omega) = \int_0^\infty \left[1 - e^{i\Omega u}\right] \text{Im}S(u) du, \quad (\text{D.1})$$

is the

$$S(u) = \frac{2\alpha}{3\sqrt{\pi}} [D(u)]^{-\frac{3}{2}} \left(e^{iu} + \frac{2}{e^\beta - 1} \cos(u) \right), \quad (\text{D.2})$$

and

$$D(u) = \frac{w^2}{\beta v^2} \left\{ a^2 - \beta^2/4 - b \cos(vu) \cosh(v\beta/2) + u^2 - i [b \sin(vu) \sinh(v\beta/2) + u\beta] \right\}, \quad (\text{D.3})$$

with $R \equiv (v^2 - w^2)/(w^2 v)$, $a^2 = \beta^2/4 + R\beta \coth(\beta v/2)$ and $b = R\beta / \sinh(\beta v/2)$, which are the same as Eqs. (47b) in FHIP [17].

Solving for the real and imaginary parts of $\Sigma(\Omega)$ gives the real and imaginary parts of $\chi(\Omega)$,

$$\operatorname{Re} \chi(\Omega) = \int_0^\infty [1 - \cos(\Omega u)] \operatorname{Im} S(u) du, \quad (\text{D.4a})$$

$$\operatorname{Im} \chi(\Omega) = \int_0^\infty \sin(\Omega u) \operatorname{Im} S(u) du. \quad (\text{D.4b})$$

As both $[1 - \cos(\Omega u)]$ and $\sin(\Omega u)$ are real we can take ‘Im’ outside the integral,

$$\operatorname{Re} \chi(\Omega) = \operatorname{Im} \int_0^\infty [1 - \cos(\Omega u)] S(u) du, \quad (\text{D.5a})$$

$$\operatorname{Im} \chi(\Omega) = \operatorname{Im} \int_0^\infty \sin(\Omega u) S(u) du. \quad (\text{D.5b})$$

Now we promote $u \in \mathbb{R}$ to a complex variable $u = x + iy \in \mathbb{C}$. The integrals then become integrals on the complex plane,

$$\operatorname{Re} \chi(\Omega) = \operatorname{Im} \int_\Gamma [1 - \cos(\Omega x) \cosh(\Omega y) + i \sin(\Omega x) \sinh(\Omega y)] S(x + iy) du, \quad (\text{D.6a})$$

$$\operatorname{Im} \chi(\Omega) = \operatorname{Im} \int_\Gamma [\sin(\Omega x) \cosh(\Omega y) + i \cos(\Omega x) \sinh(\Omega y)] S(x + iy) du, \quad (\text{D.6b})$$

where Γ is our contour of integration. To motivate a choice of contour, let’s consider the form of $D(x + iy)$ and $S(x + iy)$,

$$D(x + iy) = \frac{w^2}{\beta v^2} \left\{ \left[a^2 - \beta^2/4 - b \cos(vx) \cosh(v(y - \beta/2)) + x^2 + y(\beta - y) \right] + i \left[b \sin(vx) \sinh(v(y - \beta/2)) + 2x(y - \beta/2) \right] \right\} \quad (\text{D.7})$$

$$S(x + iy) = \frac{2\alpha}{3\sqrt{\pi}} \frac{\cos(x + i(y - \beta/2))}{\sinh(\beta/2) [D(x + iy)]^{\frac{3}{2}}}. \quad (\text{D.8})$$

Now we notice that $D(x + iy)$ and $S(x + iy)$ are trivially real when $y = \beta/2$. This gives the results,

$$D(x + i\beta/2) = \frac{w^2}{\beta v^2} [x^2 + a^2 - b \cos(vx)] \in \mathbb{R} \quad (\text{D.9})$$

$$S(x + i\beta/2) = \frac{2\alpha}{3\sqrt{\pi}} \frac{\beta^{\frac{3}{2}}}{\sinh(\beta/2)} \left(\frac{v}{w} \right)^3 \frac{\cos(x)}{[x^2 + a^2 - b \cos(vx)]^{\frac{3}{2}}} \in \mathbb{R}. \quad (\text{D.10})$$

