Ab Initio Modelling of Photoinduced Electron Dynamics in Nanostructures

A Thesis

Presented Upon Application for Admission to the Degree of

Doctor of Philosophy

in the

Faculty of Engineering and Physical Sciences

by

Ryan J. McMillan
MSci (Hons) 2013

School of Mathematics and Physics
Queen’s University Belfast
Northern Ireland

4th November, 2017
Abstract

Nanostructured materials have recently attracted much interest due to their unique properties which make them appealing for the next generation of efficient and novel optical/electrical devices. In particular, two-dimensional (atomically thin) materials such as transition metal dichalcogenides (TMDs) have been extensively researched and shown to exhibit, e.g., strong optical absorption when compared to their bulk counterparts, with potential applications in photovoltaics for solar energy. The optical absorption in such materials may be further improved by decoration with metal nanoparticles (MNPs) due to a plasmonic enhancement effect. While such an effect has been demonstrated experimentally, it is hard to show theoretically from an \textit{ab initio} point of view due to the computational demand of such calculations: the state-of-the-art approaches commonly used to determine the optical spectra of, e.g, the semiconducting TMD (i.e. density functional theory (DFT) and many-body perturbation theory) may not be applied to the full TMD-MNP structure as the MNP is often on a much larger scale than the semiconductor rendering the \textit{ab initio} methods infeasible.

In this thesis, we develop a dynamical, hybrid approach (the projected equations of motion (PEOM) method) where a composite material is split into subsystems which are then coupled electromagnetically. The primary system (e.g., the TMD) may be treated using any time-dependent theory, while the secondary system (e.g., the MNP) is modelled entirely through its frequency-dependent polarisability which is fitted to obtain parameters which enter into the PEOMs.

As a proof of concept, the PEOM method is first applied to a semiconducting quantum dot-MNP system and the obtained energy absorption rates and population dynamics are compared with results from existing analytical approaches. Good agreement between the two methods is shown, while the PEOM proves to be an improvement when investigating ultrafast excitations in such systems. The method is then further tested by comparing absorption spectra in bilayers of hexagonal boron nitride and MoS$_2$ obtained via the PEOM approach with those obtained by time-dependent DFT and the Bethe-Salpeter equation. Again, the two approaches are in good, qualitative agreement. The thesis is left open as a starting point towards investigating the TMD-MNP structures, as well as stating the limitations of the PEOM method and suggesting possible improvements.
Acknowledgements

I must begin by thanking my supervisor, Dr Myrta Grüning, for her incredible support and guidance throughout the PhD process: I could always count on her fast replies to emails, availability, cooperation with tricky mathematical derivations, and diligent advice and reading of my work. I wish also to thank Dr Lorenzo Stella for his huge input into the PEOM method devised in this thesis, and to Dr Dan Dundas both for his supervision during my Masters degree and for his guidance during this PhD, especially at the early stages. Thanks must also go to Professor Jorge Kohanoff for encouraging/persuading me to take on a PhD in the first place, and for creating such a friendly and supportive atmosphere within the Atomistic Simulation Centre. I would like to express my appreciation of the staff within the Maths and Physics department, especially to those in the departmental office and accounting department for being so friendly and for their help with organising trips to conferences and making sure that I got my money back. I’d like to thank the developers of Yambo for their assistance and for letting me mess with their wonderful code. Thanks also to Dr Malachy Montgomery (a veritable Linux genius) for all his help with everything computational and for teaching me so much about Linux and software in general. I also wish to gratefully acknowledge financial support from the UK Engineering and Physical Sciences Research Council.

Thank you to all my friends at the ASC for keeping me sane throughout these past four years: for helping me with physics, for entertaining me, for listening to me, for encouraging me, for putting up with my all-to-frequent calls for tea, for baking tasty treats, for talking nonsense, and for genuinely caring—it simply wouldn’t have been the same without you. Thanks to my wonderful, supportive and caring family: grandparents, siblings, aunts and uncles, and friends who have become family. Special thanks to my parents who have always put our needs before their own, encouraged us in education and music, provided for us in so many ways and continue set an example of how to live. Finally, thanks to my flatmate and best friend, Rachel, who has always been there for me, helped me through so many trials and has never failed to cheer me up when the burdens of life and the PhD stress have seemed overwhelming.
# Contents

1 Introduction 2

1.1 Nanostructured Media ................................................. 2
1.2 *Ab initio* Modelling: Computational Limits ..................... 3
1.3 Projected Equations of Motion Method ................................ 5
1.4 Layout of Thesis ...................................................... 6

2 Background Theory 8

2.1 Polarisation, the Dielectric Function and Absorption ............ 9
2.2 Electronic Structure Calculations .................................... 11
   2.2.1 The Time-Independent Schrödinger Equation .................. 11
   2.2.2 Density Functional Theory (DFT) ............................. 13
   2.2.3 Kohn-Sham DFT .................................................. 16
2.3 Excited State Calculations ........................................... 17
   2.3.1 The Time-Dependent Schrödinger Equation .................... 18
   2.3.2 Density Matrix Formalism .................................... 19
   2.3.3 Time-Dependent DFT and Linear Response ..................... 21
   2.3.4 Periodic Systems .............................................. 23
   2.3.5 Quasi-Particles and The Bethe-Salpeter Equation ............ 27
   2.3.6 The Time-Dependent Bethe-Salpeter Equation ................ 31

3 The Projected Equations of Motion (PEOM) Method 34

3.1 Introduction .......................................................... 34
3.2 Derivation ............................................................ 35
3.3 Test: Recovering the Fitted Polarisability .......................... 38

4 Semiconducting Quantum Dot-Metal Nanoparticle Hybrid 42

4.1 Describing the System ............................................... 43
4.2 Energy Absorption Rates ............................................. 44
   4.2.1 Analytical Approach ......................................... 45
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.2</td>
<td>PEOM Approach</td>
<td>47</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Comparison of Methods</td>
<td>48</td>
</tr>
<tr>
<td>4.3</td>
<td>Population Inversion</td>
<td>51</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Semi-Analytical Approaches</td>
<td>52</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Comparison with PEOM Approach</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td>2D Material Composites</td>
<td>58</td>
</tr>
<tr>
<td>5.1</td>
<td>Atomic Configurations</td>
<td>58</td>
</tr>
<tr>
<td>5.2</td>
<td>Absorption Spectra from Linear Response Theory</td>
<td>61</td>
</tr>
<tr>
<td>5.3</td>
<td>PEOM Approaches</td>
<td>66</td>
</tr>
<tr>
<td>5.4</td>
<td>Comparison of LR and PEOM-PEOM Spectra for Bilayers</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions and Future Work</td>
<td>78</td>
</tr>
<tr>
<td>A</td>
<td>The Projected Equations of Motion Method</td>
<td>84</td>
</tr>
<tr>
<td>A.1</td>
<td>Generalisation to Anisotropic Media</td>
<td>84</td>
</tr>
<tr>
<td>B</td>
<td>Semiconducting Quantum Dot-Metal Nanoparticle Hybrid</td>
<td>86</td>
</tr>
<tr>
<td>B.1</td>
<td>Density Matrix Equations of Motion for Isolated SQD</td>
<td>86</td>
</tr>
<tr>
<td>B.2</td>
<td>RWA Steady-State Solution for Isolated SQD</td>
<td>88</td>
</tr>
<tr>
<td>B.3</td>
<td>Effective Field for Coupled SQD-MNP System</td>
<td>89</td>
</tr>
<tr>
<td>B.4</td>
<td>RWA and Steady-State Solution for SQD-MNP System</td>
<td>92</td>
</tr>
<tr>
<td>B.5</td>
<td>Time-Derivative of $p_{\text{MNP}}(t)$</td>
<td>93</td>
</tr>
<tr>
<td>B.6</td>
<td>Energy Absorption Rate for MNP in the RWA</td>
<td>94</td>
</tr>
<tr>
<td>B.7</td>
<td>Effective Field Limitations</td>
<td>95</td>
</tr>
<tr>
<td>C</td>
<td>Fourth-Order Runge-Kutta Method for Solving First-Order ODEs</td>
<td>97</td>
</tr>
<tr>
<td>D</td>
<td>Algorithms</td>
<td>99</td>
</tr>
<tr>
<td>D.1</td>
<td>Least-Squares Fitting Algorithm (MATLAB)</td>
<td>99</td>
</tr>
<tr>
<td>D.2</td>
<td>Runge-Kutta Solution to Isolated PEOM</td>
<td>105</td>
</tr>
</tbody>
</table>
List of Figures

1.1 Schematic diagram of the unit cells corresponding to (a) an isolated MoS$_2$ monolayer and (b) the same monolayer, decorated with gold nanospheres.  

3.1 Schematic diagram showing the dipole-dipole interaction between the primary system (PS) and the secondary system (SS), separated by a distance $R$. When an external field, $E_{\text{EXT}}$, is applied, a dipole moment, $p_{\text{PS}}$, is induced in the PS, generating a field. The SS thus experiences this dipole field in addition to the external field, and we denote the total field felt by the SS as $E_{\text{SS}}$. Similarly, due to $E_{\text{SS}}$, a dipole field is generated in the SS which is in turn felt by the PS in addition to $E_{\text{EXT}}$, and we denote the total field felt by the PS as $E_{\text{PS}}$. In this way, the PS and SS dynamics are coupled through the external field. 

3.2 Time-dependent dipole moment, $p(t)$, of the gold sphere with frequency-dependent polarisability given by Eqs. (3.14) and (3.15). The system of equations in Eq. (3.16) are solved under the parameters in Table 3.1 using the RK4 method with a time-step of 0.001 fs. The inset shows the delta-like external field, $E_{\text{EXT}}(t)$, as given in Eq. (3.18) with a switch-on time of $t_{\text{start}} = 0.1$ fs. 

3.3 Real (blue) and imaginary (red) parts of the frequency-dependent polarisability, $\alpha(\omega)$, of a gold sphere. The solid lines are from the analytical expression given by Eqs. (3.14) and (3.15). The crosses are obtained by taking the Fourier transforms of the time-dependent dipole moment and external field (see Fig. 3.2). The units are $1/a^3$ where $a$ is the radius of the sphere. 

4.1 Schematic diagram of a spherical metal nanoparticle (MNP) of radius, $a$, separated by a distance, $R$, from a spherical semiconducting quantum dot (SQD) of radius, $r$. The MNP is modelled classically while the SQD is treated as a two-level quantum system with ground state, $|1\rangle$, and excited state, $|2\rangle$, separated by an energy gap of $\hbar \omega_0$. 

4.2 Schematic showing how the PEOMs are solved, coupled with the density matrix equation of motion. We discretise time into equally spaced points, \( \{t_0, t_1, \ldots \} \), and use the RK4 method (Appendix C) to solve the differential equations in Eq. (4.2) and Eq. (4.25) in parallel branches 1 and 2, respectively. After each iteration, the value of \( E_{\text{MNP}} \) \( (E_{\text{SQD}}) \) is updated using the value of \( p_{\text{SQD}} \) \( (p_{\text{MNP}}) \) from Branch 1 (2). We assume the initial conditions \( t_0 = \rho(0) = s_k(0) = p_{\text{SQD}}(0) = p_{\text{MNP}}(0) = 0 \). 47

4.3 Energy absorption rate, \( Q \), for the SQD-MNP system under illumination of a monochromatic wave of weak intensity \( (I_0 = 1 \text{ W cm}^{-2}) \) and frequency \( \omega_L \), as a function of the laser detuning, \( h(\omega_L - \omega_0) \) for separation distances \( R = 13 \text{ nm} \) (green), 15 nm (red), 20 nm (blue) and 80 nm (black). The solid lines represent the steady-state analytical solution in the RWA while the crosses are the results from the PEOM method. 49

4.4 As Fig. 4.3 but in the strong field regime where the laser intensity is \( I_0 = 1 \times 10^3 \text{ W cm}^{-2} \). 50

4.5 Excited state population dynamics for an isolated SQD \( (R \to \infty) \) interacting with a sech pulse of area \( 5\pi \) according to Eq. (4.36). The solid red line is the numerical solution to the original EOMs in Eq. (4.2) while the dashed blue line is the solution to the modified RWA EOMs in Eq. (4.39). (a) Dynamics for a 1000-cycle pulse corresponding to \( \tau_p \approx 0.11 \text{ ps} \). (b) Dynamics for a 10-cycle pulse corresponding to \( \tau_p \approx 1.1 \text{ fs} \). 53

4.6 Excited state population dynamics for an SQD-MNP system interacting with a 10-cycle sech pulse for various interparticle distances, \( R \). The field amplitude is chosen to give a \( 5\pi \) pulse area for each value of \( R \) according to Eq. (4.37). (a) Solution to the modified EOMs in Eq. (4.39) under the RWA and assuming a slowly-varying pulse envelope. (b) Solution to the original EOMs in Eq. (4.2) beyond the RWA using the effective field in Eq. (4.40) which assumes a slowly-varying pulse envelope. (c) Solution to Eq. (4.2) using the PEOM method where the auxiliary parameters are obtained by fitting \( \alpha_{\text{MNP}}(\omega) \) in Eq. (4.8) accurately over the range \( 0-10 \text{ eV} \) using \( N = 21 \) fitting functions. (d) Same as (c) but where \( \alpha_{\text{MNP}}(\omega) \) is fitted over a small range close to \( h\omega_0 \) \( (2.455-2.545 \text{ eV}) \) using \( N = 1 \) fitting functions. Insets: real (blue dashed) and imaginary (black dashed) parts of the fitted polarisability, \( \alpha_{\text{MNP}}(\omega)/a^3 \) (exact function shown in grey). 54

4.7 Time evolution of the MNP dipole moment, \( p_{\text{MNP}}(t) \), for the \( R = 13 \text{ nm} \) cases in Fig. 4.6 (b) (solid blue) and (c) (solid black) where the effective field method and PEOM method are used respectively. The corresponding external field is shown in dashed red. 56
4.8 Value of $\rho_{22}(t)$ at the end of the pulse for various pulse durations. The interparticle distance is $R = 13$ nm and the pulse area is chosen to be $5\pi$ according to Eq. (4.37)................................................................. 56

5.1 Side (top panel) and top (bottom panel) views of (a) a monolayer of MoS$_2$ (b) a bilayer of MoS$_2$ in the AA' configuration and (c) a bilayer of MoS$_2$ in the AA configuration. The solid grey lines represent the unit cell boundaries. In (b) and (c), the two layers are separated such that the Mo atoms are a distance, $d$, apart in the $z$-direction............................................................... 59

5.2 Side (top panel) and top (bottom panel) views of (a) a monolayer of $h$-BN and (b) a bilayer of $h$-BN in the AA configuration................................................................. 60

5.3 Comparison of absorption spectra for the $h$-BN monolayer obtained from linear response calculations within the IP, RPA and BSE approximations.............. 62

5.4 Comparison of absorption spectra for the $h$-BN bilayer obtained from linear response calculations within the IP, RPA and BSE approximations. The corresponding monolayer spectra (multiplied by a factor of 2) are shown in faded colours for comparison................................................................. 63

5.5 Comparison of absorption spectra for the MoS$_2$ monolayer obtained from linear response calculations within the IP and RPA approximations................................................................. 64

5.6 Comparison of absorption spectra for the $h$-BN bilayer obtained from linear response calculations within the IP and RPA approximations. The corresponding monolayer spectra (multiplied by a factor of 2) are shown in faded colours for comparison................................................................. 65

5.7 Schematic diagram of a bilayer composed of two monolayers, 1 and 2, which extend infinitely in the $x$- and $y$-directions and are separated by a distance $R$ along the $z$-axis. The monolayers are assumed to be isotropic and the external electric field, $E_{\text{EXT}}$, is directed along the monolayer plane (e.g. along the $x$-axis). 66

5.8 Time-dependent polarisation of the $h$-BN monolayer interacting with a delta-like external field of intensity $I_0 = 1$ W cm$^{-2}$ as calculated from the TD-BSE equation within the IP approximation................................................................. 68

5.9 The absorption spectrum of the isolated ($R \to \infty$) $h$-BN monolayer within the IP approximation as calculated via linear response (solid line) and the TD-BSE equation (crosses)................................................................. 69
5.10 Absorption of h-BN monolayers separated by a distance $R = 5$ a.u.. The dynamics of monolayer 1 are calculated via the TD-BSE while those of monolayer 2 are calculated via the PEOMs. The two monolayers are coupled through the external fields in Eq. (5.2) by means of the induced dipole moments. The LR absorption spectrum of an isolated monolayer is shown in grey for comparison.

5.11 Absorption spectrum of the simulated bilayer (the superposition of the spectra of monolayers 1 and 2) using the TD-BSE coupled with the PEOMS (RT-PEOM method) and two coupled sets of PEOMs (PEOM-PEOM method).

5.12 Comparison of IP absorption spectra for a bilayer of h-BN obtained by LR-TDDFT and the PEOM-PEOM method. For the PEOM-PEOM results, we compare for two different layer-separation distances: the physically correct distance of $R = 3.3$ Å and an effective distance of $R_{\text{eff}} = 8.5$ Å which gives the dominant absorption peak a similar intensity to that of the LR calculation. The spectrum for two isolated monolayers ($R \to \infty$) is shown in grey for comparison.

5.13 Comparison of the RPA absorption spectra for a bilayer of h-BN obtained by LR-TDDFT and the PEOM-PEOM method with $R_{\text{eff}} = 7$ Å. The spectrum for two isolated monolayers ($R \to \infty$) is shown in grey for comparison.

5.14 Comparison of the BSE absorption spectra for a bilayer of h-BN obtained by LR-BSE and the PEOM-PEOM method with $R_{\text{eff}} = 10$ Å. The spectrum for two isolated monolayers ($R \to \infty$) is shown in grey for comparison.

5.15 Same as Fig. 5.14 but with the PEOM-PEOM spectrum 'corrected' by incorporating an energy shift of $\omega_c = 0.59$ eV into the PEOMs.

5.16 Comparison of the IP (a) and RPA (b) absorption spectra for a bilayer of MoS$_2$ obtained within LR-TDDFT and the PEOM method with $R_{\text{eff}} = 100$ Å (a) and $R_{\text{eff}} = 120$ Å (b). The spectra for two isolated monolayers ($R \to \infty$) of MoS$_2$ are shown in grey for comparison.

5.17 (a) and (b) are the same as Fig. 5.13 and Fig. 5.16 (b) respectively but using the field with the exponential factor (see Eq. (5.12)) instead of the effective distance, $R_{\text{eff}}$. 

---

LIST OF FIGURES

ix

5.10 Absorption of h-BN monolayers separated by a distance $R = 5$ a.u.. The dynamics of monolayer 1 are calculated via the TD-BSE while those of monolayer 2 are calculated via the PEOMs. The two monolayers are coupled through the external fields in Eq. (5.2) by means of the induced dipole moments. The LR absorption spectrum of an isolated monolayer is shown in grey for comparison.

5.11 Absorption spectrum of the simulated bilayer (the superposition of the spectra of monolayers 1 and 2) using the TD-BSE coupled with the PEOMS (RT-PEOM method) and two coupled sets of PEOMs (PEOM-PEOM method).

5.12 Comparison of IP absorption spectra for a bilayer of h-BN obtained by LR-TDDFT and the PEOM-PEOM method. For the PEOM-PEOM results, we compare for two different layer-separation distances: the physically correct distance of $R = 3.3$ Å and an effective distance of $R_{\text{eff}} = 8.5$ Å which gives the dominant absorption peak a similar intensity to that of the LR calculation. The spectrum for two isolated monolayers ($R \to \infty$) is shown in grey for comparison.

5.13 Comparison of the RPA absorption spectra for a bilayer of h-BN obtained by LR-TDDFT and the PEOM-PEOM method with $R_{\text{eff}} = 7$ Å. The spectrum for two isolated monolayers ($R \to \infty$) is shown in grey for comparison.

5.14 Comparison of the BSE absorption spectra for a bilayer of h-BN obtained by LR-BSE and the PEOM-PEOM method with $R_{\text{eff}} = 10$ Å. The spectrum for two isolated monolayers ($R \to \infty$) is shown in grey for comparison.

5.15 Same as Fig. 5.14 but with the PEOM-PEOM spectrum ‘corrected’ by incorporating an energy shift of $\omega_c = 0.59$ eV into the PEOMs.

5.16 Comparison of the IP (a) and RPA (b) absorption spectra for a bilayer of MoS$_2$ obtained within LR-TDDFT and the PEOM method with $R_{\text{eff}} = 100$ Å (a) and $R_{\text{eff}} = 120$ Å (b). The spectra for two isolated monolayers ($R \to \infty$) of MoS$_2$ are shown in grey for comparison.

5.17 (a) and (b) are the same as Fig. 5.13 and Fig. 5.16 (b) respectively but using the field with the exponential factor (see Eq. (5.12)) instead of the effective distance, $R_{\text{eff}}$. 

---

LIST OF FIGURES

ix
List of Abbreviations

PV Photovoltaic
PCE Power conversion efficiency
h-BN Hexagonal boron nitride
TMD Transition metal dichalcogenide
MNP Metal nanoparticle
QD Quantum dot
SQD Semiconducting quantum dot
LR Linear response
RT Real-time
HF Hartree-Fock
CI Configuration-interaction
MP Møller-Plesset
DFT Density functional theory
TDDFT Time-dependent density functional theory
RT-TDDFT Real-time time-dependent density functional theory
LR-TDDFT Linear response time-dependent density functional theory
BSE Bethe-Salpeter equation
TD-BSE Time-dependent Bethe-Salpeter equation
LR-BSE Linear response Bethe-Salpeter equation
MBPT Many body perturbation theory
TDSE Time-dependent Schrödinger equation
TISE Time-independent Schrödinger equation
HK Hohenberg-Kohn
KS Kohn-Sham
LDA Local density approximation
ALDA Adiabatic local density approximation
GGA Generalised gradient approximation
HEG: Homogeneous electron gas
PP: Pseudopotential
BZ: Brillouin zone
GF: Green’s function
RWA: Rotating wave approximation
IP: Independent-particle
RPA: Random phase approximation
KBEs: Kadanoff-Bayn equations
COHSEX: Coulomb-hole pluse screened-exchange
QM: Quantum mechanics
MM: Molecular mechanics
RK4: Runge-Kutta fourth-order
QEH: Quantum-electrostatic heterostructure
FDTD: Finite-difference time-domain
EOM(s): Equation(s) of motion
PEOM: Projected equations of motion
PEOM-PEOM: Coupled projected equations of motion
PS: Primary system
SS: Secondary system
Chapter 1

Introduction

1.1 Nanostructured Media

In recent years much attention has been given to nanostructured materials and devices. Due to their atomic/molecular scales, nanostructures exhibit unique physical properties which can often be easily tuned simply by manipulating their size or geometry. Therefore, they have a wide range of applications including in the fields of biology, medicine, construction, technology and energy creation/storage, and are already being exploited in many consumer products. For example, metal nanoparticles can be used in the treatment of cancer using photothermal therapy [1]; nano-optical transistors may pave the way for quantum computing [2]; spray-on solar cells have been fabricated thanks to perovskite nanocrystals [3]; and quantum dot semiconductors are currently being used in the latest generation of TV panels [4].