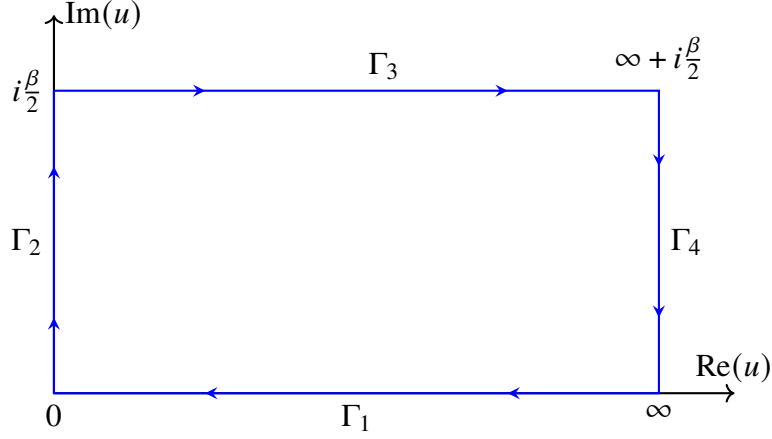


Figure D.1: The complex contour chosen to transform the integral in Eq. (D.1). No singularities lie within the closed contour so the contour integral is zero.

From this, we choose to integrate over the contours $\Gamma_1 \in (\infty + 0i, 0 + 0i] \rightarrow \Gamma_2 \in [0 + i0, 0 + i\beta/2] \rightarrow \Gamma_3 \in [0 + i\beta/2, \infty + i\beta/2) \rightarrow \Gamma_4 \in (\infty + i\beta/2, \infty + 0i)$ as shown in Fig. D.1. Since the integrands in Eqs. (D.6a) and (D.6b) are analytic in this region, this closed contour integral will be zero. (There is a pole in $\text{Im}S(x + iy)$ at $0 + i0$, but this is cancelled by the zero of the elementary/trigonometric functions in front of it at this point.) The closing piece of the contour lies at $x \rightarrow \infty$ and can be neglected as $S(x + iy) \rightarrow 0$ in this limit. Thus, for the real part of $\chi(\Omega)$ we have,

$$\begin{aligned} \int_0^\infty [1 - \cos(\Omega x)] S(x) dx &= \int_0^{\beta/2} [1 - \cosh(\Omega y)] S(iy) d(iy) \\ &+ \int_0^\infty \left[1 - \cos(\Omega x) \cosh\left(\frac{\Omega\beta}{2}\right) + i \sin(\Omega x) \sinh\left(\frac{\Omega\beta}{2}\right) \right] S\left(x + \frac{i\beta}{2}\right) dx, \end{aligned} \quad (\text{D.11})$$

and for the imaginary part of $\chi(\Omega)$ we have,

$$\begin{aligned} \int_0^\infty \sin(\Omega x) S(x) dx &= i \int_0^{\beta/2} \sinh(\Omega y) S(iy) d(iy) \\ &+ \int_0^\infty \left[\sin(\Omega x) \cosh\left(\frac{\Omega\beta}{2}\right) + i \cos(\Omega x) \sinh\left(\frac{\Omega\beta}{2}\right) \right] S\left(x + \frac{i\beta}{2}\right) dx. \end{aligned} \quad (\text{D.12})$$

We can now see more clearly why we integrate at $y = \beta/2$. Since $S(x + i\beta/2)$ is real, acting ‘Im’ on these integrals will cancel the second integral in the contour integral for $\text{Im}\chi(\Omega)$ (which is entirely real), and the third integral for both $\text{Re}\chi(\Omega)$ and $\text{Im}\chi(\Omega)$ is simplified due to the absence of any cross-terms that would have resulted for other values of y as $S(x + iy)$ would have been complex. To see that the second integral for $\text{Im}\chi(\Omega)$ is real, we

need to see if $S(iy)$ is real. First, we look at $D(iy)$, which is given by,

$$D(iy) = \frac{w^2}{\beta v^2} \left[a^2 - \frac{\beta^2}{4} + y(\beta - y) - b \cosh \left(vy - \frac{\beta v}{2} \right) \right] \in \mathbb{R}, \quad (\text{D.13})$$