So-called two-dimensional materials, such as graphene and monolayers of transition-metal dichalcogenides (TMDs), have proven to be particularly interesting due to radical shifts in their physical properties when transitioning from their bulk counterparts. For example, graphene has a much higher electron mobility than graphite (and more than 100 times that of silicon) making it extremely useful for electronic applications [5]. Similarly, a monolayer of MoS$_2$ has a direct band gap, as opposed to an indirect gap in bulk form, making it an efficient absorber of light and, therefore, a promising material for photovoltaic (PV) devices [6]. Moreover, the thinness of monolayer TMD PVs—which can be as much as 500,000 times thinner than traditional, polycrystalline silicon PVs—means cheaper production and installation costs along with a wider range of applications, such as virtually transparent solar cells that can, e.g., be placed on windows or LCD screens. However, the atomic thinness of such materials can sometimes hinder their effectiveness: because an MoS$_2$ monolayer has an inherently small optical cross section, it struggles to absorb much of the incident light. In turn, this results in poor power conversion...
efficiencies (PCEs) of MoS$_2$-based PVs: less than 10% compared with traditional technologies with PCEs typically between 20–40% [7]. It would, therefore, be advantageous to find a way to increase the absorption of light in TMD monolayers.

One method to increase absorption is to pair the semiconductor with metal nanoparticles (MNPs) where the surface plasmon resonance associated with the MNP generates a local field enhancement, thus increasing the field felt by the semiconductor. For example, in Ref. [8] the efficiency of dye-sensitised solar cells was increased by over 20% by incorporating gold nanoparticles. In Ref. [9], a 60-fold enhancement of the second-harmonic generation in RbTiOPO$_4$ crystals was reported by depositing silver nanostructures on the surface of the crystals. Further, the photocurrent [10], photoluminescence [11, 12] and absorption [12] in MoS$_2$ monolayers have all been shown to be enhanced by the presence of metallic nanostructures. These results have been demonstrated experimentally, but are hard to simulate theoretically, from an ab initio perspective, due to the computational limitations of current, state-of-the-art theory. It is the goal of this thesis to develop a method which allows such simulations to be carried out and, therefore, give insight into the physical processes involved in the plasmonic enhancement in metal-semiconductor hybrid materials.

1.2 Ab initio Modelling: Computational Limits

In principle, the electronic and optical properties of any material may be determined by knowledge of its wavefunction which can be obtained from the solution of the famous Schrödinger’s equation. Now, analytical solutions do not exist for systems of more than a few particles: however, approximate wavefunction-based theories exist such as Hartree-Fock, post-Hartree-Fock and, more recently, quantum Monte Carlo methods, although these approaches are often limited to relatively small systems due to computational demand. Non-wavefunction based reformulations of quantum mechanics have also proved a popular alternative, such as density matrix theory, density functional theory (DFT), and Green’s function based approaches, coupled with various approximations, and allow realistic calculations often to a high degree of accuracy. (See the beginning of Section 2.2.2 for a discussion on the various approaches mentioned above.)

Suppose we wish to calculate the absorption spectrum of an isolated monolayer of MoS$_2$. In reality, the monolayer will be a finite system containing a large number of electrons. For simulation purposes, the monolayer (or any solid, for that matter) is treated as an infinite system which can be described by a single unit cell, repeated periodically. For the case of MoS$_2$, the unit cell will contain just three atoms, with a volume of around 0.1 nm$^3$ (see Fig. 1.1 (a)). The current, state-of-the-art approach to obtain the spectrum is to first determine the ground state of the system via DFT, then solve the Bethe-Salpeter equation (BSE) from many body perturbation theory (MBPT) which includes excitonic effects within the system, important
in the case of MoS\textsubscript{2} (e.g. Refs [13–15]). Now suppose we wish to investigate the plasmonic enhancement created by the deposition of gold nanospheres onto the monolayer as, e.g., in Ref. [10]. Due to the size of the nanosphere (typically tens of nanometres), a large unit cell is required to simulate the system: in particular, this unit cell will contain possibly thousands more atoms than that of the isolated MoS\textsubscript{2} (see Fig. 1.1 (b)). Whilst it may be possible (though computationally costly) to calculate the spectrum within the simpler time-dependent DFT (TDDFT) framework, the sheer size of this system makes the solution of the demanding BSE unattainable.

![Figure 1.1: Schematic diagram of the unit cells corresponding to (a) an isolated MoS\textsubscript{2} monolayer and (b) the same monolayer, decorated with gold nanospheres.](image)

Now, while the MoS\textsubscript{2} monolayer exhibits strongly bound excitons, thus requiring the use of the BSE in the calculated absorption spectra [13], the nanoparticle possesses no such excitonic behaviour due to its metallic nature. Therefore, it would be computationally beneficial, and physically acceptable, to model the MNP response on a simpler level of theory than MBPT, while keeping the BSE description of the MoS\textsubscript{2}. Such hybrid methods already exist to describe, e.g., solvated molecules [16–18], protein-ligand interactions [19–21] and, indeed, other semiconductor-metal structures [22–29].

These approaches rely on the possibility to separate the composite system into two or more components whose dynamics are solved using different levels of approximation and to treat the residual interaction between the subsystems in an appropriate way. For example, a continuum solvation model (such as the polarisable continuum model) may be used in the solvated molecule problem where the molecule is treated using quantum mechanics (QM) and
the solvent treated as a dielectric continuum, the interaction being electrostatic in nature [16–
18, 30]. While the QM parts in such methods are often treated at the level of HF or DFT, more recent developments have used approaches based on MBPT, yielding a more accurate
description [31, 32]. Various quantum mechanics/molecular mechanics (QM/MM) approaches
have also been applied to model the protein-ligand interaction. In these cases, the ligand is
treated using QM and the protein environment via MM and the potentials associated with the
protein’s molecular make-up are approximated by means of classical force fields [19–21].

Hybrid methods have also been applied to model the coupling between molecules or quantum
dots (QDs) and metal nanoparticles (MNPs) upon optical excitation. For small MNPs, the
composite system may still be treated fully quantum mechanically, e.g. in Ref. [33] where a
jellium model is combined with TDDFT at the level of the local density approximation to
model a nanoparticle dimer. For larger MNPs, classical electrodynamics is employed to model
the MNP dynamics whereas a quantum description of the molecule is retained. In this case, the
interaction between the MNP and the molecule is modelled through an effective electromagnetic
coupling. These hybrid approaches make use of numerical methods such as the finite-difference
time domain (FDTD) to solve the classical electrodynamics problem — namely, the Maxwell’s
equations — while the dynamics of the molecular electrons are solved by means of TDDFT.
The overall dynamics are made self-consistent by including the electromagnetic field generated
by the MNP into the molecular evolution and vice versa [34–37].

More recently, a hybrid method has been introduced to simulate so-called Van der Waals
heterostructures such as those comprised of several layers of 2D TMDs. Similarly to the size-
difference problem illustrated in Fig. 1.1, these heterostructures require restrictively large su-
percells due to mismatches in the respective lattice parameters of the constituent TMD mono-
layers thus prohibiting accurate ab initio calculations of optical properties, especially at the
higher levels of theory. In Ref. [38], a semiclassical method called the quantum-electrostatic
heterostructure (QEH) model is developed. The QEH model takes elements of the dielectric
functions of the constituent, isolated monolayers and couples them in a purely electrostatic
sense via the Coulomb interaction by means of a coupled, Dyson-like equation to build an
approximate dielectric function of the resulting heterostructure. The computational demand,
therefore, rests solely on that of the quantum mechanical calculations of the individual dielectric
functions of the constituent monolayers.

1.3 Projected Equations of Motion Method

In this thesis, we develop a dynamical hybrid method for any complex material which can be
split into subsystems where the interaction between the systems is electromagnetic. This has
particular applicability to semiconductor-metal compounds, such as, e.g., the MoS$_2$ monolayer
decorated with gold nanoparticles [10], or the well-studied quantum dot-metal nanoparticle systems [22–29]. The method is simpler and much less computationally expensive than the existing FDTD approaches and avoids the solution of Maxwell’s equations when the near-field effects in the electromagnetic coupling between constituents are negligible.

We shall present a generalised model for treating the time-dependent interaction between a primary system (PS) and a secondary system (SS) coupled through an electromagnetic field. We shall call this method the Projected Equations of Motion (PEOM) method. By ‘primary system’, we mean the system of primary interest which may require a high level of theory in order to adequately describe its dynamics: e.g., a molecule, a QD, or a semiconductor monolayer. The choice of method for which to solve the dynamics of the PS is independent of the PEOM method, provided it is within a real-time framework. The secondary system is often a larger ‘environment’ which acts as a source of unavoidable perturbation to the primary system, though in principle it may also be a similar system to the PS: e.g., metal nanoparticles which are used to enhance the optical properties of the PS. The SS is modelled entirely from its linear, frequency-dependent polarisability. This may be obtained, e.g., by classical (or, indeed, quantum) simulations, analytical models, or alternatively by experiment. The frequency-dependent polarisability is fitted in order to produce parameters which enter into a set of projected equations of motion for the SS. These PEOMs may then be solved simultaneously with the equations of motion (EOMs) that give the dynamics of the PS. The interaction between the two systems is considered in the dipole-dipole approximation within the quasi-static limit, which respectively require the distances between the constituents to be relatively large compared to the size of the system and the wavelength of incident light to be much larger than the size of the system.

1.4 Layout of Thesis

In Chapter 2, we briefly introduce the concepts, theories and key equations involved with the state-of-the-art simulations of ground state and optical properties of electronic systems. In particular, we show what is meant by optical absorption in Section 2.1. In Section 2.2 we discuss how the ground state electronic wavefunction should be obtained by the time-independent Schrödinger equation, before introducing density functional theory. We then show how the time-dependent Schrödinger equation is required to simulate optical absorption in Section 2.3 and introduce the density matrix formalism. Here we also derive the linear response equations from time-dependent density functional theory (for periodic systems) which directly yield formulas for the absorption spectra. The Bethe-Salpeter equation from many-body perturbation theory is then discussed within both linear response and its time-dependent form.

The projected equations of motion (PEOM) method is introduced and derived in Chapter 3. In Section 3.3 a test is performed on an isolated metal nanoparticle to show that the proposed
PEOMs reproduce the frequency-dependent polarisability from which they were fitted.

In Chapter 4, the PEOM method is then applied to a semiconducting quantum dot-metal nanoparticle (SQD-MNP) hybrid system to study both the energy absorption rates (response to a monochromatic wave) and population inversion (response to pulsed radiation). In both cases, the PEOM results are compared with analytical and semi-analytical results from the literature.

In Chapter 5 the absorption spectra for bilayers of MoS$_2$ and hexagonal boron nitride (h-BN) are obtained via the standard approaches of TDDFT and the BSE within linear response. As a proof of concept, we show that similar spectra may be reproduced by coupling PEOMs (fitted from the respective monolayers of MoS$_2$ and h-BN) either with the time-dependent BSE or with an additional set of PEOMs (the so-called PEOM-PEOM method).

Finally, conclusions and future work are presented in Chapter 6.
Chapter 2

Background Theory

In this chapter, before deriving the PEOM method in Chapter 3, we introduce some underlying theory and also give an overview of existing \textit{ab initio} approaches that we shall use to simulate the optical properties of materials from a quantum mechanical perspective.

In particular, in Section 2.1 we define the polarisation and dielectric function and show how optical absorption spectra may be obtained through it. Now, in principle the physical process of absorption involves perturbing the ground state electronic configuration of a system (Section 2.2) which must first be known before absorption simulations can be performed. Therefore, in Section 2.2.2 we introduce Density Functional Theory (DFT) (in particular, within the Kohn-Sham scheme (Section 2.2.3)) as a means to obtain the ground state electronic structure.

In Section 2.3, we then present methods for simulating the interaction of the ground state system with a perturbing, external potential. These methods include density matrix formalism which is a reformulation of the wavefunction-based Schrödinger equation, within a time-dependent framework, and is useful for treating the dynamics of few-level systems. It is applied to a two-level semiconducting quantum dot in Chapter 4 to simulate energy absorption rates and population inversion in the system when coupled to a metal nanoparticle via the PEOM method.

The time-dependent version of DFT (TDDFT) is introduced in Section 2.3.3 in both its time-dependent form and within linear response (LR) where the external perturbation is considered to be sufficiently weak. DFT and LR-TDDFT are then specified for extended systems (e.g. solids) in Section 2.3.4 where periodic boundary conditions are required. In Section 2.3.5, we explain how TDDFT cannot readily describe excitonic effects (electron-hole interactions) which play an important role in the absorption spectra of certain materials and we introduce the Bethe-Salpeter equation (BSE) (within the linear response regime) which can capture such interactions through a many-body theory involving the so-called Green’s functions. The BSE
is extended beyond the linear regime in Section 2.3.6 by introducing an equation of motion for the time-dependent, non-equilibrium Green’s function which is equivalent to a time-dependent BSE (TD-BSE). LR-TDDFT and the LR-BSE are used in Chapter 5 to obtain optical spectra of monolayers and bilayers of transition metal dichalcogenides and the TD-BSE is then coupled with the PEOM method to simulate the same spectra for the bilayers as a proof of concept.

2.1 Polarisation, the Dielectric Function and Absorption

When a material interacts with an electric field, $E$, the electrons within the material are displaced from their equilibrium position. The dipole moment, $p$, is the product of a particle’s charge, $q$, and its displacement from equilibrium, $r$, i.e.

$$p = qr.$$  

(2.1)

The polarisation (or polarisation density), $P$, is the average dipole moment per unit volume,

$$P = N_a p,$$  

(2.2)

where $N_a$ is the number of particles per unit volume. In the linear regime, where the average displacements are small (e.g. for an external field of low intensity), the polarisation is linked to the field by means of the electric susceptibility, $\chi_e$,

$$P(\omega) = \chi_e(\omega)E(\omega),$$  

(2.3)

where $\omega$ is the angular frequency and we have given the definition in frequency space having assumed a uniform electric field and an isotropic, homogeneous material. Similarly, the dipole moment is related to the electric field by the polarisability, $\alpha$,

$$p(\omega) = \alpha(\omega)E(\omega).$$  

(2.4)

The electric susceptibility is related to the macroscopic dielectric function, $\epsilon_M$, by

$$\epsilon_M = 1 + 4\pi\chi_e.$$  

(2.5)

The susceptibility, $\chi_e$ (and, hence, $\epsilon_M$ and $\alpha$), are generally complex and frequency-dependent. A material is isotropic if the polarisation is parallel to the external field, in which case $\chi_e$ is

---

1We use CGS units throughout the thesis unless otherwise specified.
simply a scalar. In general though, the direction of polarisation may be different to that of the external field in which case the material is anisotropic and the susceptibility is now a rank-2 tensor,

$$\chi = \begin{bmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{bmatrix}. \quad (2.6)$$

If the polarisation and external field are written in Cartesian coordinates ($P = P_x i + P_y j + P_z k$ and $E = E_x i + E_y j + E_z k$), then the $i$-th component ($i = x, y, z$) of the polarisation is given by

$$P_i = \chi_{ix}E_x + \chi_{iy}E_y + \chi_{iz}E_z. \quad (2.7)$$

For simplicity, we always assume isotropic media in this thesis, unless otherwise stated.

The complex refractive index, $n$, of a material determines how an electromagnetic wave propagates through it. For non-magnetic materials, it is related to the dielectric function by

$$\epsilon_M = n^2. \quad (2.8)$$

Since $n$ and $\epsilon_M$ are in general complex, we shall denote them by their real and imaginary parts:

$$n = n_1 + in_2, \quad (2.9)$$

$$\epsilon_M = \epsilon_1 + i\epsilon_2. \quad (2.10)$$

For a plane wave of amplitude, $E_0$, and frequency, $\omega$, propagating (say, in the $z$-direction) through a medium of refractive index, $n$, it can be shown that the intensity, $I(z)$, of the field decreases exponentially,

$$I(z) = \frac{cn_1}{8\pi}E_0^2 e^{-2\omega n_2 z/c}, \quad (2.11)$$

where $c$ is the speed of light in a vacuum. The penetration depth, $\delta_p$, is the distance at which the intensity is reduced by $1/e$. The absorption coefficient is defined as $\alpha_{\text{abs}} = 1/\delta_p$ and from Eqs. (2.8) and (2.11) it can be shown that

$$\alpha_{\text{abs}} = \frac{\omega \epsilon_2}{cn_1}. \quad (2.12)$$

Alternatively, since $\epsilon_M$ and $n$ are linked by Eq. (2.8), then knowledge of $\epsilon_M$ (or $n$) alone gives information about the optical absorption. Therefore, it is common to define the absorption, Abs, simply as

$$\text{Abs} = \text{Im}[\epsilon_M]. \quad (2.13)$$

We also note that the real part of the dielectric function can be retrieved from the imaginary
part via the Kramers-Kronig relation (e.g. see Section 1.7 in Ref. [39]).

Now, in this section we have described absorption as a frequency-dependent property of the system. For example, in experiment one might shine light from a monochromatic source of various frequencies on a material and measure the light absorption for each frequency to construct the absorption spectrum as a function of frequency. Of course, each part of that process involves light interacting with the system in time, and so the time-dependent forms of the previous equations may also be useful. E.g., an expression for the time-dependent polarisation may be obtained by taking the Fourier transform of Eq. (2.3) within the causality condition,

$$P(t) = \int_0^\infty \chi_e(t - t')E(t')dt',$$

where we have assumed the equilibrium condition with time-translational invariance. In this case, we have a time-dependent response function, $\chi_e(t - t')$, and the polarisation depends on the entire history of the interaction of the system with the field. However, the frequency-dependent form is most useful as this is what is calculated in spectroscopic experiments and readily gives information about the properties of the system of interest. Therefore, if the time-dependent polarisation is produced from real-time simulations, it is often Fourier transformed onto frequency space for analysis and comparison with experiment.

## 2.2 Electronic Structure Calculations

In order to calculate the polarisation (and, hence, absorption) of a system, we must first have knowledge of the electronic configuration in the ground-state. Solid state matter can be considered as a collection of nuclei and electrons interacting with each other. These interactions depend on the particles’ positions as well as external forces and determine the electrical and optical properties of the material. In this section, we discuss how the electronic energies and wavefunctions may be obtained from the Schrödinger equation and briefly introduce density functional theory, highlighting the main equations and concepts relevant to this thesis. For detailed discussions and derivations, the reader is referred to literature such as Refs [40–49].

### 2.2.1 The Time-Independent Schrödinger Equation

Suppose we have a system of $N$ electrons and $M$ nuclei with spatial coordinates $r_1, \ldots, r_N$ and $R_1, \ldots, R_M$, respectively. Neglecting electronic spin, the system can be fully described by the quantum-mechanical wavefunction, $\Psi_{\text{tot}}(r_1, \ldots, r_N, R_1, \ldots, R_M)$, from which all observable properties of the system can be determined. In electronic structure calculations, the goal is to find the wavefunction which yields the lowest possible (ground-state) energy. In principle, this
is found by solving the time-independent Schrödinger equation (TISE),

\[
\hat{H}_{\text{tot}} \Psi_{\text{tot}}(r_1, \ldots, r_N, R_1, \ldots, R_M) = E_{\text{tot}} \Psi_{\text{tot}}(r_1, \ldots, r_N, R_1, \ldots, R_M),
\]

(2.15)

where \( \hat{H}_{\text{tot}} \) is the Hamiltonian operator of the system. \( \hat{H}_{\text{tot}} \) contains contributions from the kinetic energy of the electrons and nuclei, along with electron-electron, electron-nuclei and nuclei-nuclei interactions, i.e.

\[
\hat{H}_{\text{tot}} = \hat{T}_e + \hat{T}_n + \hat{V}_{e-e} + \hat{V}_{e-n} + \hat{V}_{n-n}.
\]

(2.16)

Eq. (2.15) is an eigenvalue problem, with an infinity of solutions: the solution yielding the lowest value of \( E_{\text{tot}} \) is the ground state configuration. Solving Eq. (2.15) is generally extremely complicated with an analytical solution existing only for a small subset of problems. Therefore, several approximations and methodologies exist to simplify the task.

The first approximation is to separate the electronic and nuclear motions of the system. This is known as the Born-Oppenheimer approximation and allows us to express the total wavefunction as a product of an electronic wavefunction and nuclear wavefunction (and the total energy as a sum of the electronic and nuclear contributions). It is valid provided the electrons move on a much smaller time-scale than that of the nuclei.

We, therefore, reduce the original problem to finding just the electronic wavefunction, \( \Psi(r_1, \ldots, r_N) \), which satisfies

\[
\hat{H} \Psi(r_1, \ldots, r_N) = E \Psi(r_1, \ldots, r_N).
\]

(2.17)

\( \hat{H} \) is the electronic Hamiltonian given by

\[
\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-n}.
\]

(2.18)

The explicit nuclear contributions may then be obtained separately and included ad hoc. In Eq. (2.18),

\[
\hat{T}_e = \sum_i -\frac{1}{2} \nabla_i^2
\]

(2.19)

is the operator defining the total kinetic energy of the electrons,

\[
\hat{V}_{e-e} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}
\]

(2.20)
gives the total Coulomb repulsion between the electrons, and

\[ \hat{V}_{\text{e-n}} = \sum_i v_{\text{ext}}(r_i) \]  

(2.21)

where \( v_{\text{ext}}(r) \) is the potential representing the total nuclear attraction of the electrons in addition to any other external potential. Notice that we use atomic units throughout this thesis unless otherwise stated, i.e.

\[ -e = m_e = \hbar = \frac{1}{4\pi\epsilon_0} = 1, \]  

(2.22)

where \(-e\) is the electronic charge, \(m_e\) is the mass of an electron, \(\hbar\) is the reduced Planck’s constant and \(\epsilon_0\) is the permittivity of free space.

The observable, \(A\), of any operator, \(\hat{A}\), is given by its expectation value,

\[ A \equiv \left\langle \Psi \right| \hat{A} \left| \Psi \right\rangle \]  

(2.23)

\[ = \int \Psi^*(r_1, \ldots, r_N) \hat{A} \Psi(r_1, \ldots, r_N) dr_1 \ldots dr_N, \]  

(2.24)

and it follows from Eq. (2.17) that the total (electronic) energy of the system is

\[ E = \left\langle \Psi \right| \hat{H} \left| \Psi \right\rangle. \]  

(2.25)

Now, Eq. (2.15) is extremely computationally demanding to solve even for a system of a few electrons. Therefore, various methods exist to simplify the problem including Hartree-Fock and perturbation theory where the dimensionality of the wavefunction is reduced. Alternatively, the wavefunction may be reformed into a density functional which can also be used to calculate the observables of the system: this method is known as density functional theory and is much more accurate than Hartree-Fock and much more scalable than the perturbative approaches.

### 2.2.2 Density Functional Theory (DFT)

Hartree-Fock (HF) theory provides a way of approximating the ground state energy of an interacting, \(N\)-electron system by expressing the corresponding wavefunction as a linear combination of products of one-electron atomic orbitals, \(\{\psi_k(r)\}\), (which are assumed to be orthonormal) in the form of a single Slater determinant, i.e.

\[ \Psi(r_1, \ldots, r_N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N) \end{vmatrix}. \]  

(2.26)
This enforces the antisymmetry requirement of the wavefunction imposed by the Pauli exclusion principle. By minimising the energy, $E$, in Eq. (2.17), HF finds the ‘best’ orbitals which ensures the Slater determinant wavefunction yields the lowest possible energy (i.e. the best approximation to the ground state energy given the Slater form of the wavefunction).

HF is an independent-particle model, with electron-electron interaction only accounted for by an average Coulomb potential and a non-local exchange potential arising from the antisymmetry property of the Slater determinant. The approximation, therefore, lacks any electron correlation (other than in the average sense) and may lead to large errors in the energy: for example, band gaps in some semiconductors and bond-length in some molecules are badly described. Correlation can be further included in post-Hartree-Fock methods such as configuration interaction (CI) in which the wavefunction is expanded in a linear combination of Slater determinants, and Møller-Plesset (MP) perturbation theory where the correlation potential is modelled through a perturbation to the Fock Hamiltonian. More recently, novel approaches have been developed which can yield results similar to full-CI but with much less computational demand making for viable alternatives towards treating real systems (e.g., the full configuration-interaction quantum Monte Carlo method which employs a stochastic approach [50, 51]).

While these methods may improve the results of HF (and, indeed, can be used to systematically approach the exact results), the computational expense is large and their use is limited to small systems: for example the computational requirements for MP2, MP3 and MP4 methods scales with the number of electrons as $O(N^5)$, $O(N^6)$ and $O(N^7)$ respectively. Density Functional Theory (DFT), on the other hand, provides a much more computationally efficient procedure for approximating the ground state observables with methods yielding scaling ranging from $O(N^4)$ to linear scaling $O(N)$. For example, linear-scaling DFT can be used to model systems containing tens of thousands to millions of atoms (albeit with varying degrees of accuracy).

Whereas the HF method minimises the energy of an approximate Hamiltonian with respect to an approximate wavefunction, DFT models the energy as a functional of the electron density and the exact ground state energy is, in principle, found by minimising the energy of the exact Hamiltonian with respect to the electron density. We define the one-electron density function for an $N$-electron wavefunction as

$$
\rho(r) = N \int |\Psi(r_1, r_2, \ldots, r_N)|^2 \, dr_2 \ldots dr_N.
$$

(2.27)

From Eqs. (2.18) to (2.21), we can see that the Hamiltonian is uniquely determined by the number of electrons, $N$, and the system-dependent external potential, $v_{\text{ext}}(r)$, which is defined by the positions and charges of the nuclei, and from Eq. (2.18) and Eq. (2.25), the total energy
of an \( N \)-electron system is

\[
E = \langle \psi | \hat{H} | \psi \rangle = \langle \psi | T_e | \psi \rangle + \langle \psi | V_{e-e} | \psi \rangle + \langle \psi | V_{e-n} | \psi \rangle = T_e + V_{e-e} + V_{e-n} .
\]  

\( (2.28) \)

The formulation of DFT begins with the first Hohenberg-Kohn (HK) theorem which implies that the electron density, \( \rho(r) \), uniquely determines the external potential, \( v_{\text{ext}}(r) \), and thus uniquely determines the Hamiltonian. The energy must, therefore, be a functional of the density, \( E \equiv E[\rho] \), i.e. from Eq. (2.28),

\[
\]  

\( (2.29) \)

Using Eqs. (2.21), (2.25) and (2.27), it is easy to show that

\[
V_{e-n}[\rho] = \int v_{\text{ext}}(r)\rho(r)dr ,
\]  

\( (2.30) \)

so that Eq. (2.29) can be rewritten as

\[
E[\rho] = T_e[\rho] + V_{e-e}[\rho] + \int v_{\text{ext}}(r)\rho(r)dr = F[\rho] + \int v_{\text{ext}}(r)\rho(r)dr ,
\]  

\( (2.31) \)

where \( F[\rho] \) is a universal potential, independent of the system.

Now, the second HK theorem states that the ground state energy may be obtained by minimising \( E[\rho] \) in Eq. (2.31) with respect to \( \rho \) under the constraint that the density is derived from a normalised wavefunction, which is equivalent to requiring

\[
\int \rho(r)dr = N .
\]  

\( (2.32) \)

Since Eq. (2.31) is the exact energy of the original Hamiltonian, then the density which makes \( E \) minimum is the ground state density, \( \rho_{\text{GS}} \), and the exact ground state energy is

\[
E_{\text{GS}} = E[\rho_{\text{GS}}] .
\]  

\( (2.33) \)

Hence, DFT provides a way to find the ground state energy of an \( N \)-electron system by considering the density which depends only on the three spatial variables. Conversely, the solution of the original TISE depends on \( 3N \) variables, so the computational cost is drastically reduced. Unfortunately, however, it is not possible to explicitly and exactly express \( F[\rho] \) in terms of
the electron density, $\rho(r)$, as we did for the external potential in Eq. (2.30). If it were possible, then we would have a method for determining exactly all (ground state) observables in a quantum-mechanical system by self-consistently solving Eq. (2.31) by changing the density (which depends on only the 3 spatial variables), thus avoiding trying to solve the TISE using a wavefunction approach (which in principle depends on $3N$ variables). Furthermore, though we may find a density that minimises the energy to get the ground state energy, we have no way of verifying that this density corresponds to a true (in the physical sense) wavefunction, which must obey anti-symmetry requirements set by the Pauli exclusion principle. Kohn-Sham DFT provides a solution to this as well as expressing the universal potential in Eq. (2.31) in a more explicit form to realise the calculation of the majority of the total energy.

**2.2.3 Kohn-Sham DFT**

In the Kohn-Sham (KS) scheme, similarly to HF, we derive the density from a fictitious system of $N$ independent electrons, with a wavefunction expressed by a single Slater determinant (Eq. (2.26)) composed of one-electron atomic orbitals, $\{\phi_i(r)\}$, thus ensuring the anti-symmetry property is obeyed. In KS DFT, we require the density, which, due to the determinant nature of the wavefunction, is simply (from Eqs. (2.26) and (2.27))

$$
\rho(r) = \sum_i \phi_i^*(r)\phi_i(r), \quad (2.34)
$$

to be the same as that of the exact ground state wavefunction, even though it is derived from the approximate, Slater determinant wavefunction describing the non-interacting system.

By making use of the properties of the Slater determinant, we can rewrite the total energy as

$$
E[\rho] = -\frac{1}{2} \sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle + \frac{1}{2} \int \int \frac{\rho(r')\rho(r)}{|r-r'|} dr' dr + \int v_{\text{ext}}(r)\rho(r) dr + E_{\text{xc}}[\rho]. \quad (2.35)
$$

The first two terms in Eq. (2.35) are the non-interacting contributions to the kinetic energy and average Coulomb repulsion, respectively. The first three terms describe most of the total energy of the system, and all other correlation and exchange energy not accounted for in the independent particle approximation are collected in the abstract *exchange-correlation energy*, $E_{\text{xc}}[\rho]$.

Upon minimising $E[\rho]$ in Eq. (2.35) with respect to $\rho$ with the normalisation constraint Eq. (2.32), it can be shown that the required KS orbitals satisfy the following equation,

$$
\hat{H}^{\text{KS}} \phi_i(r) = \epsilon \phi_i(r). \quad (2.36)
$$
\( \hat{H}^{\text{KS}} \) is the one-electron KS Hamiltonian,
\[
\hat{H}^{\text{KS}} = -\frac{1}{2} \nabla^2 + \int \frac{\rho(r')}{|r - r'|} dr' + v_{\text{ext}}(r) + v_{\text{xc}}[\rho](r),
\]
with \( v_{\text{xc}}[\rho](r) \) being the local multiplicative exchange-correlation potential defined as the functional derivative of the exchange-correlation energy w.r.t. the density, i.e.
\[
v_{\text{xc}}[\rho](r) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}. \tag{2.38}
\]
Since \( \hat{H}^{\text{KS}} \) depends on the density, we start with a trial density as a first approximation and solve Eq. (2.36) self consistently until the total energy in Eq. (2.35) has converged. If \( E_{\text{xc}} \) is the exact functional corresponding to the true system, then the total energy will converge to the exact ground-state, yielding also the exact ground-state density which can be used to find exactly all other ground-state observables.

Of course, \( E_{\text{xc}} \), cannot be expressed exactly and we, therefore, rely on approximations to the true exchange-correlation energy. Many such approximate functionals exist and though \( E_{\text{xc}} \) is in theory a universal functional, the approximations used are often chosen to best describe a given system of interest. The two most popular exchange-correlation potentials (at least for periodic structure calculations) are the local density approximation (LDA) and the generalised gradient approximation (GGA). The LDA is the simplest approximation, derived from a model of the homogeneous electron gas (HEG), and depends \( \text{locally} \) on the spatial value of the density. The GGA is considered an improvement over the LDA as it depends on both the local density and its gradient. Many other functionals exist often based on semi-empirical formulations which are tailored towards specific systems. For an extensive list of existing functionals see, e.g., Ref. [52].

The large number of exchange-correlation approximations available (with certain approximations involving parameters taken directly from experiment) means that KS DFT becomes a somewhat semi-empirical method and not a true \( \text{ab initio} \) theory, unlike HF. Moreover, while there may be methods of systematically improving the functionals (such as orbital-dependent functionals and the optimised effective potential method, e.g. Refs. [53, 54]), they often come with the same computational effort as post-HF and other wavefunction-based approaches. Of course, the wide use of DFT in modern quantum-chemical calculations is testament to its efficiency and overall accuracy when compared to other methods.

2.3 Excited State Calculations

In Section 2.2, we discussed methods for obtaining the ground-state electronic configuration of a system. In order to determine, e.g., optical properties, we require a time-dependent the-
ory to simulate the interaction with a time-dependent field (i.e. electromagnetic radiation) with the system. In this section, we briefly introduce the time-dependent wavefunction via the time-dependent Schrödinger equation, which in principle can be used to describe optical phenomena. We then discuss various alternative methods including the density matrix approach, time-dependent density functional theory and the Bethe-Salpeter equation from many-body perturbation theory. Again, these methods are only briefly discussed with attention given to the key equations applicable to this thesis (namely, for obtaining the macroscopic dielectric function). For detailed discussion and derivations, the reader is referred to literature including Refs [39, 55–62].

2.3.1 The Time-Dependent Schrödinger Equation

We seek the time-dependent wavefunction, \( \Psi(t) \), for the electronic system (note that the wavefunction also depends on the electronic coordinates, but we use the notation \( \Psi(t) \equiv \Psi(r_1, \ldots, r_N, t) \) for simplicity). It can be found by solving the time-dependent Schrödinger equation (TDSE),

\[
\hat{H} \Psi(t) = i \frac{\partial}{\partial t} \Psi(t) ,
\]

where the Hamiltonian is now time-dependent also (c.f. Eq. (2.18)), i.e.

\[
\hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{\text{ext}}(t) .
\]

\( \hat{V}_{\text{ext}}(t) \) includes, e.g., the nuclear attraction in addition to any externally applied potential,

\[
\hat{V}_{\text{ext}}(t) = \sum_i v_{\text{ext}}(r_i, t) .
\]

In order to solve Eq. (2.39), we require knowledge of the initial state of the system. We may assume that the system starts in the ground-state, but as discussed in Section 2.2, a many-electron, ground-state wavefunction is difficult to calculate, let alone determine its propagation in time. Time-dependent density functional theory (TDDFT) is the time-dependent counterpart to DFT, which provides an efficient, wavefunction-free method for simulating the dynamics and properties of any given system. The density matrix formalism of quantum mechanics also provides an alternative to the wavefunction-based TDSE and is useful for describing the dynamics of few-level systems.
### 2.3.2 Density Matrix Formalism

We define the matrix representation of an operator, $\hat{A}$, as

$$A_{mn} = \langle \psi_m | \hat{A} | \psi_n \rangle ,$$  \hspace{1cm} (2.42)

where $\{\psi_n\}$ is a complete set of orthonormal wavefunctions. We then expand the time-dependent, $N$-electron wavefunction as

$$\Psi(t) = \sum_n c_n(t) \psi_n ,$$  \hspace{1cm} (2.43)

where $c_n(t)$ is the time-dependent probability amplitude that the system is in the eigenstate $\psi_n$.

The density operator is defined as

$$\hat{\rho}(t) = \Psi(t) \Psi^*(t) ,$$  \hspace{1cm} (2.44)

which is simply the probability of finding the $N$ electrons in positions $r_1, \ldots, r_N$ at time $t$. From Eqs. (2.42) and (2.43), it can be shown that the matrix elements of the density operator are

$$\rho_{mn}(t) = c_m(t) c_n^*(t) ,$$  \hspace{1cm} (2.45)

Note that the diagonal elements are

$$\rho_{nn}(t) = |c_n(t)|^2 ,$$  \hspace{1cm} (2.46)

which is the probability that the system is in eigenstate $\psi_n$ at time $t$ (also known as the population of the state). The off-diagonal elements do not have a straightforward physical interpretation, but we can see that $\rho_{mn}$ will be nonzero only if $\psi_m$ and $\psi_n$ are ‘populated’ in that their coefficients, $c_m(t)$ and $c_n(t)$, must both be nonzero. $\rho_{nm}$ is, therefore, said to give the ‘coherence’ between eigenstates $m$ and $n$ and is related to the ‘mixing’ of these levels within $\Psi(t)$. From Eq. (2.45), it is also clear that the density matrix is Hermitian:

$$\rho_{nm}(t) = \rho_{mn}^*(t) .$$  \hspace{1cm} (2.47)

Provided $\Psi(t)$ is normalised, we have that $\langle \Psi(t) | \Psi(t) \rangle = 1$ so from Eq. (2.43) it can be
shown that

\[ \sum_n |c_n(t)|^2 = 1 . \quad (2.48) \]

Eq. (2.48) implies that the total population is conserved. It is easy to show that this requires the trace (sum of diagonal elements) of the density matrix to be unity:

\[ \text{tr} (\rho(t)) \equiv \sum_n \rho_{nn}(t) \]
\[ = 1 . \quad (2.49) \]

(2.50)

Usefully, the expectation value, \( A(t) \), of any operator, \( \hat{A} \), at time \( t \) reduces to

\[ A(t) = \langle \Psi(t) \mid \hat{A} \mid \Psi(t) \rangle \]
\[ = \sum_{nm} \rho_{nm}(t) A_{mn} \]
\[ = \text{tr} (\rho(t) A) . \quad (2.53) \]

Further, by substituting Eq. (2.43) into the TDSE (Eq. (2.39)), we arrive at the following density matrix expression of the TDSE, which is known as the von Neumann equation of motion or the master equation,

\[ \dot{\rho} = -i [\hat{H} , \rho] , \quad (2.54) \]

where the commutator is

\[ [\hat{A} , \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} , \quad (2.55) \]

Hence, by integrating Eq. (2.54), we can get \( \rho(t) \) and then from Eq. (2.53) we can determine the time-dependent nature of any observable.

Note that while Eq. (2.54) is a direct reformulation of the TDSE, it is also possible to include phenomenological effects which may not be easily incorporated into the system Hamiltonian. An example might be photoionisation, where population transfers out of the system, or spontaneous emission where the population transfers between states. The following is a simple model where the matrix, \( \Gamma \), contains damping coefficients,

\[ \dot{\rho} = -i [\hat{H} , \rho] - \Gamma \circ \left( \rho - \rho^{(\text{eq})} \right) , \quad (2.56) \]

where \( \circ \) is the element-wise matrix multiplication operator and \( \rho^{(\text{eq})} \) is the equilibrium value of the density matrix. In Eq. (2.56), it is worth noting that, depending on the choice of \( \Gamma \) and \( \rho^{(\text{eq})} \), the conservation of population (Eq. (2.48)) may be violated (which may, however, be the
desired effect).

2.3.3 Time-Dependent DFT and Linear Response

In TDDFT, we wish to solve the TDSE in Eq. (2.39) by means of the one-electron density, which is now time-dependent (c.f. Eq. (2.27)),

\[ \rho(r, t) = N \int |\Psi(r, r_2, \ldots, r_N, t)|^2 dr_2 \ldots dr_N. \] (2.57)

In Section 2.2.2, we mentioned that ground state DFT is founded on the Hohenberg-Kohn theorem which gives a unique mapping between the external potential, \( v_{\text{ext}}(r) \), and the one-electron density, \( \rho(r) \). Similarly, in TDDFT the Runge-Gross theorem gives a one-to-one mapping between the time-dependent potential, \( v_{\text{ext}}(r, t) \), and the density, \( \rho(r, t) \), where the \( N \)-electron wavefunction, \( \Psi(r_1, \ldots, r_N, t) \) evolves from the ground state wavefunction, \( \Psi_{\text{GS}}(r_1, \ldots, r_N) \) (or, indeed, any fixed initial state). Thus, any time-dependent observable may be represented in terms of the density.

In the Kohn-Sham scheme we again represent the \( N \)-electron wavefunction as a Slater determinant (c.f. Eq. (2.26)) with a set of time-dependent orbitals, \( \{\varphi_i(r, t)\} \), so that the density can be written as

\[ \rho(r, t) = \sum_i |\varphi_i(r, t)|^2. \] (2.58)

Analogously to Eq. (2.36) in KS-DFT, each of the orbitals obey the following time-dependent KS equation (from the TDSE, Eq. (2.39)),

\[ \hat{H}^{\text{KS}}\varphi_i(r, t) = i \frac{\partial}{\partial t}\varphi_i(r, t), \] (2.59)

where \( \hat{H}^{\text{KS}} \) is the time-dependent KS Hamiltonian (c.f. Eq. (2.37)),

\[ \hat{H}^{\text{KS}} = -\frac{\nabla^2}{2} + v_{\text{H}}[\rho](r, t) + v_{\text{ext}}(r, t) + v_{\text{xc}}[\rho](r, t), \] (2.60)

where

\[ v_{\text{H}}[\rho](r, t) = \int \frac{\rho(r', t)}{|r - r'|} dr'. \] (2.61)

is the time-dependent Hartree potential and \( v_{\text{xc}}[\rho](r, t) \) is the time-dependent exchange-correlation potential which in practice must be approximated.

While directly solving the time-dependent Kohn-Sham equations in Eq. (2.59) is feasible (we call this framework real-time TDDFT (RT-TDDFT)), it is often computationally demanding, especially for large systems. Nevertheless, obtaining a fully time-resolved description of the system dynamics may be necessary to model certain phenomena such as high harmonic
generation where short, intense laser pulses are involved which cause large fluctuations in the electron density. Indeed, several implementations of RT-TDDFT do exist such as in the popular Octopus \cite{63} and NWChem \cite{64} codes. On the other hand, if the incident radiation is relatively weak (such as in the case of most optical absorption experiments), then the electron density varies only a small amount from the ground state density and one may consider the linear response (LR) regime which directly yields frequency-dependent observables.

Now, the absorption of light in a material can be described by the imaginary part of its macroscopic dielectric function, $\epsilon_M$ (see Section 2.1), which may be obtained by an appropriate averaging of the microscopic dielectric function which is given by

$$\epsilon^{-1}(r, r', t-t') = \delta(r - r')\delta(t - t') + \int \frac{1}{|r - r''|} \chi(r', r'', t - t') dr'' . \tag{2.62}$$

$\chi$ is the (linear) density-density response of the system to the external potential, $v_{\text{ext}}(r, t)$, defined via

$$\delta \rho(r, t) = \iint \chi(r, r', t - t') v_{\text{ext}}(r', t') dt' dr' , \tag{2.63}$$

and describes the first-order perturbation to the electron density.

From Eq. (2.60), the total, time-dependent potential felt by the Kohn Sham system is

$$v_{\text{eff}}(r, t) = v_H[\rho](r, t) + v_{\text{xc}}[\rho](r, t) + v_{\text{ext}}(r, t) .\tag{2.64}$$

Analogously to Eq. (2.63), the perturbation to the KS electron density is then given by

$$\delta \rho(r, t) = \iint \chi_0(r, r', t - t') v_{\text{eff}}(r', t') dt' dr' , \tag{2.65}$$

where $\chi_0(r, r', t - t')$ is known as the non-interacting density-density response, as it describes the response of the non-interacting, artificial KS system to the effective, average KS potential, $v_{\text{eff}}(r, t)$.

It can be shown that $\chi_0$ may be written as a sum of independent transitions from valence to conduction states, in the following Lehmann representation,

$$\chi_0(r, r', \omega) = \sum_{i,j} \frac{f_i - f_j}{\omega - (\epsilon_j - \epsilon_i) + i\eta} \varphi_i^*(r) \varphi_j(r) \varphi_j^*(r') \varphi_i(r') , \tag{2.66}$$

where $\{\varphi_i(r)\}$ are the Kohn-Sham orbitals obtained by solving the ground state KS equations in Eq. (2.36), $f_i$ is the occupation number of $\varphi_i$, and the limit $\eta \to 0^+$ should be taken. In practice, however, $\eta$ is taken to be finite in order to broaden the spectra to match experimental data, representing phenomenological damping caused by external interactions (in this case, $\eta$ is known as the damping term). The original, exact density-density response can then be found
via $\chi_0$ by the following Dyson-like equation,

$$\chi(r, r', t - t') = \chi_0(r, r', t - t') + \iiint \chi_0(r, r_1, t - t_1) K(r_1, r_2, t_1 - t_2) \chi(r_2, r', t_2 - t') dt_1 dr_1 dt_2 dr_2 , \quad (2.67)$$

where $K$ is the kernel given by

$$K(r, r', t - t') = \frac{1}{|r - r'|} \delta(t - t') + f_{xc}(r, r', t - t') , \quad (2.68)$$

where $f_{xc}$ is the exchange-correlation kernel (analogous to Eq. (2.38)) given formally by

$$f_{xc}(r, r', t - t') = \left. \frac{\delta v_{xc}[\rho](r, t)}{\delta \rho(r', t')} \right|_{\rho = \rho_{GS}} , \quad (2.69)$$

which is evaluated at the ground state density, $\rho_{GS}(r)$. As in ground state DFT, the choice of the exchange-correlation kernel determines the accuracy of the results obtained.