and then $S(iy)$ is given by,

$$S(iy) = \frac{2\alpha}{3\sqrt{\pi}} \frac{\beta^{3/2}}{\sinh(\beta/2)} \left(\frac{v}{w} \right)^3 \frac{\cosh(y - \beta/2)}{\left[a^2 - \beta^2/4 + y(\beta - y) - b \cosh(v(y - \beta/2)) \right]^{3/2}} \in \mathbb{R}, \quad (\text{D.14})$$

so $S(iy)$ is indeed real. Since the second integral for $\text{Im}\chi(\Omega)$ has two complex i s and $S(iy)$ is real, the whole integral is entirely real and so it doesn't contribute to $\text{Im}\chi(\Omega)$. Unfortunately, $\text{Re}\chi(\Omega)$ does not simplify as nicely as $\text{Im}\chi(\Omega)$ because the second integral is imaginary, and so is still present after taking only the imaginary parts. Nonetheless, for $\text{Re}\chi(\Omega)$ we get,

$$\begin{aligned} \text{Re}\chi(\Omega) &= \text{Im} \int_0^\infty [1 - \cos(\Omega x)] S(x) dx \\ &= \frac{2\alpha}{3\sqrt{\pi}} \frac{\beta^{3/2}}{\sinh(\beta/2)} \left(\frac{v}{w} \right)^3 \left\{ \sinh \left(\frac{\Omega\beta}{2} \right) \int_0^\infty \frac{\sin(\Omega x) \cos(x) dx}{[x^2 + a^2 - b \cos(vx)]^{3/2}} \right. \\ &\quad \left. + \int_0^{\beta/2} \frac{[1 - \cosh(\Omega x)] \cosh(x - \beta/2) dx}{[a^2 - \beta^2/4 + x(\beta - x) - b \cosh(v(x - \beta/2))]^{3/2}} \right\}, \end{aligned} \quad (\text{D.15})$$

and for $\text{Im}\chi(\Omega)$ we get,

$$\begin{aligned} \text{Im}\chi(\Omega) &= \text{Im} \int_0^\infty \sin(\Omega x) S(x) dx \\ &= \frac{2\alpha}{3\sqrt{\pi}} \frac{\beta^{3/2}}{\sinh(\beta/2)} \left(\frac{v}{w} \right)^3 \int_0^\infty \frac{\cos(\Omega x) \cos(x) dx}{[x^2 + a^2 - b \cos(vx)]^{3/2}}. \end{aligned} \quad (\text{D.16})$$

Im χ expansion in Bessel-K functions

In Devreese et al. [18], the integral in Eq. (D.16) is expanded in an infinite sum of modified Bessel functions of the second kind. Here, we follow the same procedure and arrive at the same result but provide detailed workings. Specifically, we are interested in solving the integral,

$$\int_0^\infty \frac{\cos(\Omega x) \cos(x) dx}{[x^2 + a^2 - b \cos(vx)]^{3/2}}. \quad (\text{D.17})$$

We start by noticing that,

$$\left| \frac{b \cos(vx)}{x^2 + a^2} \right| < 1 \quad \text{if } v > 0 \text{ and } \beta > 0, \quad (\text{D.18})$$

so we can do a binomial expansion of the denominator,

$$\begin{aligned} & \int_0^\infty \frac{\cos(\Omega x) \cos(x)}{(x^2 + a^2)^{3/2}} \left[1 - \frac{b \cos(vx)}{x^2 + a^2} \right]^{-3/2} dx \\ &= \int_0^\infty dx \frac{\cos(\Omega x) \cos(x)}{(x^2 + a^2)^{3/2}} \sum_{n=0}^\infty \binom{-3/2}{n} \frac{(-b)^n \cos^n(vx)}{(x^2 + a^2)^n} dx \quad (\text{D.19}) \\ &= \sum_{n=0}^\infty \binom{-3/2}{n} (-b)^n \int_0^\infty \frac{\cos(\Omega x) \cos(x) \cos^n(vx)}{(x^2 + a^2)^{n+3/2}} dx, \end{aligned}$$

where $\binom{-3/2}{n}$ is a binomial coefficient. Next we expand $\cos^n(vx)$ using the power-reduction formula,