Within TDDFT, there exist several approximations governed by the choice of kernel. In particular, for no kernel ($K = 0$), we have simply from Eq. (2.68) that $\chi = \chi_0$ which is just the case of the non-interacting KS system of Eq. (2.66). This is known as the independent-particle (IP) approximation. If we keep the first term in Eq. (2.68) (the bare Coulomb part), but set $f_{xc} = 0$, then this approximation is known as the random-phase-approximation (RPA).

In general, $f_{xc}$ will have a non-local spatial dependence and will also depend on the entire history of the system in time. However, the adiabatic approximation has proved to be very popular and is the most widely applied. In this approximation, $v_{xc}[\rho](r, t)$ is taken simply to be the time-independent potential $v_{xc}[\rho](r)$ in Eq. (2.38), evaluated at the instantaneous value of the density, $\rho(r, t)$. Most commonly, the adiabatic approximation is used in conjunction with the ground state LDA potential, yielding the adiabatic LDA (ALDA) approximation. Despite the popularity of the ALDA, there are certain systems where such an approximation fails, particularly in the case of semiconductors with strong electron-hole interactions (excitonic effects). In this case, one must resort to a higher level of theory than TDDFT such as the Bethe-Salpeter equation (BSE) from MBPT, or use more complicated exchange-correlation potentials such as those derived from the BSE [65, 66].

### 2.3.4 Periodic Systems

Part of our work shall focus on the optical properties of solids which can be considered as periodic arrays of atoms which form a crystalline structure. In general, the solid is treated as an infinite array which poses a problem from a practical point of view as we cannot perform a DFT calculation on an infinite number of atoms. In this section, we reformulate the Kohn-
Sham wavefunctions and TDDFT equations into reciprocal space to make use of the system’s periodicity and reduce computational effort.

The positions of the sites of the atoms within the structure are given by the direct lattice vectors

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 ,$$

(2.70)

where the \(n_i\) are integers and \(\mathbf{a}_i\) are called the primitive vectors which span the real space. The set of all such lattice vectors forms what is called the Bravais lattice. The unit cell is the region of space enclosed by the parallelepiped formed by the primitive vectors and contains atoms lying on its sides, corners or centre. The crystal structure can then be formed by translating the unit cell by integer amounts in the primitive vector directions.

Since the atoms are positioned periodically via the direct lattice vectors \(\mathbf{R}\), the external potential generated by the nuclei, \(v_{\text{ext}}(\mathbf{r})\), must also share the same periodicity, i.e.

$$v_{\text{ext}}(\mathbf{r} + \mathbf{R}) = v_{\text{ext}}(\mathbf{r}) .$$

(2.71)

The reciprocal lattice is defined as the set of all wave vectors, \(\mathbf{G}\), corresponding to plane waves with the same periodicity as the Bravais lattice. The reciprocal lattice vectors are defined as

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 ,$$

(2.72)

where \(m_i\) are integers and \(\mathbf{b}_i\) are the reciprocal lattice basis vectors which span the whole reciprocal space:

$$\mathbf{b}_1 = \frac{2\pi}{\Omega_{\text{cell}}} \mathbf{a}_2 \times \mathbf{a}_3 ,$$

(2.73a)

$$\mathbf{b}_2 = \frac{2\pi}{\Omega_{\text{cell}}} \mathbf{a}_3 \times \mathbf{a}_1 ,$$

(2.73b)

$$\mathbf{b}_3 = \frac{2\pi}{\Omega_{\text{cell}}} \mathbf{a}_1 \times \mathbf{a}_2 ,$$

(2.73c)

where \(\Omega_{\text{cell}}\) is the volume of the unit cell in direct space. The equivalent of the unit cell in reciprocal space is called the Brillouin zone (BZ).

By Bloch’s theorem, we can express the energy eigenstates of an electron of momentum, \(|\mathbf{k}|\), in the periodic field (Eq. (2.71)) by an expansion of plane waves,

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}} \sum_{\mathbf{G}} c_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} ,$$

(2.74)

where the \(c_{n,\mathbf{k}+\mathbf{G}}\) are the expansion coefficients, to be determined. For given \(\mathbf{k}\), the energy of the Bloch wave in state \(n\) is \(\varepsilon_{n\mathbf{k}}\): by considering the energy as a function of \(\mathbf{k}\), \(\varepsilon_{n\mathbf{k}}(\mathbf{k})\), we can build up an energy profile of the crystal structure, which is normally depicted in band diagrams.
Since the orbitals in Eq. (2.74) now depend on the wave vectors, $k$, any observables are given by integrating over all reciprocal space in the BZ. For example, the density in Eq. (2.34) becomes

$$\rho(r) = \sum_n \int_{\text{BZ}} |\varphi_{nk}(r)|^2 \, dk,$$

and the total energy will be

$$E = \sum_n \int_{\text{BZ}} \varepsilon_{nk} dk.$$

In practice, these integrals are calculated numerically involving a sum over a chosen subset of wave vectors (also called $k$-points) in the BZ. This is known as $k$-point sampling. The total energy is usually converged by using more vectors in the sum: several methods exist so as to reduce the number of vectors required whilst maintaining accuracy, by ‘intelligently’ sampling the reciprocal space based on the symmetry of the BZ. The simplest is the Monkhorst-Pack method which samples over an equally spaced grid in the BZ.

We also note that in calculating the orbitals in Eq. (2.74), we need to sum over an infinite number of reciprocal lattice vectors, $G$. In order to truncate the summation, we sum over all plane waves with kinetic energy less than $E_{\text{cut}}$, i.e. those satisfying

$$\frac{1}{2} |k + G|^2 < E_{\text{cut}},$$

which yields a finite number, $N_{\text{basis}}$, of plane wave basis functions in the calculation of the orbitals and hence the total energy. The energy is then converged by increasing the number of basis functions (i.e. by increasing $E_{\text{cut}}$).

Since an electronic wavefunction in a given state must be orthonormal to the wavefunctions in all other states, there appear a large number of oscillations in the wavefunction form, especially for atoms with many electrons which, in turn, requires a large number of plane waves in the expansion. As a method of reducing $N_{\text{basis}}$, we neglect a number of core (or inner) electrons and introduce a modified nuclear potential called a pseudopotential (PP) which matches the true potential after some cut-off radius, $r_{\text{cut}}$, but is made softer for $r < r_{\text{cut}}$ whilst retaining the effective Coulomb potential of the neglected electrons. As well as reducing the total number of electrons treated in the system, the introduction of PPs reduces $N_{\text{basis}}$ and significantly reduces the computation time of periodic DFT calculations.

In the time-dependent framework, the response functions depend on two spatial coordinates

---

2The summations, $\sum_n$, are over occupied states unless otherwise stated.
as well as time. Similarly to Eq. (2.74), we can expand, e.g., \( \chi(r, r', t - t') \) in plane waves as

\[
\chi(r, r', \omega) = \frac{1}{\sqrt{V_{\text{cell}}}} \int_{\text{BZ}} \sum_{G \neq G'} e^{i(q + G') \cdot r} \chi_{GG'}(q, \omega) e^{-i(q + G') \cdot r'} dq, \tag{2.78}
\]

where \( q \) is a vector in the BZ (the Bloch vector of the incident radiation) and \( \chi_{GG'}(q, \omega) \) are the Fourier coefficients given by

\[
\chi_{GG'}(q, \omega) \equiv \chi(q + G, q + G', \omega) = \int \int \int \int e^{-i(q + G') \cdot r} \chi(r, r', t - t') e^{i(q + G') \cdot r'} e^{-i\omega(t - t')} dr dr' dt. \tag{2.79}
\]

In this form, the non-interacting response function from Eq. (2.66) is written as

\[
\chi_{GG'}^0(q, \omega) = \frac{1}{\sqrt{V_{\text{cell}}}} \int_{\text{BZ}} \sum_{i,j} \frac{f_{ik} - f_{j,k+q}}{\omega - (\epsilon_{j,k+q} - \epsilon_{ik}) + i\eta} \times \\
\left\langle \psi_{ik} \left| e^{-i(q + G) \cdot r} \psi_{j,k+q} \right\rangle \left\langle \psi_{j,k+q} \left| e^{i(q + G') \cdot r'} \right\rangle \psi_{i,k} \right\rangle dk, \tag{2.80}
\]

and Eq. (2.67), which relates the full-interacting response, becomes

\[
\chi_{GG'}(q, \omega) = \chi_{GG'}^0(q, \omega) + \sum_{G_1G_2} \chi_{G_1G_2}^0(q, \omega) K_{G_1G_2}(q, \omega) \chi_{G_2G'}(q, \omega). \tag{2.83}
\]

The kernel from Eq. (2.68) may be written as

\[
K_{GG'}(q, \omega) = v(q + G) \delta_{GG'} + K_{GG'}^{xc}(q, \omega), \tag{2.84}
\]

where

\[
v(q + G) = \frac{4\pi}{|q + G|^2}, \tag{2.85}
\]

is the Coulomb potential in reciprocal space and \( K_{GG'}^{xc}(q, \omega) \) is the Fourier representation of the exchange-correlation kernel, Eq. (2.69).

Now, the microscopic dielectric function from Eq. (2.62) becomes

\[
\epsilon^{-1}_{GG'}(q, \omega) = \delta_{GG'} + \frac{4\pi}{|q + G|^2} \chi_{GG'}(q, \omega), \tag{2.86}
\]

and it can be shown that the macroscopic dielectric function is simply the \( G = 0 \) component of the above, i.e.,

\[
\epsilon_M(q, \omega) = \frac{1}{\epsilon^{-1}_{G=G'=0}(q, \omega)}. \tag{2.87}
\]

For optical absorption, we need only consider the case of vanishing momentum \( q \to 0 \) (known...
as the optical limit). We define

$$\epsilon_M(\omega) = \lim_{q \to 0} \epsilon_M(q, \omega),$$

and then the absorption is defined by the imaginary part of $\epsilon_M$ as in Eq. (2.13).

We shall later on be investigating absorption spectra of isolated systems: by this we mean that the system is not periodic in one or more directions. This could, e.g., be a molecule, a nanotube/wire or (in the case of this thesis) a two-dimensional monolayer. In practice, the unit cells must then have sufficient ‘vacuum distance’ in the non-periodic directions to avoid spurious interactions with neighbouring cells. However, clearly as the unit cell fills with vacuum, the imaginary part of the dielectric function will tend to zero. It is, therefore, preferable to examine rather than Abs (which will depend on the unit cell size), the polarisability which we define as

$$\alpha(\omega) = \frac{\Omega_{\text{non-per}}}{4\pi} (\epsilon_M(\omega) - 1),$$

where $\Omega_{\text{non-per}}$ is the unit cell ‘volume’ in the non-periodic direction. E.g., in the case of a molecule (0D system), this will be a volume; an area in the case of a nanowire (1D system); and a length in the case of a monolayer (2D system). In this way, a constant proportionality is assured so that $\alpha$ is independent of the amount of vacuum distance (see, e.g., Ref. [67]).

### 2.3.5 Quasi-Particles and The Bethe-Salpeter Equation

In Sections 2.3.3 and 2.3.4, we described how to simulate the linear response of the electronic density to a small perturbation within the framework of TDDFT, from which one can obtain the optical spectra of solids. In principle, TDDFT provides an exact method for describing so-called neutral excitations where the total number of electrons in the system is conserved (such as is the case of optical absorption). However, the common approximations used for the exchange-correlation potential, $v_{xc}$, in TDDFT often results in poor optical spectra for many semiconductors when compared with experiment. The failure of such approximations of $v_{xc}$ is often attributed to their inability to describe electron-hole ($e-h$) interactions (so-called ‘excitonic’ effects) which are important processes in describing the absorption of light in semiconductors. In this section we introduce the concept of quasi-particles and many-body perturbation theory: the reader is referred to Refs. [57, 59–62] for detailed discussions and derivations.

Now, as described in Section 2.3.3, TDDFT is formulated around reforming the many-electron wavefunction into an electron density composed of one-electron, non-interacting wavefunctions in an effective potential. In order to describe, e.g., $e-h$ interactions which involve the correlated movement of two particles, one often turns instead to many-body perturbation
theory (MBPT). In MBPT, rather than the electron interacting strongly with every other electron via the (bare) Coulomb potential, it is viewed as a ‘screened’ electron, surrounded by a ‘cloud’ of other electrons. In such a picture, the screened electron is called a quasi-particle and will interact much more weakly with other quasi-particles via a screened Coulomb potential when compared with the respective, unscreened electrons. These quasi-particles will, of course, exhibit different properties to the bare electrons and will, therefore, possess different energies and wavefunctions which may be obtained by solving the following quasi-particle equation,

\[ \hat{h}_0(r) \Psi_i(r, \omega) + \int \Sigma(r, r', \omega) \Psi_i(r', \omega) dr' = E_i(\omega) \Psi_i(r, \omega) , \]  

(2.90)

where

\[ \hat{h}_0(r) = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + v_{\text{H}}(r) \]  

(2.91)

is the Hamiltonian of the bare electron interacting with the external potential, \( v_{\text{ext}}(r) \), and the Hartree potential, \( v_{\text{H}}(r) \), and \( \Sigma \) is the self-energy which contains the exchange and correlation effects of the quasi-particle associated with the MBPT. This one-particle equation is similar to the KS-DFT equation with Hamiltonian in Eq. (2.37), with the important difference that, as opposed to the exchange-correlation potential \( v_{\text{xc}} \) in DFT, \( \Sigma \) is non-local. The self-energy is also energy-dependent and, in general, non-Hermitian.

It can be shown that the solution to Eq. (2.90) may be related to a Green’s function (GF), the notion of which we shall briefly discuss. If \( |N \rangle \) is the ground state of a system of \( N \) interacting particles, then the time-ordered, single-particle GF is defined as

\[ G(1, 2) = -i \langle N | T [\psi(1) \psi^\dagger(2)] | N \rangle , \]  

(2.92)

where \( \psi \) and \( \psi^\dagger \) are the creation and annihilation field operators which add or subtract a particle from the system respectively. The symbol, \((i)\), represents the position coordinates \( r_i \) and time, \( t_i \) (i.e. \( G(1, 2) \equiv G(r_1, t_1, r_2, t_2) \)). \( T \) is the time-ordered product given by

\[ T [A(t_1)B(t_2)] = \begin{cases} 
A(t_1)B(t_2) & t_1 > t_2 \\
-B(t_2)A(t_1) & t_1 < t_2 
\end{cases} . \]  

(2.93)

Eq. (2.92), therefore, describes the propagation of an electron created at position \( r_2 \), time \( t_2 \) to position \( r_1 \) at time \( t_1 \) provided \( t_1 > t_2 \). Conversely, if \( t_2 > t_1 \) then it describes the propagation of a hole. It can be shown that the GF may be written in its spectral form as

\[ G(r, r', \omega) = \sum_i \frac{\Psi_i(r, \omega) \Psi_i^\dagger(r', \omega)}{\omega - E_i(\omega)} , \]  

(2.94)
so that the poles of the GF are the quasi-particle energies, or the electron addition and removal energies. The GFs approach is, therefore, a natural way to model photoemission experiments where electrons are ejected from the system: indeed, the imaginary part of G is called the spectral function and is related to photoemission spectra.

In practice, it can be shown that the GF can be found by solving the following Dyson equation,

$$G(1, 2) = G^0(1, 2) + \int G^0(1, 3)\Sigma(3, 4)G(4, 2)d(34),$$

where $G_0$ is the non-interacting GF associated with the solution of Eq. (2.90) with $\Sigma = 0$ (i.e., the equation describing the bare electrons in the Hartree potential). Its spectral representation is

$$G_0^0(r, r', \omega) = \sum_i \varphi_i(r)\varphi_i^*(r'),$$

where the $\{\varphi_i, \epsilon_i\}$ are the non-interacting electron orbitals and energies (e.g., from KS-DFT).

A common approximation for the self-energy is the so-called GW (or $G_0W_0$) approximation where $\Sigma = G_0W_0$ where $W_0$ is the screened Coulomb interaction, $W_0 = e^{-1}v$ (i.e., the bare Coulomb potential, ‘screened’ by the dielectric function, $\epsilon$).

Now, while the method above describes very well phenomena involving one-particle excitations, the e-h interactions mentioned at the start of this chapter clearly involve two-particle excitations. Similarly, they can be described via the two-particle GF,

$$G(1, 2, 3, 4) = -\langle N \mid T \psi(1)\psi(3)\psi(4)\psi^\dagger(2) \mid N \rangle. \quad (2.97)$$

In particular, the independent-particle polarisability, $L^0$, for the e-h describes the propagation of the electron and the hole independently and is given by

$$L^0(1, 2, 3, 4) = iG(1, 3)G(4, 2). \quad (2.98)$$

The interacting polarisability, $\tilde{L}$, is then given by the following Dyson equation (analogous to Eq. (2.67)) which is known as the Bethe-Salpeter Equation (BSE),

$$\tilde{L}(1, 2, 3, 4) = L^0(1, 2, 3, 4) + \int L^0(1, 2, 3, 4)\Xi(5, 6, 7, 8)\tilde{L}(7, 8, 3, 4)d(5678),$$

where $\Xi$ is the BSE kernel,

$$\Xi = \delta(5, 6)\delta(7, 8)v(5, 7) + i\frac{\delta\Sigma(5, 7)}{\delta G(6, 8)} \quad (2.100)$$

and $v$ is the Coulomb potential.

It can be shown that the macroscopic dielectric function is given via the two-point contrac-
tion of \( \tilde{L} \), i.e.
\[
\epsilon_m(\omega) = 1 - \lim_{q \to 0} \nu(q) \int e^{i(q \cdot (r - r'))} \tilde{L}(r, r, r', r', \omega) drdr'.
\] (2.101)

\( \tilde{L}(r, r, r', r', \omega) \) may be obtained by assuming that the electron and the hole propagate simultaneously (i.e. an e-h pair created in (1) and annihilated in (3): \( \tilde{L}(r, r, r', r', \omega) \equiv \tilde{L}(1 = 2, 3 = 4) \)) and by considering time translational invariance so that we can now omit the time-dependence from the variables (i) and take the Fourier transform in time such that now \( \tilde{L}(1, 2, 3, 4) \) becomes \( \tilde{L}(r_1, r_2, r_3, r_4, \omega) \).

In order to solve Eq. (2.99), we first change the basis into pairs of KS orbitals and transform \( \tilde{L} \) into momentum space to get
\[
\tilde{L}_{mn'k'}(\omega) = \int \tilde{L}(r_1, r_2, r_3, r_4, \omega) \varphi_{nk}(r_1) \varphi_{n'k'}^{*}(r_2) \varphi_{nk'}^{*}(r_3) \varphi_{n'k}(r_4) dr_1 dr_2 dr_3 dr_4 .
\] (2.102)

It can then be shown that the BSE in Eq. (2.99) may be expressed as the following eigenvalue problem,
\[
H_{mn'k'} A_{mn'k'}^{\lambda} = E_{\lambda} A_{mn'k'}^{\lambda} ,
\] (2.103)
where \( H_{mn'k'} \) is the Hamiltonian,
\[
H_{mn'k'} = (\epsilon_{nk} - \epsilon_{n'k'}) \delta_{nm} \delta_{n'm'} \delta_{kk'} + (f_{nk} - f_{n'k'}) \Xi_{mn'k'} ,
\] (2.104)
where \( \epsilon_{nk} \) and \( f_{nk} \) are the energies and occupation values of the KS state \( \varphi_{nk}(r) \). Note that Eq. (2.104) only includes positive frequency transitions and is known as the resonant part of the Hamiltonian. \( \Xi_{mn'k'} \) is the BSE kernel (Eq. (2.100)) expressed in the new basis and where we have used the GW approximation for the self-energy:
\[
\Xi_{mn'k'} = W_{mn'k'} - 2 \tilde{V}_{mn'k'} ,
\] (2.105)
where
\[
\tilde{V}_{mn'k'} = \frac{1}{\Omega} \sum_{G \neq 0} v(G) \langle n'k' | e^{-iGr} | nk \rangle \langle mk' | e^{-iG'r} | m'k' \rangle
\] (2.106)
describes the e-h exchange effects (from the Hartree potential), and
\[
W_{mn'k'} = \frac{1}{\Omega} \sum_{G,G'} v(q + G)e^{-iG_{C}(q)} \langle n'k' | e^{i(q + G)r} | m'k' \rangle \langle mk' | e^{-i(q+G')r} | nk \rangle \delta_{q-k-k'}
\] (2.107)
describes the e-h interaction via the screened Coulomb potential. \( \epsilon_{GG'}^{-1} \) is the microscopic dielectric function of Eq. (2.86) at \( \omega = 0 \) (static screening).
Finally, it can then be shown that the macroscopic dielectric function, Eq. (2.101), becomes

$$\varepsilon_M(\omega) = 1 - \lim_{q \rightarrow 0} \frac{8\pi}{|q|^2 q^4} \sum_{m'k'} \langle n'k | e^{-i\omega \cdot r} | n'k' \rangle \langle m'k' | e^{i\omega \cdot r} | m'k - q \rangle \sum_{\lambda} \frac{A_{n'kk}^\lambda (A_{m'k'k}^\lambda)^*}{\omega - E_{\lambda}}.$$  

(2.108)

### 2.3.6 The Time-Dependent Bethe-Salpeter Equation

In Sections 2.3.3 and 2.3.5, we have shown how the optical absorption spectra of solids may be obtained via TDDFT and the BSE (from MBPT). In both cases, we considered only the linear response (LR), where the electronic system responds to a weak perturbation, yielding directly the frequency-dependent macroscopic dielectric function. However, clearly these LR methods do not allow one to probe non-linear effects in the system via, e.g., strong, short-pulse laser interactions. Of course, one can go beyond the LR-TDDFT by solving the TDDFT equations of Section 2.3.3 in real-time such as implemented, e.g., in the Octopus code [63]. However, as discussed in the previous section, one must include many-body effects to model important electron-hole interactions in semiconductors, which cannot be easily incorporated into the TDDFT scheme. One should, therefore, prefer a real-time implementation of the BSE in order to describe such interactions for non-linear phenomena. Indeed, this approach (named the time-dependent BSE (TD-BSE)) is described in Ref. [68] and implemented (alongside the standard LR-TDDFT and LR-BSE methods) in the Yambo code [59].

We wish to solve the time evolution of a system responding to an external field, including many-body effects. As described in the previous chapter, the many-body effects are modelled using the Green’s function, $G(r_1, t_1, r_2, t_2)$ (see Eq. (2.92)). In a similar way as in Eq. (2.102), we define the GF in momentum space choosing as a basis the KS orbitals:

$$G_{n_1n_2k}(t_1, t_2) = \int \varphi_{n_1k}^*(r_1) G(r_1, t_1, r_2, t_2) \varphi_{n_2k}(r_2) dr_1 dr_2. \quad (2.109)$$

For notation purposes, we also define $[G_{k}(t_1, t_2)]_{n_1n_2} = G_{n_1n_2k}$. Notice that we explicitly include the time variables here: as we are interested in non-equilibrium phenomena, the time-translation invariance is broken and so we cannot define a single frequency, $\omega$, by means of the Fourier transform as in Eq. (2.102). We, hence, define the advanced ($G^a$), retarded ($G^r$), lesser ($G^<$) and greater ($G^>$) GFs which depend on the ordering of $t_1$ and $t_2$.

We define the Hamiltonian

$$\hat{H} = \hat{h} + \hat{H}_{mb} + \hat{U}, \quad (2.110)$$

which composes of $\hat{U}$ which describes the interaction with the externally applied field, $\hat{H}_{mb}$.
which describes the many-body effects, and the KS Hamiltonian, \( \hat{h} \), (see Eq. (2.37))

\[
\hat{h} = -\sum_i \frac{\nabla^2_i}{2} + \hat{V}^{\text{ext}}(\mathbf{r}) + \hat{V}^H[\rho] + \hat{V}^{xc}[\rho],
\]

(2.111)

where \( \hat{V}^{\text{ext}} \) represents the interaction of the electrons with the nuclei, and \( \hat{V}^H \) and \( \hat{V}^{xc} \) are the Hartree and exchange-correlation potentials. \( \rho \) is the electron density of the system at equilibrium (\( \hat{U} = 0 \)),

\[
\rho = \sum_{nk} f_{nk} |\varphi_{nk}(\mathbf{r})|^2,
\]

(2.112)

where \( f_{nk} \) are the Kohn-Sham occupation numbers.

The dynamics of the GF (namely the lesser and greater GFs) may be found by solving the so-called Kadanoff-Baym equations (KBEs) [69]. We first introduce some approximations. In particular, for the self-energy in \( \hat{H}_{\text{mb}} \) we choose the Coulomb-hole plus screened-exchange (COHSEX) approximation, \( \Sigma^{\text{COHSEX}} = \Sigma^{\text{COH}} + \Sigma^{\text{SEX}} \). \( \Sigma^{\text{COH}} \) is given by

\[
\Sigma^{\text{COH}}(\mathbf{r}, \mathbf{r}'; t) = \frac{1}{2} W(\mathbf{r}, \mathbf{r}'; \mathbf{G}^{<}) \delta(\mathbf{r} - \mathbf{r}'),
\]

(2.113)

where \( W(\mathbf{r}, \mathbf{r}'; \mathbf{G}^{<}) \) is the screened Coulomb interaction (within the static GW approximation) and \( \Sigma^{\text{SEX}} \) is given by

\[
\Sigma^{\text{SEX}}(\mathbf{r}, \mathbf{r}'; t) = i W(\mathbf{r}, \mathbf{r}'; \mathbf{G}^{<}) G^{<}(\mathbf{r}, \mathbf{r}', t).
\]

(2.114)

The \( G_0W_0 \) correction to the KS eigenvalues are included via a scissor operator, \( \Delta h \),

\[
\Delta h_{n_1n_2,k} = (E_{n_1k} - \epsilon_{n_1k}) \delta_{n_1n_2},
\]

(2.115)

where \( E_{nk} \) are the \( G_0W_0 \) quasi-particle energies (see Eq. (2.90)) and \( \epsilon_{nk} \) are the KS eigenvalues.

It may then be shown that the KBEs can be reduced to solving the following differential equation for \( G^{<} \) [68],

\[
\frac{\partial}{\partial t} G^{<}_{n_1n_2k}(t) = -i \left[ \mathbf{h}_k + \Delta \mathbf{h}_k + \mathbf{U}_k + \mathbf{V}_k^H[\rho] - \mathbf{V}_k^H[\rho] \right]
+ \Sigma^{\text{COHSEX}}_k[G^{<}] - \Sigma^{\text{COHSEX}}_k[\tilde{G}^{<}], G^{<}_k(t) \bigg|_{n_1n_2},
\]

(2.116)

where

\[
\rho(\mathbf{r}, t) = i \sum_{n_1n_2k} \varphi_{n_1k}(\mathbf{r}) \varphi^*_{n_2k}(\mathbf{r}) G^{<}_{n_2n_1k}(t),
\]

(2.117)

where \( G^{<}_{n_2n_1k}(t) \equiv G^{<}_{n_2n_1k}(t, t) \) is the time-diagonal lesser GF with \( t = (t_1 + t_2)/2 \) and

\[
\tilde{G}^{<}_{nm'k} = i f_{nk} \delta_{nm'},
\]

(2.118)
is the equilibrium solution for $\hat{U} = 0$. In Eq. (2.116), $h_{n_1n_2k}$, $U_{n_1n_3k}$, $V^H_{n_1n_2k}$ and $\Sigma^{\text{COHSEX}}_{n_1n_2k}$ are the KS, external, Hartree and self-energy potentials (as in Eqs. (2.110), (2.111), (2.113) and (2.114)) expressed in the KS orbital basis (see Eq. (2.109)). Note the similarities of Eq. (2.116) with the master equation in density matrix theory (Eq. (2.54)).

For the external interaction $\hat{U}$, we use the dipole approximation

$$\hat{U} = -r \cdot E(t),$$

(2.119)

where $E(t)$ is a homogeneous electric field. It can then be shown that the time-dependent polarisation is given by

$$P(t) = -\frac{1}{\Omega} \sum_{nmk} r_{mnk} G^{\infty}_{nmk}(t),$$

(2.120)

where $r_{mnk}$ are the dipole matrix elements, $r_{mnk} = \langle m \mid r \mid nk \rangle$. The frequency-dependent susceptibility may then be obtained by taking the Fourier transform of $P(t)$ (see Eq. (2.3)),

$$\chi_e(\omega) = \frac{P(\omega)}{E(\omega)},$$

(2.121)
Chapter 3

The Projected Equations of Motion (PEOM) Method

3.1 Introduction

In Ref. [23] a method is developed for modelling the interaction between a semiconducting quantum dot (SQD) and a metal nanoparticle (MNP) under illumination (see Section 4.1). In this model, the SQD is treated as a two-level atomic-like system using the density matrix formalism of quantum mechanics (see Section 2.3.2) while the MNP is treated via classical electrodynamics by knowledge of its frequency-dependent, bulk dielectric constant. Due to quantum confinement effects, the SQD responds strongly at its exciton frequency and so a two-level model adequately describes the dynamics (see, e.g., Ref. [70]).

The dynamics of the two systems are then coupled through the externally applied field using a dipole-dipole approximation. The dynamics of this hybrid complex can be solved analytically within the so-called rotating wave approximation (RWA). This analytical solution is valid provided the applied field is a slowly-varying monochromatic pulse of frequency close to the frequency gap of the SQD. Moreover, close to this frequency, the frequency-dependent dipole moment of the MNP is assumed to be much broader than that of the SQD which is inherently narrow due to its two-level nature and relatively long dephasing times. As it stands, the solution will not hold for ultrafast pulse excitation which is an area of current interest for such systems. Further, if the SQD is replaced with, e.g., a semiconducting monolayer (or any other large electronic system), the two-level quantum description will not suffice and the profile of the MNP response function can no longer be considered ‘broad’. Therefore, the method should be generalised to lift the restrictive approximations commonly used, giving rise to the
proposed project equations of motion (PEOM) approach.

The bulk of this chapter and the subsequent Chapter 4 is adapted from the paper, “Projected equations of motion approach to hybrid quantum/classical dynamics in dielectric-metal composites” of which RM is the first author [71].

3.2 Derivation

In order to introduce the PEOM method, we consider a general composite comprising two isolated subsystems in a vacuum: a primary system (PS) and a secondary system (SS). The dynamics of the SS shall be solved by a set of PEOMs which are fitted from its frequency-dependent polarisability. This polarisability may arise from classical or quantum simulations, analytical approximations or from experiment. On the other hand, the dynamics of the PS shall be solved within the remits of any given time-dependent theory: this may be, e.g., quantum mechanics in the form of TDDFT, classical electrodynamics, or indeed even by a further set of PEOMs. For example, in the case of the SQD-MNP system in Ref. [23], the SQD would be the PS, whose dynamics are solved by the density matrix master equation while the MNP would be the SS whose frequency-dependent polarisability is described analytically from classical electrodynamics. The two systems shall then be coupled through an external field.

![Diagram](image)

**Figure 3.1:** Schematic diagram showing the dipole-dipole interaction between the primary system (PS) and the secondary system (SS), separated by a distance $R$. When an external field, $E_{\text{EXT}}$, is applied, a dipole moment, $p_{\text{PS}}$, is induced in the PS, generating a field. The SS thus experiences this dipole field in addition to the external field, and we denote the total field felt by the SS as $E_{\text{SS}}$. Similarly, due to $E_{\text{SS}}$, a dipole field is generated in the SS which is in turn felt by the PS in addition to $E_{\text{EXT}}$, and we denote the total field felt by the PS as $E_{\text{PS}}$. In this way, the PS and SS dynamics are coupled through the external field.

We consider the PS and SS to be separated by some distance, $R$, with the unit vector, $\hat{n}$, pointing along the line of separation. An external field, $E_{\text{EXT}}(t) \equiv E_{\text{EXT}}(t)\hat{e}$, is applied which induces a dipole-dipole interaction between the two systems as described in Fig. 3.1. To
simplify the notation, we assume that the PS and SS are isotropic media so that their dipole moments are along $\hat{e}$. For the generalisation to the anisotropic case see Appendix A.1. The fields felt by the PS and SS are then, respectively [23, 72, 73],

$$E_{PS}(t) = E_{EXT}(t) + \frac{p_{SS}(t)}{R^3}g,$$

$$E_{SS}(t) = E_{EXT}(t) + \frac{p_{PS}(t)}{R^3}g,$$

where $p_{SS}(t)$ ($p_{PS}(t)$) is the total dipole moment of the SS (PS), and

$$g = 3\hat{n} (\hat{e} \cdot \hat{n}) - \hat{e}.$$  

The acquisition of the time-dependent dipole moment of the PS, $p_{PS}(t)$, depends on the chosen theory: e.g., within TDDFT (see Section 2.3.3), the dipole moment would be

$$p_{PS}(t) = \int r \rho(r, t) dr,$$

where $\rho(r, t)$ is found by solving the Kohn-Sham EOMs in Eq. (2.59) and using Eq. (2.57). Similarly, within density matrix theory (see Section 2.3.2), we have

$$p_{PS}(t) = \text{tr} (\rho(t) \mu),$$

where $\mu$ is the transition dipole moment operator matrix and $\rho(t)$ is found by solving the master equation of motion (Eq. (2.56)).

For the SS, rather than calculate the dipole moment explicitly, we assume that its frequency dependent polarisability, $\alpha(\omega)$, is already known. This may have been previously obtained, however, from $\textit{ab initio}$ calculations similar to the PS, or from experimental data or classical approximations. Its dipole moment can then be described via (see Section 2.1)

$$p_{SS}(\omega) = \alpha(\omega) E_{SS}(\omega).$$

In the time domain, however, the dipole moment is written in terms of the response function $\alpha(t)$, as

$$p_{SS}(t) = \int_{-\infty}^{t} \alpha(t - t') E_{SS}(t') dt'.$$

Now, the EOMs that determine $p_{PS}(t)$ depend on $E_{PS}(t)$ which in turn depends on $p_{SS}(t)$ from Eq. (3.1a). They are generally solved using an iterative algorithm, where the time domain is split into a set of discrete points. However, computing the integral in Eq. (3.6) at each time-step in the solution is cumbersome and the values of $E_{SS}(t)$ and $\alpha(t)$ for each time-step must be
held in memory which may not be feasible for long simulations.

In Ref. [74], a method (originally devised for memory kernels in the Generalised Langevin Equation) is presented for avoiding the memory-dependent time-convolution inherent in Eq. (3.6). Inspired by this, we introduce $N$ complex auxiliary degrees of freedom, $\{s_k(t)\}$ which satisfy the following projected equations of motion (PEOMs)

$$
\dot{s}_k = - (\gamma_k + i\omega_k) s_k + iE_{SS}(t) \quad \text{for} \quad k = 1, 2, \ldots, N .
$$

(3.7)

We then state that $p_{SS}(t)$ can be written as

$$
p_{SS}(t) \approx \sum_{k=1}^{N} c_k \text{Re}[s_k(t)] ,
$$

(3.8)

so that the memory-dependent integral in Eq. (3.6) is replaced with an expansion over the functions $s_k$ which are found by solving the differential equations in Eq. (3.7). As these differential equations no longer contain a time-convolution (i.e., they are “memoryless”), they can be efficiently integrated using, e.g., the same iterative algorithm as for the PS EOMs. All that is required is to find suitable values for the (real) parameters $\{c_k, \gamma_k, \omega_k\}$ in Eq. (3.7). The formal solution of Eq. (3.7) is

$$
s_k(t) = \int_{-\infty}^{t} e^{-(\gamma_k+i\omega_k)(t-t')} E_{SS}(t') dt' .
$$

(3.9)

Substituting the real part of Eq. (3.9) into Eq. (3.8) and rearranging yields

$$
p_{SS}(t) \approx \int_{-\infty}^{t} \left( \sum_{k=1}^{N} c_k e^{-\gamma_k(t-t')} \sin[\omega_k(t-t')] \right) E_{SS}(t') dt' ,
$$

(3.10)

and comparing with Eq. (3.6) we see that

$$
\alpha(t) \approx \sum_{k=1}^{N} c_k e^{-\gamma_k t} \sin(\omega_k t) .
$$

(3.11)

Taking the Fourier transform of Eq. (3.11) (using the causality condition) gives

$$
\alpha(\omega) \approx \sum_{k=1}^{N} \frac{c_k}{2} \left[ \frac{1}{\omega + \omega_k + i\gamma_k} - \frac{1}{\omega - \omega_k + i\gamma_k} \right] .
$$

(3.12)

Hence, the parameters $\{c_k, \gamma_k, \omega_k\}$ may be found by fitting the frequency-dependent polarisability of the SS (which is known) to the functions on the RHS of Eq. (3.12), e.g. using the least squares method (see, e.g., Chapter 8 of Ref. [75] and Appendix D.1). We describe the
quality of the fit by the estimated percentage error which we define as
\[
\text{p.e.} = \max \left( \frac{\text{abs}(\alpha_i^{\text{approx.}} - \alpha_i)}{\alpha_i} \right),
\]
where \(\alpha_i^{\text{approx.}}\) and \(\alpha_i\) are the approximated (Eq. (3.12)) and exact polarisabilities evaluated at \(\omega_i\) and the maximum is taken over \(i\) where \(\omega\) has been discretised to \(\{\omega_i\}\) over some interval.

### 3.3 Test: Recovering the Fitted Polarizability

In the previous section, we stated that if the known frequency-dependent polarisability is fitted to Eq. (3.12), then the solution of the PEOMs in Eq. (3.7) with the obtained parameters when substituted into the approximation Eq. (3.8) yields the corresponding time-dependent dipole moment. In this section, we shall perform this procedure for the polarisability of a gold nanosphere, then take the Fourier transform of the resulting time-dependent dipole moment to ensure that the original polarisability is indeed recovered.

Consider a small metal sphere of radius, \(a\), with frequency-dependent bulk dielectric constant, \(\epsilon(\omega)\). It can be shown that its polarizability is given by (see e.g. Chapter 2 of Ref. [76])
\[
\alpha(\omega) = a^3\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}.
\]
(3.14)

We choose a gold sphere and approximate the dielectric constant by the analytical model given by Etchegoin et al. [77], i.e.
\[
\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i \omega \Gamma} + \sum_{i=1,2} A_i \omega_i \left[ \frac{e^{-i\phi_i}}{\omega + \omega_i + i \Gamma_i} - \frac{e^{i\phi_i}}{\omega - \omega_i + i \Gamma_i} \right],
\]
(3.15)

where, from the Drude model, \(\epsilon_\infty = 1.53\) is the high-frequency limit dielectric constant, \(\omega_p = 8.55\) eV is the plasmon frequency and \(\Gamma = 7.29\) meV is the damping term. The remaining parameters from Etchegoin’s model are \(A_1 = 0.94, \phi_1 = -\pi/4, \omega_1 = 2.65\) eV, \(\Gamma_1 = 0.539\) eV, \(A_2 = 1.36, \phi_2 = -\pi/4, \omega_2 = 3.74\) eV and \(\Gamma_2 = 1.32\) eV.

We fit the polarizability of the gold sphere from Eqs. (3.14) and (3.15) to the model in Eq. (3.12) using a least-squares algorithm in MATLAB (see Appendix D.1). The function is fitted over the range 0–10 eV and we choose \(N = 12\) basis functions which gives a fit with estimated percentage error of 0.8%. The obtained parameters are shown in Table 3.1.

We now wish to solve the PEOMs in Eq. (3.7). The gold sphere is isotropic so we need not consider the vector notation as the dipole moment will be in the direction of the field. Further, the sphere (the secondary system) is isolated (\(R \rightarrow \infty\)) so that the field felt by it is simply the externally applied field, \(E_{SS}(t) = E_{EXT}(t)\). Therefore, we must solve the following set of
Table 3.1: Table of parameters obtained from the least-squares fit of the polarisability from Eqs. (3.14) and (3.15) to the model in Eq. (3.12). The fit is performed over the range 0–10 eV for \( N = 12 \) basis functions with an estimated percentage error of 0.8%.

<table>
<thead>
<tr>
<th>( k )</th>
<th>( c_k ) (eV)</th>
<th>( \omega_k ) (eV)</th>
<th>( \gamma_k ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.0206</td>
<td>1.1029</td>
<td>0.6799</td>
</tr>
<tr>
<td>2</td>
<td>-8.8410</td>
<td>2.5306</td>
<td>0.4677</td>
</tr>
<tr>
<td>3</td>
<td>0.1247</td>
<td>2.4209</td>
<td>0.1571</td>
</tr>
<tr>
<td>4</td>
<td>8.6495</td>
<td>2.5353</td>
<td>0.4599</td>
</tr>
<tr>
<td>5</td>
<td>0.2901</td>
<td>3.1248</td>
<td>0.7446</td>
</tr>
<tr>
<td>6</td>
<td>0.1056</td>
<td>3.9888</td>
<td>1.0782</td>
</tr>
<tr>
<td>7</td>
<td>0.3387</td>
<td>5.2148</td>
<td>1.2975</td>
</tr>
<tr>
<td>8</td>
<td>0.3256</td>
<td>6.0966</td>
<td>1.1638</td>
</tr>
<tr>
<td>9</td>
<td>0.3448</td>
<td>6.9571</td>
<td>1.2901</td>
</tr>
<tr>
<td>10</td>
<td>0.4798</td>
<td>8.0455</td>
<td>1.8002</td>
</tr>
<tr>
<td>11</td>
<td>0.7379</td>
<td>10.2476</td>
<td>2.8363</td>
</tr>
<tr>
<td>12</td>
<td>4.3978</td>
<td>30.8060</td>
<td>2.3264</td>
</tr>
</tbody>
</table>

For \( N = 12 \) with the parameters \( \{c_k, \gamma_k, \omega_k\} \) as given in Table 3.1.

Now, for a given external field, \( E_{\text{EXT}}(t) \), we can solve Eq. (3.16) and substitute into Eq. (3.8) to obtain the time-dependent polarisation, \( \mathbf{p}(t) \). By taking the Fourier transforms of \( E_{\text{EXT}}(t) \) and \( \mathbf{p}(t) \), we can use the relation Eq. (3.5) to get the frequency-dependent polarisability,

\[
\alpha(\omega) = \frac{\mathbf{p}(\omega)}{E_{\text{EXT}}(\omega)}.
\]

Ideally, the external field should contain all frequency components in order to reproduce the polarisability at all frequencies. This can be accomplished by choosing a \( \delta \) function as the external field. We, therefore, choose the following delta-like function,

\[
E_{\text{EXT}}(t) = \begin{cases} 
E_0 & , t = t_{\text{start}} \\
0 & , \text{otherwise}
\end{cases}
\]

where \( t_0 \) can be considered as the ‘switch-on’ time of the field and \( E_0 \) is the amplitude.

Now that the external field is defined, we can solve Eq. (3.16) numerically using the iterative Runge-Kutta fourth-order (RK4) method (see, e.g., Chapter 5 of Ref. [75] and Appendices C and D.2). For the RK4 method, we require the initial conditions of the solution. We assume...
the external field, Eq. (3.18), is initially zero ($t_{\text{start}} > 0$) and that the system is originally unpolarised so that $p(t = 0) = 0$ which means $s_k(t = 0) = 0$ ∀$k$ from Eq. (3.8). The RK4 solution is shown in Fig. 3.2 where we have used a time-step of 0.001 fs.

By taking the Fourier transforms of $p(t)$ and $E_{\text{EXT}}(t)$ and using Eq. (3.17), we can see from Fig. 3.3 that the fitted polarisability from Eqs. (3.14) and (3.15) is indeed recovered by the PEOM approach.
Figure 3.3: Real (blue) and imaginary (red) parts of the frequency-dependent polarisability, $\alpha(\omega)$, of a gold sphere. The solid lines are from the analytical expression given by Eqs. (3.14) and (3.15). The crosses are obtained by taking the Fourier transforms of the time-dependent dipole moment and external field (see Fig. 3.2). The units are $1/a^3$ where $a$ is the radius of the sphere.
Chapter 4

Semiconducting Quantum Dot-Metal Nanoparticle Hybrid

Quantum dots (QDs) are small (nanoscale) semiconductors which exhibit atomic-like properties due to quantum confinement effects. By quantum confinement, we mean that in contrast to bulk semiconductors, which exhibit a continuous energy spectrum, QDs display a discrete set of energy levels. QDs are, hence, also commonly referred to as artificial atoms.