$$\cos^n(vx) = \frac{2}{2^n} \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \cos((n-2k)vx) + \frac{(1 - n \bmod 2)}{2^n} \binom{n}{\frac{n}{2}}, \quad (\text{D.20})$$

where the second term comes from even n contributions only. Substituting this into our integral gives,

$$\begin{aligned} & \sum_{n=0}^\infty \binom{-3/2}{n} \left(-\frac{b}{2}\right)^n \left[2 \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \int_0^\infty \frac{\cos(\Omega x) \cos(x) \cos((n-2k)vx)}{(x^2 + a^2)^{n+3/2}} dx \right. \\ & \quad \left. + (1 - n \bmod 2) \binom{n}{\frac{n}{2}} \int_0^\infty \frac{\cos(\Omega x) \cos(x)}{(x^2 + a^2)^{n+3/2}} dx \right]. \quad (\text{D.21}) \end{aligned}$$

We can now combine the cosines inside of the integrals into sums of single cosines using,

$$\begin{aligned} & \cos(\Omega x) \cos(x) \cos(vx(n-2k)) = \\ & \quad \frac{1}{4} \{ \cos(x(\Omega + 1 + v(n-2k))) + \cos(x(\Omega - 1 + v(n-2k))) \\ & \quad + \cos(x(\Omega + 1 - v(n-2k))) + \cos(x(\Omega - 1 - v(n-2k))) \} \quad (\text{D.22}) \\ & \equiv \frac{1}{4} \sum_{z_4} \cos(x z_{k,4}^n) \end{aligned}$$

where for brevity we have defined $z_{k,4}^n \in \{\Omega + 1 + v(n - 2k), \Omega - 1 + v(n - 2k), \Omega + 1 - v(n - 2k), \Omega - 1 - v(n - 2k)\}$. Likewise,

$$\begin{aligned} \cos(\Omega x) \cos(x) &= \frac{1}{2} \{ \cos(x(\Omega + 1)) + \cos(x(\Omega - 1)) \} \\ &\equiv \frac{1}{2} \sum_{z_2} \cos(x z_2) \end{aligned} \quad (\text{D.23})$$

where for brevity we have defined $z_2 \in \{\Omega + 1, \Omega - 1\}$. Substituting these into our expansion gives,

$$\begin{aligned} \sum_{n=0}^{\infty} \binom{-3/2}{n} \left(-\frac{b}{2}\right)^n \left[2 \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \sum_{z_4} \int_0^{\infty} \frac{\cos(x z_{k,4}^n(\Omega))}{(x^2 + a^2)^{n+3/2}} dx \right. \\ \left. + (1 - n \bmod 2) \binom{n}{\frac{n}{2}} \sum_{z_2} \int_0^{\infty} \frac{\cos(x z_2(\Omega))}{(x^2 + a^2)^{n+3/2}} dx \right]. \end{aligned} \quad (\text{D.24})$$

We now have a lot of integrals of the form,

$$\int_0^{\infty} \frac{\cos(xz)}{(x^2 + a^2)^{n+3/2}} dx, \quad (\text{D.25})$$

which is an integral representation of modified Bessel functions of the second kind,

$$\begin{aligned} \int_0^{\infty} \frac{\cos(xz)}{(x^2 + a^2)^{n+3/2}} dx &= \frac{\sqrt{\pi}}{\Gamma(n + 3/2)} K_{n+1}(|z|a) \left| \frac{z}{2a} \right|^{n+1} \\ &\equiv B_n(z) \end{aligned} \quad (\text{D.26})$$

Thus, overall we can expand $\text{Im}\chi(\Omega)$ in a series of these Bessel functions,

$$\begin{aligned} \text{Im}\chi(\Omega) &= \frac{2\alpha\beta^{\frac{3}{2}}}{3\sqrt{\pi}} \frac{\sinh(\frac{\Omega\beta}{2})}{\sinh(\frac{\beta}{2})} \left(\frac{v}{w}\right)^3 \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(-\frac{b}{2}\right)^n \left[\sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \sum_{z_4} B_n(z_{k,4}^n(\Omega)) \right. \\ &\quad \left. + (1 - n \bmod 2) \binom{n}{\frac{n}{2}} \sum_{z_2} B_n(z_2(\Omega)) \right] \end{aligned} \quad (\text{D.27})$$

where $a^2 = \beta^2/4 + R\beta \coth(\beta v/2)$, $b = R\beta / \sinh(\beta v/2)$ and $R = (v^2 - w^2)/(w^2 v)$. Also, $z_{k,4}^n(\Omega) \in \{\Omega + 1 + v(n - 2k), \Omega - 1 + v(n - 2k), \Omega + 1 - v(n - 2k), \Omega - 1 - v(n - 2k)\}$ and $z_2(\Omega) \in \{\Omega + 1, \Omega - 1\}$.

Re χ expansion in Bessel-I, Struve-L and ${}_1F_2$ hypergeometric functions

Motivated by the expansion of $\text{Im}\chi(\Omega)$ in Devreese et al. [18], we provide a similar expansion for $\text{Re}\chi(\Omega)$. I follow a similar procedure as for $\text{Im}\chi(\Omega)$ and notice that our efforts focus on solving the integrals,

$$\int_0^\infty \frac{\sin(\Omega x) \cos(x) dx}{[x^2 + a^2 - b \cos(vx)]^{3/2}}, \quad (\text{D.28})$$

$$\int_0^{\beta/2} \frac{[1 - \cosh(\Omega x)] \cosh(x - \beta/2) dx}{[a^2 - \beta^2/4 + x(\beta - x) - b \cosh(v(x - \beta/2))]^{3/2}}. \quad (\text{D.29})$$

The first integral is similar to Eq. (D.17), with a cosine swapped out for a sine. Following a similar procedure as for Eq. (D.17) gives,

$$\begin{aligned} \int_0^\infty \frac{\sin(\Omega x) \cos(x) dx}{[x^2 + a^2 - b \cos(vx)]^{3/2}} &= \sum_{n=0}^\infty \binom{-3/2}{n} \left(-\frac{b}{2}\right)^n \left[2 \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \sum_{z_4} \int_0^\infty \frac{\sin(x z_{k,4}^n(\Omega))}{(x^2 + a^2)^{n+3/2}} dx \right. \\ &\quad \left. + (1 - n \bmod 2) \binom{n}{\frac{n}{2}} \sum_{z_2} \int_0^\infty \frac{\sin(x z_2(\Omega))}{(x^2 + a^2)^{n+3/2}} dx \right], \end{aligned} \quad (\text{D.30})$$

where we now look for any special functions for which,

$$\int_0^\infty \frac{\sin(xz)}{(x^2 + a^2)^{n+3/2}} dx \quad (\text{D.31})$$

is the integral representation. We found that,

$$\begin{aligned} \int_0^\infty \frac{\sin(xz)}{(x^2 + a^2)^{n+3/2}} dx &= \frac{\sqrt{\pi}}{2} \frac{\Gamma(-\frac{1}{2} - n) \text{sgn}(z) |z|^{n+1}}{(2a)^{n+1}} [I_{n+1}(|z|a) - \mathbf{L}_{-(n+1)}(|z|a)] \\ &\equiv J_n(z) \end{aligned} \quad (\text{D.32})$$

for $n \geq 0$ and $a \geq 0$. Here $\text{sgn}(x)$ is the signum function, $I_n(x)$ is the modified Bessel function of the first kind, $\mathbf{L}_n(x)$ is the modified Struve function. Therefore, for $\text{Re}\chi(\Omega)$

we have,

$$\begin{aligned} \text{Re}\chi(\Omega) = & \frac{2\alpha\beta^{3/2}}{3\sqrt{\pi}} \frac{\sinh\left(\frac{\Omega\beta}{2}\right)}{\sinh(\beta/2)} \left(\frac{v}{w}\right)^3 \left\{ \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(\frac{b}{2}\right)^n \left[\sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \sum_{z_4} J_n(z_{k,4}^n(\Omega)) \right. \right. \\ & \left. \left. + (1 - n \bmod 2) \binom{n}{\frac{n}{2}} \sum_{z_2} J_n(z_2(\Omega)) \right] \right\} \\ & + \frac{2\alpha}{3\sqrt{\pi}} \frac{\beta^{3/2}}{\sinh(\beta/2)} \left(\frac{v}{w}\right)^3 \int_0^{\beta/2} \frac{[1 - \cosh(\Omega x)] \cosh(x - \beta/2) dx}{[a^2 - \beta^2/4 + x(\beta - x) - b \cosh(v(x - \beta/2))]^{3/2}} \end{aligned} \quad (\text{D.33})$$