The discrete nature of the energy levels in QDs gives them useful optical and electronic properties. In particular, QDs emit light strongly at specific frequencies which can be tuned by altering the size or geometry of the particle. The way in which a semiconducting QD (SQD) responds to light may also be altered by the presence of a metal nanoparticle (MNP) due to electromagnetic coupling between the two systems. Indeed, it has been previously shown that both energy absorption rates and population dynamics can be greatly affected when the MNP is in close proximity to the SQD [22–29].

In this chapter, we begin by providing a description of the electromagnetic coupling between the systems (Section 4.1) where the SQD is treated using density matrix theory (Section 2.3.2) and the MNP is treated classically. In Section 4.2 we show how the energy absorption rates may be obtained within the analytical rotating wave approximation (RWA) and compare the results with the PEOM method of Chapter 3. Similarly, semi-analytical methods for describing the population dynamics are described in Section 4.3 and compared with the PEOM method for ultra-short pulses.
Figure 4.1: Schematic diagram of a spherical metal nanoparticle (MNP) of radius, $a$, separated by a distance, $R$, from a spherical semiconducting quantum dot (SQD) of radius, $r$. The MNP is modelled classically while the SQD is treated as a two-level quantum system with ground state, $|1\rangle$, and excited state, $|2\rangle$, separated by an energy gap of $\hbar \omega_0$.

### 4.1 Describing the System

Consider a spherical, gold MNP of radius, $a$, separated by a distance, $R$, from a spherical SQD of radius, $r$, as shown in Fig. 4.1. From Eq. (3.1), when an external field $E_{\text{EXT}}(t)$ is applied, the fields felt by the SQD and MNP are, respectively,

$$E_{\text{SQD}}(t) = E_{\text{EXT}}(t) + g \frac{p_{\text{MNP}}(t)}{R^3}, \quad (4.1a)$$

$$E_{\text{MNP}}(t) = E_{\text{EXT}}(t) + g \frac{p_{\text{SQD}}(t)}{R^3}, \quad (4.1b)$$

where $p_{\text{SQD}}(t)$ ($p_{\text{MNP}}(t)$) is the dipole moment of the SQD (MNP). We assume the MNP and SQD are isotropic, and have taken the external field to be polarised along the line connecting the centres of the particles so that $\hat{n} = \hat{e}$. From Eq. (3.2), we have that $g = 2\hat{e}$ and so all fields are pointing in the direction of the external field, $\hat{e}$, allowing us to drop the vector notation.

The SQD is treated as a 2-level, atomic-like system with ground state, $|1\rangle$, and excited state, $|2\rangle$, separated by an energy gap of $\hbar \omega_0$ ($\omega_0$ is known as the exciton frequency). We use the density matrix formalism (see Section 2.3.2) so that the SQD can be described by a $2 \times 2$ density matrix, $\rho(t)$, and its dynamics are governed by the following equations (see Appendix B.1)

$$\dot{\Delta} = -4\tilde{\mu}_{21} E_{\text{SQD}}(t) \text{Im} [\rho_{21}] - \Gamma_{11} (\Delta - 1), \quad (4.2a)$$

$$\dot{\rho}_{21} = - (\Gamma_{21} + i\omega_0) \rho_{21} + i\tilde{\mu}_{21} E_{\text{SQD}}(t) \Delta, \quad (4.2b)$$

where $\Delta(t) = \rho_{11}(t) - \rho_{22}(t)$ is the population difference between the ground and excited states, and $\rho_{12} = \rho_{21}^*$. $\Gamma_{11}$ and $\Gamma_{21}$ are the population decay and dephasing rates of the system respectively. The SQD is assumed to be a dielectric sphere with dielectric constant $\epsilon_S$ and so
it has a screened dipole matrix element,

\[ \tilde{\mu}_{21} = \frac{\mu_{21}}{\epsilon_{\text{eff}S}}, \]  

where \( \mu_{21} \) is the bare dipole matrix element and

\[ \epsilon_{\text{eff}S} = \frac{2}{3} + \epsilon_S. \]  

The dipole moment of the SQD is

\[ p_{\text{SQD}}(t) = \text{tr} (\rho \mu) = \tilde{\mu}_{21} (\rho_{12} + \rho_{21}), \]  

where \( \text{tr} (\cdots) \) is the matrix trace operator.

The MNP’s frequency-dependent dipole moment is given as

\[ p_{\text{MNP}}(\omega) = \alpha_{\text{MNP}}(\omega) E_{\text{MNP}}(\omega), \]  

where \( \alpha_{\text{MNP}}(\omega) \) is the frequency-dependent polarisability. For comparison with previous literature, we approximate \( \alpha_{\text{MNP}}(\omega) \) by the Clausius-Mossotti formula,

\[ \alpha_{\text{MNP}}(\omega) = \frac{a^3}{\epsilon_M(\omega) + 2}, \]  

where \( \epsilon_M(\omega) \) is the frequency-dependent dielectric function of the bulk metal (see, e.g., Ref. [78]).

### 4.2 Energy Absorption Rates

The energy absorption rate (EAR) of the SQD-MNP system is a steady-state property in response to the following monochromatic wave,

\[ E_{\text{EXT}}(t) = E_0 \cos(\omega_L t), \]  

where \( \omega_L \) is the frequency of the wave and \( E_0 \) is the amplitude.

Suppose a steady-state is achieved where \( \Delta = 0 \) at some time, \( t = T^{s.s} \). Then we define

\[ \Delta^{s.s.} = \Delta (T^{s.s}) \]
CHAPTER 4. SEMICONDUCTING QUANTUM DOT-METAL NANOPARTICLE HYBRID

The EAR of the SQD is defined as

$$Q_{\text{SQD}} = \frac{1}{2} \hbar \omega_0 \Gamma_{11} \left( 1 - \Delta^2 \right), \quad (4.11)$$

while that of the MNP is

$$Q_{\text{MNP}} = \left\langle \int j(t) E_{\text{MNP}}^{(\text{in})}(t) \, dV \right\rangle , \quad (4.12)$$

where

$$j(t) = \frac{1}{V} \frac{d}{dt} p_{\text{MNP}}(t) \quad (4.13)$$

is the current density in the MNP [24] and $E_{\text{MNP}}^{(\text{in})}(t)$ is the field inside the MNP. For a sphere it can be shown that [78]

$$E_{\text{MNP}}^{(\text{in})}(t) = E_{\text{MNP}}(t) - \frac{4}{3} \pi p_{\text{MNP}}(t). \quad (4.14)$$

We define the time-average of a function $h(t)$ as

$$\langle h(t) \rangle = \frac{1}{\delta T} \int_{T}^{T+\delta T} h(t') \, dt', \quad (4.15)$$

and choose $T = T^{s.s.}$, and $\delta T$ to be one period of the wave,

$$\delta T = \frac{2\pi}{\omega_L}. \quad (4.16)$$

In Section 4.2.1, we show how $Q_{\text{SQD}}$ and $Q_{\text{MNP}}$ may be obtained analytically by means of the rotating wave approximation. In Section 4.2.2, we describe how one can use the PEOM method of Chapter 3 to find the same absorption rates. The two methods are then compared in Section 4.2.3.

4.2.1 Analytical Approach

By choosing Eq. (4.9) as the external field, Eq. (4.2) can be solved analytically under the so-called rotating wave approximation (RWA) where the frequency of incident radiation is assumed to be close to the frequency gap of the two-level system, i.e. $\omega_L \approx \omega_0$. Under the RWA, any fast oscillations in the system dynamics are neglected, and in Appendix B.4 we show that Eq. (4.2) becomes

$$\dot{\Delta} = 4 \text{Im} \left[ (\Omega_{\text{eff}} + G \rho_{21}) \rho_{21}^{*} \right] + \Gamma_{11} \left( 1 - \Delta \right), \quad (4.17a)$$

$$\dot{\rho}_{21} = i (\omega_L - \omega_0 + G \Delta) \rho_{21} - \Gamma_{21} \rho_{21} + i \Omega_{\text{eff}} \Delta. \quad (4.17b)$$
where we have introduced

\[ \Omega_{\text{eff}} = \Omega_0 \left( 1 + \frac{g}{R^3} \alpha_{\text{MNP}}(\omega_L) \right) , \]

\[ \Omega_0 = \frac{\tilde{\mu}_{21} E_0}{2} , \]

\[ G = \frac{g^2 \tilde{\mu}_{21}^2}{R^6} \alpha_{\text{MNP}}(\omega_L) . \]

and separated \( \rho_{21}(t) \) into slowly and quickly oscillating parts,

\[ \rho_{21}(t) = \tilde{\rho}_{21} e^{-i \omega_L t} , \]

where \( \tilde{\rho}_{21} \) is assumed to vary on a much larger timescale than \( 2\pi/\omega_L \). Eq. (4.17a) describes the change in the population with time. Using the conservation of total population (see Eq. (2.50)) and the definition, \( \Delta = \rho_{21} - \rho_{22} \), we first note that \( 1 - \Delta = 2\rho_{22} \), so we see that the rate of change of population difference depends on the population of the excited state, \( \rho_{22} \), which is damped by the decay constant, \( \Gamma_{11} \). It also depends on the coherence of the excited and ground states as described by \( \tilde{\rho}_{21} \) which is influenced in a non-trivial manner by the effective Rabi frequency, \( \Omega_{\text{eff}} \), and the term, \( G \), both of which depend on the MNP polarisability evaluated at the applied field frequency, \( \omega_L \). Similarly, the change in coherence is described by Eq. (4.17b) which depends both on the population difference and the coherence itself. Here, \( \tilde{\rho}_{21} \) is damped by the term \( \Gamma_{21} \) which determines the lifetime of the exciton of frequency \( \omega_0 \). Notice that if the system is initially in the ground state, we will have that \( \Delta = 1 \) and \( \tilde{\rho}_{21} = 0 \). Hence, by examining Eqs. (4.17a) and (4.17b), we see that the coupling between the population and coherence dynamics is introduced solely by the term \( \Omega_{\text{eff}} \) which depends on the strength of the applied electric field (see Eq. (4.19)) so that the equations are coupled self-consistently through the field.

Eq. (4.17) may be solved analytically under the steady-state conditions \( \dot{\Delta} = \dot{\tilde{\rho}}_{21} = 0 \) to obtain

\[ \tilde{\rho}_{21}^{s.s.} = \frac{-\Omega_{\text{eff}} \Delta^{s.s.}}{\omega_L - \omega_0 + G \Delta^{s.s.} + i \Gamma_{21}} , \]

where \( \Delta^{s.s.} \) is found by solving a cubic equation (see Appendix B.4). Thus, \( Q_{\text{SQD}} \) is found by Eq. (4.11). In the above equation, \( \omega_0 \) is the exciton frequency of the bare SQD while \( \Gamma_{21} \) is the exciton lifetime. In Eq. (4.19), \( \Omega_0 \) is the Rabi frequency of the bare SQD and \( \Omega_{\text{eff}} \) is then the Rabi frequency, renormalised due to the presence of the MNP. In Section 4.2.3 we show how these parameters are affected by the MNP interaction term, \( G \), for a weak field.

Finally, in Appendix B.6 we show that \( Q_{\text{MNP}} \) is given in the RWA by

\[ Q_{\text{MNP}} = 2\omega_L \text{Im}[\alpha_{\text{MNP}}(\omega_L)] \left| \frac{E_0}{2} + \frac{g \tilde{\mu}_{21}}{R^3} \tilde{\rho}_{21}^{s.s.} \right|^2 . \]
4.2.2 PEOM Approach

In the PEOM method (see Chapter 3), the SQD is treated as the primary system and $p_{SQD}(t)$ is calculated directly from the time-dependent density matrix elements (Eq. (4.6)) which are found by numerically integrating Eq. (4.2) using the fourth-order Runge-Kutta (RK4) method (see Appendix C). Conversely, the MNP is treated as the auxiliary system and $p_{MNP}(t)$ is approximated by (Eq. (3.8))

$$p_{MNP}(t) = \sum_{k=1}^{N} c_k \text{Re} [s_k(t)] ,$$

(4.24)

where the $\{s_k(t)\}$ are found by numerically solving

$$\dot{s}_k = -(\gamma_k + i\omega_k)s_k - iE_{MNP}(t) \quad \text{for} \ k = 1, 2, \ldots, N .$$

(4.25)

using the same RK4 method as for $p_{SQD}(t)$. Eqs. (4.2) and (4.25) can be solved in a coupled fashion as shown in Fig. 4.2.

Figure 4.2: Schematic showing how the PEOMs are solved, coupled with the density matrix equation of motion. We discretise time into equally spaced points, \{t_0, t_1, \ldots\}, and use the RK4 method (Appendix C) to solve the differential equations in Eq. (4.2) and Eq. (4.25) in parallel branches 1 and 2, respectively. After each iteration, the value of $E_{MNP}$ ($E_{SQD}$) is updated using the value of $p_{SQD}$ ($p_{MNP}$) from Branch 1 (2). We assume the initial conditions $t_0 = \rho(0) = s_k(0) = p_{SQD}(0) = p_{MNP}(0) = 0$.

The parameters $\{\gamma_k, \omega_k, c_k\}$ are found by a least-squares fit of the frequency-dependent
polarisability in Eq. (4.8) (see Section 3.3 and Appendix D.1).

\[ \Delta_{ss}, \text{ and therefore } Q_{SQD} \text{ (Eq. (4.11)), can be calculated trivially, assuming the simulation time is long enough that a steady-state can be said to have been reached (this can be inspected visually or by numerically checking that } \Delta \text{ is close to zero).} \]

To calculate \( Q_{MNP} \) from Eq. (4.12), one must first calculate the current density from Eq. (4.13). The derivative, \( \frac{dp_{MNP}}{dt}(t) \), may be calculated numerically, though it can be shown that (see Appendix B.5)

\[ \frac{dp_{MNP}}{dt} = \sum_{k=1}^{N} c_k \left( \omega_k \text{Im}[s_k(t)] - \gamma_k \text{Re}[s_k(t)] \right). \] (4.26)

The time-average in Eq. (4.12) can then be found by numerical integration. For a small time-step, \( h \), in the RK4 solution, we found the crude approximation,

\[ \int_{t_{m}}^{t_{n}} f(t') dt' \approx h \sum_{i=n}^{m} f(t_i), \] (4.27)

to be sufficient.

### 4.2.3 Comparison of Methods

In this section, we wish to test the validity of the PEOM model by comparing the results of the EARs for the weak and strong field regimes as described in Ref. [23]. We take the SQD system parameters from Ref. [23], which are typical of a CdSe quantum dot. The dielectric constant is taken to be \( \epsilon_S = 6 \) with (bare) transition dipole moment \( \mu_{21} = 0.65e \text{ nm} \) and exciton energy \( \hbar \omega_0 = 2.5 \text{ eV} \) close to the plasmon peak of the gold MNP which has a diameter of \( a = 7.5 \text{ nm} \). The decay and dephasing times are given by \( \Gamma_{11}^{-1} = 0.8 \text{ ns} \) and \( \Gamma_{21}^{-1} = 0.3 \text{ ns} \). The MNP frequency-dependent response is approximated by the Clausius-Mossotti formula and the PEOM parameters are obtained by a least-squares fit using 12 basis functions (see Section 3.3 and Table 3.1).

The field strength is given in terms of the intensity, \( I_0 \), by

\[ I_0 = \frac{c}{8\pi} E_0^2, \] (4.28)

where \( c \) is the speed of light. We define the total EAR as

\[ Q = Q_{SQD} + Q_{MNP}. \] (4.29)

Fig. 4.3 shows the total EAR for the hybrid system as a function of the laser detuning, \( \hbar(\omega_L - \omega_0) \), in the weak-field regime \( (I_0 = 1 \text{ W cm}^{-2}) \) for various separation distances of the
two particles. As in Ref. [23], we see the quenching of $Q$ and the red-shift of the hybrid exciton energy as the particles are brought together. This effect is clear by considering that for a weak field, there is little difference in the population levels, i.e. $\Delta = 1$, and indeed the effect is apparent upon examination of the steady-state value of $\bar{\rho}_{21}$ from Eq. (4.22),

$$\bar{\rho}_{21} = \frac{-\Omega_{\text{eff}}}{(\omega_L - \omega_0 + \text{Re}[G]) + i(\Gamma_{21} + \text{Im}[G])}.$$ (4.30)

From Eq. (4.30), we can see that the hybrid exciton frequency is shifted by the real part of $G$ while the damping coefficient is increased by the imaginary part of $G$.

![Figure 4.3](image)

**Figure 4.3:** Energy absorption rate, $Q$, for the SQD-MNP system under illumination of a monochromatic wave of weak intensity ($I_0 = 1\ \text{W cm}^{-2}$) and frequency $\omega_L$, as a function of the laser detuning, $h(\omega_L - \omega_0)$ for separation distances $R = 13\ \text{nm}$ (green), $15\ \text{nm}$ (red), $20\ \text{nm}$ (blue) and $80\ \text{nm}$ (black). The solid lines represent the steady-state analytical solution in the RWA while the crosses are the results from the PEOM method.

The strong-field regime ($I_0 = 1 \times 10^3 \text{W cm}^{-2}$) is shown in Fig. 4.4. We see a so-called asymmetric, fano shape which becomes more pronounced for smaller inter-particle distances. The effect is attributed to non-linear interference between the external field and the field generated by the SQD at the MNP [23, 79].

In Figs. 4.3 and 4.4, the analytical RWA solutions are shown in solid lines while the crosses are the results taken from the numerical integration in the PEOM method. In both the weak and strong field regimes, we see perfect agreement between the two methods due to the validity of the RWA for the case of a sinusoidal external field with frequency very close to resonance with the SQD exciton frequency.
Figure 4.4: As Fig. 4.3 but in the strong field regime where the laser intensity is $I_0 = 1 \times 10^3 \text{W cm}^{-2}$.
4.3 Population Inversion

Population inversion occurs when the SQD is excited from the ground state to the excited state so that $\rho_{11} = 0$, $\rho_{22} = 1$ and is associated with short laser pulses (see, for example, Ref. [80]). We consider a pulsed external field given by

$$E_{\text{EXT}}(t) = E_0 f(t) \cos(\omega_L t) \ ,$$

(4.31)

where $f(t)$ is a dimensionless pulse envelope. The pulse area for an isolated SQD is defined as

$$\theta = \Omega_0 \int_{-\infty}^{\infty} f(t) dt \ ,$$

(4.32)

and it is known that population inversion occurs at the end of the pulse for $\theta = (2n + 1)\pi$ ($n = 0, 1, 2, \ldots$) [81].

We shall use a hyperbolic secant envelope defined by

$$f(t) = \text{sech} \left( \frac{t - \tau_0}{\tau_p} \right) \ ,$$

(4.33)

where $\tau_0$ is the centre of the pulse and $\tau_p$ characterises the pulse width. We choose the central frequency, $\omega_L$, to be resonant with the exciton frequency, i.e. $\hbar \omega_L = \hbar \omega_0 = 2.5$ eV, and we describe the pulse shape in terms of the number of cycles, $n$, by defining the pulse duration as

$$T = \frac{4\pi}{\omega_L} n \ ,$$

(4.34)

and choosing

$$\tau_0 = T/2 \ , \ \tau_p = T/30 \ .$$

(4.35)

In this way we ensure the maximum amplitude, $E_0$, is achieved at the centre of the pulse and that the external field is sufficiently close to zero at $t = 0$ and $t = T$ for the values of $E_0$ considered here.

For the sech pulse in Eq. (4.33), it can easily be shown from Eq. (4.32) that for an isolated SQD, $\theta = \pi \Omega_0 \tau_p$, and then a pulse of given duration can be described in terms of the pulse area by choosing the following field amplitude,

$$E_0 = \frac{\hbar \theta}{\pi \mu_{21} \tau_p} \ .$$

(4.36)

In Ref. [26] it was shown that the pulse area for an SQD when coupled to the MNP may be
written approximately as $\theta = \pi |\Omega_{\text{eff}}| \tau_p$ so that Eq. (4.36) becomes

$$E_0 = \hbar \theta \left( \pi \tilde{\mu}_{21} \tau_p \left| 1 + \frac{g}{R^3} \alpha_{\text{MNP}}(\omega_L) \right| \right)^{-1}. \quad (4.37)$$

In particular, it was stated that for short pulses ($\tau_p \sim 0.1 \text{ ps}$) with amplitude given by Eq. (4.37), the resulting dynamics should be independent of $R$ as the influence of the parameter $G$ (see Eq. (4.20)) becomes weaker.

In Section 4.3.1, we describe how the SQD-MNP dynamics may be solved numerically within the RWA and by an effective field method (both of which are common approaches in the literature) and outline their limitations. In Section 4.3.2, we go on to compare the results of these semi-analytical methods with the PEOM approach.

### 4.3.1 Semi-Analytical Approaches

In previous studies relating to pulsed excitations in SQD-MNP systems, the time-scales have generally been limited to relatively long pulses. For example in Ref. [82, 83], the external field is switched on over tens of nanoseconds while in Ref. [26, 84], picosecond pulses are used. In such cases the pulse envelope, $f(t)$, is slowly varying, and the population dynamics can be found by solving the RWA EOMs in Eq. (4.17) but replacing $\Omega_{\text{eff}}$ with the time-dependent form (see Appendices B.3 and B.4),

$$\Omega(t) = f(t)\Omega_{\text{eff}}, \quad (4.38)$$

giving

$$\begin{cases} 
\hat{\Delta} = 4\text{Im} \left[ (\Omega(t) + G\tilde{\mu}_{21}) \hat{\rho}_{12} \right] + \Gamma_{11} (1 - \Delta) \\
\hat{\rho}_{21} = i (\omega_L - \omega_0 + G\Delta) - \Gamma_{21} \hat{\rho}_{21} + \frac{|\Omega(t)|^2}{2} \Delta 
\end{cases} \quad (4.39)$$

The above equations can then be solved numerically to obtain the population difference, $\Delta(t)$.

Now, the use of the RWA and slowly-varying envelope approximations respectively imply that solutions to (4.39) are only valid if $\tilde{\mu}_{21}(t)$ and $f(t)$ vary much more slowly than $2\pi/\omega_L$. Recalling that $\hbar\omega_L = 2.5 \text{ eV}$, we therefore require the pulse duration to be much greater than $\sim 2 \text{ fs}$.