where a , b , z_4 and z_2 are the same as before. Expanding the second integral with the hyperbolic integrand is more complicated. We start by doing a change of variables $x \rightarrow (1 - x)\beta/2$ to transform the denominator into a similar form as before and to change the limits to $[0, 1]$,

$$\begin{aligned} & \int_0^{\beta/2} \frac{[1 - \cosh(\Omega x)] \cosh(x - \beta/2) dx}{[a^2 - \beta^2/4 + x(\beta - x) - b \cosh(v(x - \beta/2))]^{3/2}} \\ & \rightarrow \frac{\beta}{2} \int_0^1 \frac{[1 - \cosh(\Omega\beta[1 - x]/2)] \cosh(\beta x/2) dx}{[a^2 - (\beta x/2)^2 - b \cosh(\beta v x/2)]^{3/2}}. \end{aligned} \quad (\text{D.34})$$

Now we see that for $x \in [0, 1]$

$$\left| \frac{b \cosh(\beta v x/2)}{a^2 - (\beta x/2)^2} \right| < 1 \quad \text{if } v > 0 \text{ and } \beta > 0 \quad (\text{D.35})$$

so we can do a binomial expansion of the denominator as before,

$$\sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(\frac{2}{\beta}\right)^{2n+2} (-b)^n \int_0^1 \frac{[1 - \cosh(\Omega\beta[1 - x]/2)] \cosh(\beta x/2) \cosh^n(\beta v x/2)}{((2a/\beta)^2 - x^2)^{n+3/2}} dx. \quad (\text{D.36})$$

Then, I do another binomial expansion of the remaining denominator

$$\begin{aligned} & \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(\frac{2}{\beta}\right)^{2n+2} (-b)^n \sum_{m=0}^{\infty} \binom{-n - \frac{3}{2}}{m} (-1)^m \left(\frac{\beta}{2a}\right)^{2n+2m+3} \\ & \quad \times \int_0^1 \left[1 - \cosh\left(\frac{\Omega\beta[1 - x]}{2}\right) \right] \cosh\left(\frac{\beta x}{2}\right) \cosh^n\left(\frac{\beta v x}{2}\right) x^{2m} dx. \end{aligned} \quad (\text{D.37})$$

We can then expand the product of hyperbolic cosines in the integrand,

$$\begin{aligned}
& \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(\frac{2}{\beta}\right)^{2n+2} (-b)^n \sum_{m=0}^{\infty} \binom{-n-\frac{3}{2}}{m} (-1)^m \left(\frac{\beta}{2a}\right)^{2n+2m+3} \frac{1}{2^n} \\
& \times \left\{ \binom{n}{\frac{n}{2}} (1 - n \bmod 2) \left[\int_0^1 \frac{\cosh\left(\frac{\beta z_1 x}{2}\right)}{x^{-2m}} dx \right. \right. \\
& \left. \left. - \frac{1}{2} \sum_{z_2} \left(\cosh\left(\frac{\Omega\beta}{2}\right) \int_0^1 \frac{\cosh\left(\frac{\beta z_2 x}{2}\right)}{x^{-2m}} dx - \sinh\left(\frac{\Omega\beta}{2}\right) \int_0^1 \frac{\sinh\left(\frac{\beta z_2 x}{2}\right)}{x^{-2m}} dx \right) \right] \right. \\
& \left. + \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \left[\sum_{z_3} \int_0^1 \frac{\cosh\left(\frac{\Omega\beta z_3 x}{2}\right)}{x^{-2m}} dx \right. \right. \\
& \left. \left. - \frac{1}{2} \sum_{z_4} \left(\cosh\left(\frac{\Omega\beta}{2}\right) \int_0^1 \frac{\cosh\left(\frac{\Omega\beta z_4 x}{2}\right)}{x^{-2m}} dx - \sinh\left(\frac{\Omega\beta}{2}\right) \int_0^1 \frac{\sinh\left(\frac{\Omega\beta z_4 x}{2}\right)}{x^{-2m}} dx \right) \right] \right\} \quad (D.38)
\end{aligned}$$

where $z_1 = 1$, $z_2(\Omega) \in \{\Omega + 1, \Omega - 1\}$, $z_{k,3}^n \in \{1 + v(n - 2k), 1 - v(n - 2k)\}$ and $z_{k,4}^n(\Omega) \in \{\Omega + 1 + v(n - 2k), \Omega - 1 + v(n - 2k), \Omega + 1 - v(n - 2k), \Omega - 1 - v(n - 2k)\}$.

Now we have two integrals of the forms

$$\int_0^1 \cosh(zx) x^{2m} dx, \quad \int_0^1 \sinh(zx) x^{2m} dx, \quad (D.39)$$

which are the integral forms of the generalised hypergeometric functions

$$\int_0^1 \cosh(zx) x^{2m} dx = {}_1F_2 \left[\begin{matrix} m + \frac{1}{2} \\ \frac{1}{2}, m + \frac{3}{2} \end{matrix}; \frac{z^2}{4} \right] = \sum_{t=0}^{\infty} \frac{z^{2t}}{(2t + 2m + 1)(2t)!}, \quad m > -\frac{1}{2} \quad (D.40a)$$

$$\int_0^1 \sinh(zx) x^{2m} dx = \frac{z}{2m + 2} {}_1F_2 \left[\begin{matrix} m + 1 \\ \frac{3}{2}, m + 2 \end{matrix}; \frac{z^2}{4} \right] = \sum_{t=0}^{\infty} \frac{z^{2t+1}}{(2t + 2m + 2)(2t + 1)!}, \quad m > -1. \quad (D.40b)$$

For brevity, we will define

$${}_1F_2^c(z) \equiv {}_1F_2 \left[\begin{matrix} m + \frac{1}{2} \\ \frac{1}{2}, m + \frac{3}{2} \end{matrix}; \frac{\beta^2 z^2}{16} \right] = \sum_{t=0}^{\infty} \frac{(\beta z/2)^{2t}}{(2t + 2m + 1)(2t)!} \quad (D.41a)$$

$${}_1F_2^s(z) \equiv \frac{\beta z}{4m + 4} {}_1F_2 \left[\begin{matrix} m + 1 \\ \frac{3}{2}, m + 2 \end{matrix}; \frac{\beta^2 z^2}{16} \right] = \sum_{t=0}^{\infty} \frac{(\beta z/2)^{2t+1}}{(2t + 2m + 2)(2t + 1)!} \quad (D.41b)$$

so that Eq. (D.38) becomes

$$\begin{aligned}
& \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(\frac{2}{\beta}\right)^{2n+2} (-b)^n \sum_{m=0}^{\infty} \binom{-n-\frac{3}{2}}{m} (-1)^m \left(\frac{\beta}{2a}\right)^{2n+2m+3} \frac{1}{2^n} \\
& \times \left\{ \binom{n}{\frac{n}{2}} (1 - n \bmod 2) \left[{}_1F_2^c(z_1) - \frac{1}{2} \sum_{z_2} \left(\cosh\left(\frac{\Omega\beta}{2}\right) {}_1F_2^c(z_2) - \sinh\left(\frac{\Omega\beta}{2}\right) {}_1F_2^s(z_2) \right) \right] \right. \\
& \left. + \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \left[\sum_{z_3} {}_1F_2^c(z_3) - \frac{1}{2} \sum_{z_4} \left(\cosh\left(\frac{\Omega\beta}{2}\right) {}_1F_2^c(z_4) - \sinh\left(\frac{\Omega\beta}{2}\right) {}_1F_2^s(z_4) \right) \right] \right\} \quad (D.42)
\end{aligned}$$