Indeed, it is known that the RWA is not reliable for ultrashort (femto- and subfemto-second) pulses [85–87]. This is demonstrated in Figure 4.5 where we compare the solution of the original EOMs in Eq. (4.2) with those of the modified RWA EOMs in Eq. (4.17), showing the excited state population dynamics for an isolated SQD ($R \to \infty$) interacting with a picosecond and femtosecond pulse of area $5\pi$ (according to Eq. (4.36)). Figure 4.5 (a) shows $\rho_{22}(t)$ for a 1000-cycle pulse ($\tau_p \approx 0.11 \text{ ps}$) and we can see that the RWA in this case provides an adequate description of the dynamics, with population inversion occurring at the end of the pulse as expected for a $5\pi$ pulse. The inset shows a magnified region in which we can see the effect of
the RWA neglecting the quickly oscillating terms: however, in the picosecond time-scale, these effects have negligible influence on the overall dynamics. Fig. 4.5 (b) shows $\rho^{22}(t)$ for a 10-cycle pulse ($\tau_p \approx 1.1$ fs) where the pulse duration is of a comparable time-scale to $2\pi/\omega_L$. In this case, we can see that the quickly oscillating terms neglected in the RWA solution have a more significant effect on the overall dynamics: importantly, complete population inversion is not achieved at the end of the pulse, and there is a much more oscillatory behaviour.

**Figure 4.5:** Excited state population dynamics for an isolated SQD ($R \to \infty$) interacting with a sech pulse of area $5\pi$ according to Eq. (4.36). The solid red line is the numerical solution to the original EOMs in Eq. (4.2) while the dashed blue line is the solution to the modified RWA EOMs in Eq. (4.39). (a) Dynamics for a 1000-cycle pulse corresponding to $\tau_p \approx 0.11$ ps. (b) Dynamics for a 10-cycle pulse corresponding to $\tau_p \approx 1.1$ fs.

In Ref. [87], a numerical solution to Eq. (4.2) for pulsed excitation in SQD-MNP systems beyond the RWA is proposed. In deriving Eq. (4.39), $E_{\text{SQD}}(t)$ is expressed by separating out the positive and negative frequency parts as

$$E_{\text{SQD}}(t) \approx \hbar \frac{1}{2} \left[ \left( \frac{\Omega(t)}{2} e^{-i\omega_L t} + G\rho_{21}(t) \right) + \text{c.c.} \right].$$

Instead of invoking the usual RWA to arrive at Eq. (4.39), Yang et al. numerically solve Eq. (4.2) using as $E_{\text{SQD}}(t)$ the field in Eq. (4.40) (we shall call this method the effective field method). However, in deriving Eq. (4.40), one must first separate out the slowly oscillating components of the off-diagonal density matrix elements as in Eq. (4.21) (see e.g. Ref. [24]) and the slowly-varying envelope approximation must also be used (see Appendix B.3). Thus, while the quickly oscillating terms are included, improving over the RWA, the pulse duration must still be longer than $2\pi/\omega_L$.

In the next section, we compare results obtained by the RWA and effective field method with the PEOM approach which requires no slowly-oscillating approximations.
4.3.2 Comparison with PEOM Approach

In the previous section, we described how the SQD-MNP dynamics interacting with a short pulse may be obtained either by solving the modified RWA equations of Eq. (4.39) or by solving the original density matrix EOMs in Eq. (4.2) with a slowly-varying effective field (Eq. (4.40)). In this section, we compare results from both methods with those obtained by directly solving the original EOMs of Eq. (4.2) using the PEOM method as outlined in Fig. 4.2, which requires no RWA or slowly-varying pulse approximations.

Figure 4.6: Excited state population dynamics for an SQD-MNP system interacting with a 10-cycle sech pulse for various interparticle distances, $R$. The field amplitude is chosen to give a $5\pi$ pulse area for each value of $R$ according to Eq. (4.37). (a) Solution to the modified EOMS in Eq. (4.39) under the RWA and assuming a slowly-varying pulse envelope. (b) Solution to the original EOMs in Eq. (4.2) beyond the RWA using the effective field in Eq. (4.40) which assumes a slowly-varying pulse envelope. (c) Solution to Eq. (4.2) using the PEOM method where the auxiliary parameters are obtained by fitting $\alpha_{\text{MNP}}(\omega)$ in Eq. (4.8) accurately over the range $0–10$ eV using $N = 21$ fitting functions. (d) Same as (c) but where $\alpha_{\text{MNP}}(\omega)$ is fitted over a small range close to $\hbar\omega_0$ ($2.455–2.545$ eV) using $N = 1$ fitting functions. Insets: real (blue dashed) and imaginary (black dashed) parts of the fitted polarisability, $\alpha_{\text{MNP}}(\omega)/a^3$ (exact function shown in grey).

In Fig. 4.6, we compare the solutions for $\rho_{22}(t)$ based on the RWA, effective field method and the PEOM method. In each case, the SQD-MNP system interacts with a 10-cycle sech pulse of area $5\pi$ with $R$-dependent amplitude given by Eq. (4.37) and the excited state population.
dynamics are shown for various interparticle distances.

In Fig. 4.6 (a), the modified RWA EOMS in Eq. (4.17) are solved and we can see that complete population inversion occurs at the end of the pulse and the dynamics are identical for each $R$ as expected from Ref. [26] and Eq. (4.37).

In Fig. 4.6 (b), the original EOMS in Eq. (4.2) are solved beyond the RWA by taking $E_{SQD}(t)$ of the form in Eq. (4.40) similar to the calculations performed in Ref. [87]. In this case we see that the dynamics are almost identical to the isolated SQD as shown in Fig. 4.5 (b) where the original EOMs are solved exactly. At difference with the RWA solution in Fig. 4.6 (a), complete population inversion does not occur as a consequence of the RWA-breakdown. On the other hand, the dynamics remain independent of $R$ as predicted by Ref. [26]. We note at this point that Ref. [26, 87] employ a multipole description for the MNP response while our calculations use the simpler dipole model. However, we have compared results using the same multipole approximation and noticed no difference due to the short time-scales involved here.

In Fig. 4.6 (c), we solve the original EOMs in Eq. (4.2) using the PEOM method. We obtain the auxiliary parameters describing the MNP dipole moment by fitting $\alpha_{MNP}(\omega)$ in Eq. (4.8) to the functions in Eq. (3.12). This is achieved by a least-squares fit over the range 0–10 eV using $N = 21$ fitting functions to gain a fit of sufficient accuracy (see inset). We see that for large $R$ ($R = 80$ nm), $\rho_2(t)$ resembles the results in (b). However, as the interparticle distance decreases, the dynamics change considerably, with larger effect towards the end of the pulse. For each $R$, the dynamics are similar up to around 18 fs by which point the pulse is almost over (see Fig. 4.7 (b)). After this point, the population for each $R$ reaches the same maximum value (around 0.95), but at different times: $\sim 23$ fs for $R = 80$ nm, $\sim 21$ fs for $R = 20$ nm and $\sim 20$ fs for $R = 13$ nm. The population then decreases more steeply as $R$ decreases, reaching as low as 0.6 for $R = 13$ nm.

We ascribe the different results obtained with the PEOM in Fig. 4.6 (c) and the effective field method in Fig. 4.6 (b) to the fact that femtosecond pulses ($\sim 10$ cycles) excite a broad range of frequencies: in particular, much broader than the sub-picosecond pulses ($\sim 100$ cycles) for which the effective field method [87] was originally developed. As stated earlier, in writing Eq. (4.40), $f(t)$ must be slowly varying and the off-diagonal density matrix elements must also first be separated into slowly and quickly oscillating components. Under these approximations, the MNP has a ‘local’ response in time: it can be shown that the response function, $\alpha(t,t')$, is delta-like so that the response is flat in the frequency domain, i.e. the frequency-dependent polarisability is effectively constant (see Appendix B.7). However, the femtosecond pulse has a large bandwidth ($> 1$ eV), thus exciting a broad range of frequencies in the MNP response. Moreover, $\alpha_{MNP}(\omega)$ changes significantly over this range close to $\hbar \omega_0 = 2.5$ eV due to the formation of the plasmon peak and thus one would expect the resulting time-dependent dipole moment, $p_{MNP}(t)$, (and therefore $E_{SQD}(t)$) to be modified compared with that for long pulses.
of smaller bandwidths. In Fig. 4.7, $p_{\text{MNP}}(t)$ is shown for the $R = 13 \text{ nm}$ cases in Fig. 4.6 (b) and (c). We can see that in the effective field method, the MNP responds in phase with the external field, while in the PEOM method the dipole moment continues to propagate well after the pulse is over, thus contributing to the decline in population of the SQD.

**Figure 4.7:** Time evolution of the MNP dipole moment, $p_{\text{MNP}}(t)$, for the $R = 13 \text{ nm}$ cases in Fig. 4.6 (b) (solid blue) and (c) (solid black) where the effective field method and PEOM method are used respectively. The corresponding external field is shown in dashed red.

**Figure 4.8:** Value of $\rho_{22}(t)$ at the end of the pulse for various pulse durations. The interparticle distance is $R = 13 \text{ nm}$ and the pulse area is chosen to be $5\pi$ according to Eq. (4.37).

We have stated that in the effective field method, the MNP has a local response in time and, therefore, an effectively constant polarisability. This approximation is valid for monochromatic waves (e.g. Eq. (4.9)) and for long pulses. On the other hand, for very short pulses the frequency-dependence of the polarisability is important due to the larger bandwidth. The
PEOM method overcomes this limitation as $\alpha_{\text{MNP}}(\omega)$ can be fitted over an arbitrary frequency range (as in Fig. 4.6 (c)) so that the relevant frequencies can be included in the dynamics. The constant polarisability of the effective field method can be simulated within the PEOM method by choosing a single, broad function ($N = 1$) which agrees with $\alpha_{\text{MNP}}(\omega)$ at $\omega_L$ and is approximately constant over the pulse bandwidth region (see inset of Fig. 4.6 (d)). Fig. 4.6 (d) then shows that the effective field results from Fig. 4.6 (c) are indeed recovered.

Fig. 4.8 summarises the results and shows the range of pulse durations for which the different approximations are valid. The three different methods agree for $n > 100$ cycles ($\tau_p > 10$ fs). The effective field method correctly describes the fall in final population as the pulse duration approaches 10 cycles due to the breakdown of the RWA, but we can see that when the full response of the MNP is taken into consideration in the PEOM method, the effect is much more enhanced.

Overall, the results of this section show that when examining the response of ultrashort pulses (fewer than $\sim 60$ cycles), one cannot rely on the RWA or the slowly-varying pulse approximation as in the effective field method. Therefore, one should consider more advanced approaches. The PEOM methods is a valid alternative as it is not bound by such approximations, yet still its computational cost and complexity is similar to that of, e.g., the RWA or effective field method.
Chapter 5

2D Material Composites

In Chapter 4, we have tested the PEOM method on a small SQD-MNP system and it was shown to reproduce analytical and semi-analytical results while proving advantageous over existing methods for simulating the interaction with an ultra-short pulse. In this section, we test the PEOM method when applied to larger systems as a further proof of concept. In particular, we investigate the optical absorption spectra of bilayers of MoS$_2$ and hexagonal boron nitride (h-BN). The absorption spectra for the bilayers can be obtained readily both via TDDFT and the more intensive Bethe-Salpeter equation (BSE) within linear response; the results are shown in Section 5.2. In Section 5.3 we describe how the PEOM method can be used both by coupling the PEOMs to the time-dependent BSE and by using two coupled PEOMs (the PEOM-PEOM method). The spectra obtained via the standard linear response methods are compared with those from the PEOM-PEOM approach in Section 5.4.

5.1 Atomic Configurations

Before any response calculations can be carried out, we require knowledge of the crystal structure of the materials, e.g., the unit cell symmetry and the atomic positions within the unit cell. Both MoS$_2$ and h-BN have a layered form with hexagonal symmetry. The primitive lattice vectors are then given by (see Eq. (2.70))

$$a_1 = (a, 0, 0) ,$$  \hspace{1cm} (5.1a)

$$a_2 = \left(-\frac{1}{2}a, \frac{\sqrt{3}}{2}a, 0\right) ,$$  \hspace{1cm} (5.1b)

$$a_3 = (0, 0, c) ,$$  \hspace{1cm} (5.1c)
where \( a \) and \( c \) are the system-specific lattice parameters. In particular \( c \) describes the inter-layer separation distance. The lattice parameters may be obtained experimentally or by ab initio simulations via geometry optimisation. Now, we wish to simulate isolated layers of the materials which requires no periodicity in the layer-normal direction (i.e. in the \( z \)-axis). This can be mimicked by choosing \( c \) large enough so that any spurious interactions between the layers are negligible. We shall refer to the distance between the uppermost atom of a unit cell and the bottommost atom in the repeated cell directly above (in the layer-normal direction) as the vacuum distance.

We begin by looking at \( \text{MoS}_2 \). In the case of the monolayer, the simplest unit cell contains just three atoms, the Mo atom and the two S atoms which we label \( \text{Mo}_1, \text{S}_1 \) and \( \text{S}_2 \) respectively. As described in Ref. \cite{88}, we choose the bulk experimental parameters with lattice constant, \( a = 3.16 \AA \), Mo–S bond length of 2.417 \( \AA \) and S–Mo–S bond angle of 82.0\(^\circ\). This configuration is depicted in Fig. 5.1 (a) and the atomic positions within the unit cell are given in Table 5.1.

Similarly, the bilayer unit cell contains six atoms which we denote \( \text{Mo}_1, \text{S}_1, \text{S}_2, \text{Mo}_2, \text{S}_3 \) and \( \text{S}_4 \). Now, the layers in \( \text{MoS}_2 \) crystallise in several different fashions. In nature, the most common form is the so-called 2\( H \) phase, or \( \text{AA}' \) stacking, where the Mo atom fully eclipses the S atoms as shown in Fig. 5.1 (b). Much less common is the \( \text{AA} \) stacking formation where the Mo atom fully eclipses the Mo atom as shown in Fig. 5.1 (c). We label the distance (in the \( z \)-direction) between the two Mo atoms in the unit cell as \( d \) (see Fig. 5.1), and from Ref. \cite{88} we take \( d = 6.25 \AA \) for the \( \text{AA}' \) form and \( d = 6.77 \AA \) for the \( \text{AA} \) form. For both the monolayer and bilayer, we take a vacuum distance of 20 \( \AA \). The atomic positions within the unit cell are given in Table 5.1.

![Figure 5.1](image)

**Figure 5.1:** Side (top panel) and top (bottom panel) views of (a) a monolayer of \( \text{MoS}_2 \) (b) a bilayer of \( \text{MoS}_2 \) in the \( \text{AA}' \) configuration and (c) a bilayer of \( \text{MoS}_2 \) in the \( \text{AA} \) configuration. The solid grey lines represent the unit cell boundaries. In (b) and (c), the two layers are separated such that the Mo atoms are a distance, \( d \), apart in the \( z \)-direction.

We now turn to the second of our systems, hexagonal boron nitride (\( h \)-BN). Like \( \text{MoS}_2 \),
Table 5.1: Atomic, Cartesian coordinates (in Å) within the hexagonal unit cell described by Eq. (5.1) with the lattice constant \( a = 3.16 \text{ Å} \) and \( c \) is chosen so as to have a vacuum distance of 20 Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Monolayer</th>
<th>Bilayer (AA')</th>
<th>Bilayer (AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo (_1)</td>
<td>(0.000, 1.824, 2.586)</td>
<td>(0.000, 1.824, 8.836)</td>
<td>(0.000, 1.824, 2.586)</td>
</tr>
<tr>
<td>S (_1)</td>
<td>(1.580, 0.912, 1.000)</td>
<td>(1.580, 0.912, 7.250)</td>
<td>(1.580, 0.912, 1.000)</td>
</tr>
<tr>
<td>S (_2)</td>
<td>(1.580, 0.912, 4.171)</td>
<td>(1.580, 0.912, 10.421)</td>
<td>(1.580, 0.912, 4.171)</td>
</tr>
<tr>
<td>Mo (_2)</td>
<td>-</td>
<td>(1.580, 0.912, 2.586)</td>
<td>(0.000, 1.824, 9.356)</td>
</tr>
<tr>
<td>S (_3)</td>
<td>-</td>
<td>(0.000, 1.824, 1.000)</td>
<td>(1.580, 0.912, 7.770)</td>
</tr>
<tr>
<td>S (_4)</td>
<td>-</td>
<td>(0.000, 1.824, 4.171)</td>
<td>(1.580, 0.912, 10.941)</td>
</tr>
</tbody>
</table>

\( h \)-BN is also considered as a 2D material. In fact, it may be viewed as a ‘truer’ 2D system as, like Graphene, all the atoms lie in a single plane as opposed to \( \text{MoS}_2 \) (and other TMDs) which is effectively 3 atoms thick. We use the lattice parameter \( a = 2.50 \text{ Å} \) [89]. The atomic positions are shown in Fig. 5.2 (a) and detailed in Table 5.2.

\( h \)-BN also has many different stacking arrangements, with the \( AA' \) configuration being the most stable [90]. However, we present here only the less common \( AA \) formation and use the experimental interlayer distance of 3.3 Å [89]. For both the monolayer and bilayer, a vacuum distance of around 20 Å is used. The bilayer is shown in Fig. 5.2 (b) and the atomic coordinates are given in Table 5.2.

![Figure 5.2](image)

**Figure 5.2:** Side (top panel) and top (bottom panel) views of (a) a monolayer of \( h \)-BN and (b) a bilayer of \( h \)-BN in the \( AA \) configuration.

Now that we have defined the periodic structure of the two systems, we may obtain the ground state properties of the systems via DFT (see Section 2.2) and then perform calculations to obtain the optical absorption spectra. The intention is to compare results from standard approaches with those obtained through a method involving the PEOM.
### Table 5.2: Atomic, Cartesian coordinates (in Å) within the hexagonal unit cell described by Eq. (5.1) with the lattice constant $a = 2.50$ Å and $c$ is chosen so as to have a vacuum distance of around 20 Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Monolayer</th>
<th>Bilayer (AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>(1.248, 0.720, 0.500)</td>
<td>(1.248, 0.720, 3.500)</td>
</tr>
<tr>
<td>$N_1$</td>
<td>(0.000, 1.440, 0.500)</td>
<td>(0.000, 1.440, 3.500)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>-</td>
<td>(1.248, 0.720, 6.800)</td>
</tr>
<tr>
<td>$N_2$</td>
<td>-</td>
<td>(0.000, 1.440, 6.800)</td>
</tr>
</tbody>
</table>

#### 5.2 Absorption Spectra from Linear Response Theory

To calculate the absorption spectrum of a system, we must first determine the ground state electronic configuration. The ground state Kohn-Sham orbitals and energies are calculated using the Quantum Espresso package \[91\] which is an implementation of the self-consistent field (SCF) method using a plane wave basis and pseudopotentials.

In the SCF calculation for MoS$_2$ we use a GGA exchange-correlation functional and for convergence of the total ground state energy we required a plane wave energy cut-off of $E_{\text{cut}} = 60$ Ry and used a $8 \times 8 \times 1$ $k$-point sampling grid. For $h$-BN, we use an LDA functional and required $E_{\text{cut}} = 80$ Ry and with a $6 \times 6 \times 1$ $k$-point sampling. In both cases, the total energy was converged to within 0.001 Ry.

Once the orbitals and energies have been calculated, excited state calculations can be performed in YAMBO \[59\] to determine the absorption spectra. In this section we show the linear response (LR) spectra for the two materials within the independent particle (IP) approximation and random phase approximation (RPA) (see Section 2.3.3). Spectra from the Bethe-Salpeter equation (BSE) are also obtained (see Section 2.3.5). Note that in this chapter, we refer to the absorption as the imaginary part of the polarisability as described in Eq. (2.89) for finite systems, and not the general definition in Eq. (2.13).

We compare the absorption spectra for a monolayer of $h$-BN within different levels of approximation. For convergence of the IP spectrum, we required a $64 \times 64 \times 1$ $k$-point sampling and we use 20 bands for the non-interacting response function. In the RPA, we build the response function using $G$-vectors with an energy up to 10 Ry (we shall call this the response block size). In the BSE, the exchange block size is 40 Ry and that of the screened interaction is 10 Ry (i.e. that of the converged RPA spectrum). We choose only the highest valence band and lowest conduction band in the BSE kernel (i.e., one band either side of the Fermi level) which give the largest contribution to the resulting spectrum. Note that it is conventional to use the $GW$-corrected energies in the solution of the BSE which often results in an almost rigid blue-shift of the spectra. However, for the purposes of this thesis we are interested more in the
Figure 5.3: Comparison of absorption spectra for the $h$-BN monolayer obtained from linear response calculations within the IP, RPA and BSE approximations.

qualitative effects for comparison with the PEOM method and we neglect the $GW$ calculations and instead use the LDA energies within the BSE equation (the use of $GW$ depends on the dielectric screening and it is unclear that the PEOM should capture such effects). In all cases, we use a damping of $0.2 \text{ eV}$.

From Fig. 5.3, in the simplest, IP approximation we see a strong peak at around $5.6 \text{ eV}$. The RPA is only a little different to the IP, with a slight blue-shift and decrease in the peak height, thus suggesting that local field effects do not play a large role. However, it is well documented that excitonic effects are important in $h$-BN [92–94], which is demonstrated in the BSE spectrum. We see a large red-shift (of $3.6 \text{ eV}$) and a sharpening of the dominant peak, as well as an additional excitonic peak at around $3 \text{ eV}$. These results are in good agreement with the literature [92, 93]. We note that in Ref. [92], the BSE peak remains in roughly the same position as that of the RPA in contrast what is reported here. This feature was ascribed to the excitonic red-shift almost exactly cancelling the blue-shift of the $GW$ correction (which we have not included) which was around $3.5 \text{ eV}$, in good agreement with the shift shown in Fig. 5.3.

We now turn to the bilayer of $h$-BN as described in Fig. 5.2. For convergence, we again require a $64 \times 64 \times 1$ $k$-point sampling. We use 30 bands in the IP response function. The RPA and BSE block sizes are the same as in the monolayer calculation, while we use two bands either side of the Fermi level in the BSE.

Fig. 5.4 shows the spectra calculated in the same way as in Fig. 5.3 but for the bilayer (which is simply two monolayers separated by a distance of $d = 3.3 \text{ Å}$). If there were no
interaction between the layers, then we would expect the absorption spectrum to be simply the superposition of the spectra of two independent monolayers (such would be the case if $d$ was very large). This superposition is shown in corresponding faded colours in Fig. 5.4 for comparison. We can see that in the IP and RPA cases, there appears to be little interaction between the layers, with a small reduction of the dominant peak with respect to two well-separated monolayers. On the other hand, the BSE shows not only a reduction of the peaks, but a blue-shift of the spectrum of just under 1 eV, suggesting that excitonic effects are an important part of the inter-layer interaction.