which we can reduce further by defining,

$$M_n^{c/s}(z) \equiv \sum_{m=0}^{\infty} \binom{-n-\frac{3}{2}}{m} (-1)^m a^{-2(n+m+1)} \left(\frac{\beta}{2}\right)^{2m+1} {}_1F_2^{c/s}(z), \quad (D.43)$$

to give,

$$\begin{aligned}
& \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(\frac{-b}{2}\right)^n \left\{ \binom{n}{\frac{n}{2}} (1 - n \bmod 2) \left[M_n^c(z_1) - \frac{1}{2} \sum_{z_2} \left(\cosh\left(\frac{\Omega\beta}{2}\right) M_n^c(z_2) \right. \right. \right. \\
& \quad \left. \left. \left. - \sinh\left(\frac{\Omega\beta}{2}\right) M_n^s(z_2) \right) \right] \right. \\
& \quad \left. + \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \left[\sum_{z_3} M_n^c(z_3) - \frac{1}{2} \sum_{z_4} \left(\cosh\left(\frac{\Omega\beta}{2}\right) M_n^c(z_4) \right. \right. \right. \\
& \quad \left. \left. \left. - \sinh\left(\frac{\Omega\beta}{2}\right) M_n^s(z_4) \right) \right] \right\}. \quad (D.44)
\end{aligned}$$

Combining this with the rest of $\text{Re}\chi(\Omega)$ gives,

$$\begin{aligned}
\text{Re}\chi(\Omega) &= \frac{2\alpha\beta^{3/2}v^3}{3\sqrt{\pi}w^3 \sinh(\beta/2)} \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(-\frac{b}{2}\right)^n \\
&\times \left\{ \binom{n}{\frac{n}{2}} (1 - n \bmod 2) \left[M_n^c(1) + \frac{1}{2} \sum_{z_2} \left(\sinh\left(\frac{\Omega\beta}{2}\right) [M_n^s(z_2(\Omega)) + J_n(z_2(\Omega))] \right. \right. \right. \\
&\quad \left. \left. \left. - \cosh\left(\frac{\Omega\beta}{2}\right) M_n^c(z_2(\Omega)) \right) \right] \right. \\
&+ \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \left[\sum_{z_3} M_n^c(z_{k,3}^n) + \frac{1}{2} \sum_{z_4} \left(\sinh\left(\frac{\Omega\beta}{2}\right) [M_n^s(z_{k,4}^n(\Omega)) + J_n(z_{k,4}^n(\Omega))] \right. \right. \\
&\quad \left. \left. \left. - \cosh\left(\frac{\Omega\beta}{2}\right) M_n^s(z_{k,4}^n(\Omega)) \right) \right] \right\}. \tag{D.45}
\end{aligned}$$

So, altogether, I have the expansion for the memory function,

$$\begin{aligned}
\chi(\Omega) &= \frac{2\alpha\beta^{3/2}v^3}{3\sqrt{\pi}w^3 \sinh(\beta/2)} \sum_{n=0}^{\infty} \binom{-\frac{3}{2}}{n} \left(-\frac{b}{2}\right)^n \\
&\times \left\{ \binom{n}{\frac{n}{2}} (1 - n \bmod 2) \left[M_n^c(1) + \frac{1}{2} \sum_{z_2} \left(\sinh\left(\frac{\Omega\beta}{2}\right) [M_n^s(z_2) + J_n(z_2) + iB_n(z_2)] \right. \right. \right. \\
&\quad \left. \left. \left. - \cosh\left(\frac{\Omega\beta}{2}\right) M_n^c(z_2(\Omega)) \right) \right] \right. \\
&+ \sum_{k=0}^{\lfloor \frac{n-1}{2} \rfloor} \binom{n}{k} \left[\sum_{z_3} M_n^c(z_{k,3}^n) + \frac{1}{2} \sum_{z_4} \left(\sinh\left(\frac{\Omega\beta}{2}\right) [M_n^s(z_{k,4}^n) + J_n(z_{k,4}^n) + iB_n(z_{k,4}^n)] \right. \right. \\
&\quad \left. \left. \left. - \cosh\left(\frac{\Omega\beta}{2}\right) M_n^s(z_{k,4}^n) \right) \right] \right\}. \tag{D.46}
\end{aligned}$$