For the MoS$_2$ monolayer and bilayer, we use a $51 \times 51 \times 1$ $k$-point sampling for convergence of the spectra. In the case of the monolayer, we use 22 bands in the IP response function and the RPA block size is 7 Ry. For the bilayer, we use 34 bands and a block size of 7 Ry.

In Fig. 5.5, in the IP spectrum of the MoS$_2$ monolayer, we see a dominant peak at around 2.8 eV and two smaller peaks at around 3.8 eV and 4.3 eV. When local field effects are included in the RPA, we see that the profile remains largely unchanged. There is a reduction of the dominant peak and a blue-shift of around 0.2 eV. The smaller peaks are less affected with just a small decrease in peak height.

In Fig. 5.6, we see the same spectra but for the bilayer. Compared with two isolated MoS$_2$ monolayers, in the IP we see a reduction of the dominant peak and a slight broadening of the second peak, while the third remains largely unchanged. In the RPA case, there is very little difference between the two spectra. As with h-BN, we would expect a greater level of difference
between the monolayer and bilayer spectra for a BSE calculation, though we do not currently explore this.

In the subsequent sections, we wish to simulate a bilayer of h-BN or MoS$_2$ by treating one layer using \textit{ab initio} approaches and simulating the additional layer using the PEOM approach. The \textit{ab initio} approach we use is that outlined in Section 2.3.6, i.e. the so-called time-dependent BSE method which can be directly coupled with the PEOM method in a similar fashion to the SQD-MNP system described in Chapter 4. Before showing this, however, we demonstrate in the next section that the results obtained from the time-dependent BSE coincide with the linear response theory and show that to further reduce computational cost, we may instead couple two sets of PEOMs.
Figure 5.6: Comparison of absorption spectra for the $h$-BN bilayer obtained from linear response calculations within the IP and RPA approximations. The corresponding monolayer spectra (multiplied by a factor of 2) are shown in faded colours for comparison.
5.3 PEOM Approaches

![Schematic diagram of a bilayer composed of two monolayers, 1 and 2, which extend infinitely in the x- and y-directions and are separated by a distance R along the z-axis. The monolayers are assumed to be isotropic and the external electric field, $E_{\text{EXT}}$, is directed along the monolayer plane (e.g. along the x-axis).](image)

In the previous section, we have seen how absorption spectra for monolayers and bilayers of h-BN and MoS$_2$ may be obtained from linear response (LR) TDDFT and BSE calculations. In this section we show how one may use the PEOM method to simulate the absorption spectrum of a bilayer, given that the polarisability of the monolayer is known.

As depicted in Fig. 5.7, the bilayer may be thought of as two monolayers separated by a distance, $R$, along the layer-normal ($z$) axis. We label the monolayers 1 and 2. In a similar fashion to the SQD-MNP system of Chapter 4, we model monolayer 1 using a high level of theory (namely the TD-BSE approach in Section 2.3.6). We assume the frequency-dependent polarisability of monolayer 2, $\alpha_2(\omega)$, is known (e.g. from LR calculations as shown in the previous section). We also assume that the monolayers are isotropic and the external field, $E_{\text{EXT}}$, is directed along the x-axis. Similarly to Eq. (4.1), the fields felt by monolayers 1 and 2 are, respectively,

$$E_1(t) = E_{\text{EXT}}(t) - \frac{p_2(t)}{R}, \quad (5.2a)$$
$$E_2(t) = E_{\text{EXT}}(t) - \frac{p_1(t)}{R}, \quad (5.2b)$$

where $p_1$ and $p_2$ are the dipole moments associated with monolayers 1 and 2 respectively and we have set the factor $g = -1$ (see Eq. (3.2)). Note that compared with Eq. (4.1), there is a $1/R$ dependence rather than the original $1/R^3$ dependence since the layer separation is confined to one-dimension and the monolayer dipole moment has units of length rather than volume due to its two-dimensional nature (see discussion at the end of Section 2.3.4).

Now, the polarisation density for monolayer 1, $P_1(t)$, shall be obtained from the TD-BSE
method. From Eq. (2.2), it is clear that the dipole moment is given by

$$ p_1 = \Omega_1 P_1, $$

(5.3)

where $\Omega_1$ is the volume of the unit cell of the TD-BSE simulation. In fact, as discussed at Eq. (2.89), since the monolayer is periodic in the $x - y$ plane, $\Omega_1$ is simply the height of the simulation unit cell.

The dipole moment of monolayer 2 is obtained by the following PEOMs (see Chapter 3),

$$ s_k^{(2)} = - \left( \gamma_k^{(2)} + i \omega_k^{(2)} \right) s_k^{(2)} + i E_1(t), $$

(5.4)

and is given by

$$ p_2(t) = \sum_k \Re \left[ s_k^{(2)}(t) \right], $$

(5.5)

where the parameters are found by a fit of its frequency-dependent polarisability, $\alpha_2(\omega)$. We must renormalise the dipole moment to take into account that the TD-BSE simulation is performed in the simulation cell of volume $\Omega_1$. Since we know the polarisation density of monolayer 2 is simply (c.f. Eq. (5.3))

$$ P_2 = \frac{p_2}{\Omega_2}, $$

(5.6)

where $\Omega_2$ is the volume of the unit cell from which $\alpha_2(\omega)$ was calculated. Hence, in Eq. (5.2a) we rather use a dipole moment, $p_2^{\text{norm}}$, renormalised to the unit cell of monolayer 1,

$$ p_2^{\text{norm}} = \Omega_1 P_2, $$

$$ = \frac{\Omega_1}{\Omega_2} p_2. $$

As an example, we take as monolayer 1 the $h$-BN monolayer from the previous section. We work within the independent particle approximation and use the same convergence parameters as in the LR calculation of Fig. 5.3 but with a reduced $k$-point sampling of $6 \times 6 \times 1$.

We first perform the TD-BSE calculation for an isolated monolayer ($R \to \infty$) to compare with the standard LR results. In the LR calculation, we have a damping term which causes a Lorentzian broadening of the resulting spectra in order to match experimental results. This is obtained in the TD approach by adding a dephasing rate, $\Gamma$. For a damping in the spectra of $0.2 \text{ eV}$ (as in the LR calculations for $h$-BN in the previous section), we require $\Gamma = 3.291 \text{ fs}$. Note that it is important to add in this dephasing during the simulation (rather than in a post-processing step) when we introduce the PEOM coupling since the PEOM parameters will have been fitted from an already-damped spectrum. In all simulations in this chapter, we choose a time-step of $0.05 \text{ fs}$ for the Runge-Kutta propagation, and the external field is the delta-like
function given in Eq. (3.18) with an intensity of $I_0 = 1 \text{ W cm}^{-2}$ and a start-time equal to the Runge-Kutta time-step.

![Graph showing time-dependent polarization](image)

**Figure 5.8:** Time-dependent polarisation of the $h$-BN monolayer interacting with a delta-like external field of intensity $I_0 = 1 \text{ W cm}^{-2}$ as calculated from the TD-BSE equation within the IP approximation.

Fig. 5.8 shows the time-dependent polarisation of the $h$-BN monolayer calculated from the TD-BSE equation within the IP. The polarisability is obtained via Eq. (2.121) and the resulting absorption spectrum is compared with the equivalent linear response (IP) calculation in Fig. 5.9. We see good agreement between the two methods, as expected.

We now introduce coupling with the PEOMs. First of all, we determine the fitting parameters by performing a least-squares fit of the LR spectrum for the isolated monolayer (as shown in Fig. 5.9). This fit required $N = 23$ basis functions over the range 0–10 eV for an estimated percentage error of around 0.7%. Once the parameters have been determined, we can solve the TD-BSE equation (Eq. (2.116)) for the $h$-BN monolayer 1 coupled with the PEOMs in Eq. (5.4) which describe the $h$-BN monolayer 2 via the fields in Eq. (5.2).

We wish to demonstrate that monolayer 2 as artificially described by the PEOMs do indeed mimic the same response to the external field as monolayer 1 which is described quantum-mechanically by the TD-BSE equation. At this point, we are not trying to simulate a bilayer so we choose an arbitrary separation distance of $R = 5 \text{ a.u.}$. From Fig. 5.10, we can see that, compared with the isolated monolayer, when the coupling is introduced the absorption peaks blue-shift and broaden, with the effect being stronger at lower energies.

Moreover, we can see that the monolayer whose dynamics are solved by the TD-BSE responds in the same way to that mimicked by the PEOMs which is to be expected. Therefore, it
is also possible to simulate both monolayers using PEOMs, thus reducing computational effort. We shall call this approach the PEOM-PEOM method, while the former we refer to as the RT-PEOM method. We introduce a set of EOMs to describe monolayer 1,

$$s_k^{(1)} = - \left( \gamma_k^{(1)} + i\omega_k^{(1)} \right) s_k^{(1)} + iE_2(t),$$  \hspace{1cm} (5.9)

and is given by

$$p_1(t) = \sum_k \text{Re} \left[ s_k^{(1)}(t) \right],$$  \hspace{1cm} (5.10)

where the parameters are found by fitting the polarisability of monolayer 1, \(\alpha_1(\omega)\). Of course, in this case the parameters will be the same as those for monolayer 2. Eqs. (5.4) and (5.9) may then be solved in a coupled fashion through the fields Eq. (5.2). Note that we do not need to renormalise the dipole moments here.

Now, so far we have shown the spectra for the individual monolayers of \(h\)-BN. This is a benefit of the PEOM method as one cannot separate out the separate responses of the constituent monolayers with standard LR approaches. The absorption spectrum of a bilayer will simply be the superposition of the spectra of monolayers 1 and 2. (Note, however, that we are not presently interested with the physically correct bilayer response as we have chosen an arbitrary separation distance.) Fig. 5.11 shows the absorption spectrum of the bilayer as computed within the RT-PEOM method and the PEOM-PEOM method. We see that the two methods
Figure 5.10: Absorption of $h$-BN monolayers separated by a distance $R = 5$ a.u. The dynamics of monolayer 1 are calculated via the TD-BSE while those of monolayer 2 are calculated via the PEOMs. The two monolayers are coupled through the external fields in Eq. (5.2) by means of the induced dipole moments. The LR absorption spectrum of an isolated monolayer is shown in grey for comparison.

produce the same results.

Note that solving the TD-BSE is generally computationally demanding, while the numerical solution of the PEOMs is not only straightforward to implement, but significantly quicker with negligible memory requirements. In the next section, we use the PEOM-PEOM method to simulate bilayers of $h$-BN and MoS$_2$ and compare the absorption spectra (within different levels of approximation) with the LR calculations for the bilayers.
Figure 5.11: Absorption spectrum of the simulated bilayer (the superposition of the spectra of monolayers 1 and 2) using the TD-BSE coupled with the PEOMS (RT-PEOM method) and two coupled sets of PEOMs (PEOM-PEOM method).
5.4 Comparison of LR and PEOM-PEOM Spectra for Bilayers

In this section, we wish to compare the absorption spectra obtained via linear response theory for bilayers of $h-BN$ and MoS$_2$ (as in Section 5.2) with those obtained by the PEOM-PEOM method as outlined in the previous section.

We begin by looking at the $h$-BN bilayer and work within the independent particle (IP) approximation. The first step of any PEOM calculation is to obtain the fitting parameters to be used in the EOMs (c.f. Eqs. (5.4) and (5.9)). As we wish to mimic the bilayer response within the IP approximation—i.e. two monolayers separated by a distance of $d = 3.3\,\text{Å}$ (see Fig. 5.2 and Table 5.2)—we fit the LR, IP response of the $h$-BN monolayer (see Fig. 5.3). This least-squares fit required $N = 17$ basis functions to achieve an estimated percentage error of around 0.87% over the range 0–18 eV.

![Figure 5.12: Comparison of IP absorption spectra for a bilayer of $h$-BN obtained by LR-TDDFT and the PEOM-PEOM method. For the PEOM-PEOM results, we compare for two different layer-separation distances: the physically correct distance of $R = 3.3\,\text{Å}$ and an effective distance of $R_{\text{eff}} = 8.5\,\text{Å}$ which gives the dominant absorption peak a similar intensity to that of the LR calculation. The spectrum for two isolated monolayers ($R \rightarrow \infty$) is shown in grey for comparison.](image)

Fig. 5.12 shows the LR, IP absorption spectrum for the $h$-BN bilayer as in Fig. 5.4. The spectrum for two isolated monolayers is also shown for comparison. The LR results are compared with those obtained by the PEOM-PEOM method by solving Eqs. (5.4) and (5.9) using the fields in Eq. (5.2). As the layers in the LR simulation are separated by a distance of $d = 3.3\,\text{Å}$, it is natural to choose in Eq. (5.2) the distance of $R = 3.3\,\text{Å}$. The results from this PEOM-PEOM simulation are shown in Fig. 5.12. As in the test case in the previous section,
we see a broadening of the peak and a blue-shift. However, the spectrum obtained in this way is not in good agreement with the LR spectrum as the effect is too strong: compared with the isolated monolayers, the bilayer LR spectrum has a decrease in peak-height of around 2 a.u. (arbitrary units) and no blue-shift, while the PEOM-PEOM shows a decrease of around 4.5 a.u. with a blue-shift of around 0.4 eV.

We can match the LR results better by decreasing the coupling between the two systems. This is achieved by choosing a larger, effective distance between the two simulated EOMs, which we denote $R_{\text{eff}}$. We can see in Fig. 5.12 that choosing $R_{\text{eff}} = 8.5 \text{ Å}$ yields a better description of the dominant absorption peak in terms of peak-intensity, although there is still an unwanted blue-shift of around 0.2 eV.

![Figure 5.13: Comparison of the RPA absorption spectra for a bilayer of h-BN obtained by LR-TDDFT and the PEOM-PEOM method with $R_{\text{eff}} = 7 \text{ Å}$. The spectrum for two isolated monolayers ($R \rightarrow \infty$) is shown in grey for comparison.](image)

We now compare the LR, RPA spectrum of the h-BN bilayer with the PEOM-PEOM approach. The LR spectrum (c.f. Fig. 5.4) is shown in Fig. 5.13 and, similarly to the IP spectrum, we notice a decrease in the peak-intensity of around 2 a.u.. The PEOM parameters are obtained by fitting the LR, RPA spectrum for the monolayer (Fig. 5.3) which required $N = 17$ basis functions to achieve an estimated percentage error of around 0.56% over the range 0–18 eV. To match the peak-intensity of the LR calculation, we require an effective separation distance of $R_{\text{eff}} = 7 \text{ Å}$, which also, however, induces an unwanted blue-shift of around 0.1 eV. Notice that the effective distance here is almost 18% smaller than that required for in the previous IP case, suggesting that there is a stronger electromagnetic coupling between the layers when local field effects are included.
Finally, we consider the absorption spectra within the framework of the BSE. The PEOM parameters are found by fitting the LR, BSE spectrum for the monolayer (Fig. 5.3) which required \( N = 12 \) basis functions to achieve and estimated percentage error of around 0.08\% over the range 0–10 eV. The LR spectrum (c.f. Fig. 5.4) is shown in Fig. 5.14 and as described in Section 5.2, compared with the two isolated monolayers, we see both a decrease in peak-intensities along with a blue-shift of around 1 eV. To gain the same decrease in peak-intensity requires an effective distance in the PEOM-PEOM calculation of \( R_{\text{eff}} = 10 \, \text{Å} \). Note that this is almost 18\% larger than the equivalent \( R_{\text{eff}} \) in the IP calculation, suggesting perhaps that the electromagnetic coupling between the layers within the BSE is weaker and that excitonic effects are more important in describing the difference in spectra between the monolayer and bilayer. Moreover, by examining Fig. 5.4, we may attribute the blue-shift between the monolayer and bilayer within the BSE to the screening of the additional layer since this shift is not apparent in the IP and RPA cases. This additional screening is clearly not accounted for in the PEOM model, which is fitted only from an isolated monolayer. Nonetheless, the profile of the spectrum is well described by the PEOM-PEOM method, although the blue-shift is only around 0.1 eV as compared to 0.7 eV in the LR calculation.

In each of the IP, RPA and BSE simulations of the \( h \)-BN bilayer, we see that provided an appropriate effective distance is chosen in the PEOM-PEOM method, the PEOM-PEOM spectra and the LR spectra agree qualitatively, apart from the description of the blue-shift in the peak position which is over-estimated in the IP and RPA calculations and under-estimated
in the BSE calculation. Note, however, that the energy-shift of the spectra may be reproduced in an empirical fashion by including an additional parameter in the EOMs. E.g., we can simply move the peak positions by adding on a constant energy shift, $\omega_c$, in Eqs. (5.4) and (5.9):

$$
\gamma_k^{(1,2)} = - \left( \gamma_k^{(1,2)} + i(\omega_k^{(1,2)} + \omega_c) \right) s_k^{(1,2)} + iE_k^{(1,2)}(t).
$$

\hspace{1cm} (5.11)

Figure 5.15: Same as Fig. 5.14 but with the PEOM-PEOM spectrum ‘corrected’ by incorporating an energy shift of $\omega_c = 0.59$ eV into the PEOMs.

In Fig. 5.15, we repeat the PEOM-PEOM calculation as in Fig. 5.14 but include the energy shift $\omega_c = 0.59$ eV when solving the PEOMs. We can see that the first peak in the PEOM-PEOM spectrum now matches the LR spectrum almost perfectly, while the second peak is displaced by around 0.1 eV. Of course, this \textit{ad hoc} approach is not desirable from an \textit{ab initio} point of view, however.

Figure 5.16 compares the absorption spectra from LR-TDDFT and the PEOM-PEOM method for the MoS$_2$ bilayer within the RPA and IP approximations. In the IP case, the PEOM parameters are obtained by fitting the LR, IP spectrum (see Fig. 5.5) which required $N = 20$ basis functions for an estimated percentage error of 0.75% over the range 0-6 eV. Similarly, the PEOM parameters for the RPA are obtained by fitting the LR, RPA spectrum of Fig. 5.5, requiring $N = 20$ basis functions for an error of 0.59%.

In both the IP and RPA spectra for the MoS$_2$ bilayer (as discussed at Fig. 5.6), we see there is very little difference between the isolated monolayers and the bilayer, implying that there is little interaction between the layers within these approximations (we would, however, expect there to be a greater difference within the BSE). Therefore, in the PEOM-PEOM method, we
Figure 5.16: Comparison of the IP (a) and RPA (b) absorption spectra for a bilayer of MoS$_2$ obtained within LR-TDDFT and the PEOM method with $R_{\text{eff}} = 100 \, \text{Å}$ (a) and $R_{\text{eff}} = 120 \, \text{Å}$ (b). The spectra for two isolated monolayers ($R \to \infty$) of MoS$_2$ are shown in grey for comparison.

require a very large value for $R_{\text{eff}}$ ($R_{\text{eff}} = 100 \, \text{Å}$ in the IP and $R_{\text{eff}} = 120 \, \text{Å}$ in the RPA) to replicate the LR results. Theses values of $R_{\text{eff}}$ are around 17 times that of the ‘physical’ layer separation distance of $R = 6.77 \, \text{Å}$ (see Fig. 5.1 and Table 5.1) compared to those for the $h$-BN bilayer which were within 18% of the physical distance. This apparent dependence on the system can be taken care of as follows.

We introduce an exponential factor which depends on the lattice parameter of the system, $e^{-R/a}$, which appears in front of the dipole moment in the fields felt by the layers, e.g., Eq. (5.2a) becomes

$$E_1(t) = E_\text{EXT}(t) - e^{-R/a} \frac{p_\alpha(t)}{R},$$

where $a$ is the lattice parameter. This factor proportionately decreases the coupling between the layers which dispenses with the need of the effective distance, $R_{\text{eff}}$, which varied greatly between the $h$-BN and MoS$_2$ systems. The factor may be justified, e.g., as a near-field effect with system-dependent decay, depending on the surface geometry of the system. A similar factor is obtained in Chapter 2.1 of Ref. [95] which describes a static, permanent near-field at the surface of ionic crystals.

In Fig. 5.17 we show the RPA spectra using this method for (a) the $h$-BN and (b) MoS$_2$ bilayers and we see equally good agreement between the PEOM and LR approaches in both cases. Compared with using $R_{\text{eff}}$, however, the peak heights are not in quite so good agreement: this is to be expected as $R_{\text{eff}}$ was tailored precisely to align the peak heights. One could then further combine the exponential factor with an effective distance which can describe the differences in approximations (IP, RPA or BSE) while the additional factor ensures an independence of the system-dependent lattice parameter.

In summary, we have found that the PEOM-PEOM method can give qualitatively similar
Figure 5.17: (a) and (b) are the same as Fig. 5.13 and Fig. 5.16 (b) respectively but using the field with the exponential factor (see Eq. (5.12)) instead of the effective distance, $R_{\text{eff}}$.

results in the optical absorption spectra to those of the traditional linear response TDDFT and BSE calculations for bilayers of $h$-BN and MoS$_2$. However, we find that an effective value, $R_{\text{eff}}$, for the interlayer distance is required for better agreement between the methods in terms of, e.g., peak-strength and is dependent on the level of approximation used in the abinitio calculation.
Chapter 6

Conclusions and Future Work

In this thesis, we have proposed the projected equations of motion (PEOM) method for modelling the dynamics of two separated systems, coupled through an electric field. The PEOM method is beneficial when a composite system may be separated into a primary and secondary system, where the primary system in general requires a high level of theory in order to accurately describe its dynamics. On the other hand, the secondary system is modelled by knowledge of its frequency-dependent polarisability, from which parameters may be fitted which enter into a set of EOMs (the PEOMs). The two systems are then coupled via an externally applied field through a dipole-dipole interaction. The method was then applied to several systems and results were compared with existing methods as a proof of concept and demonstrating the benefits of the PEOM method.

Introduction

In Chapter 1, we discussed the recent interest in nanostructured media both in research and commercially. In particular, we mentioned that the useful, optical properties of nanostructured semiconductors (such as two-dimensional semiconductors and quantum dots) may be enhanced, or affected, by the presence of metal nanoparticles. We then went on to describe the state of the art in simulating the optical and electronic properties of such systems from an *ab initio* perspective. It was stated that the higher levels of theory for accurately describing the ground and excited states of the electronic systems are limited to relatively small systems. Consequently, since metal nanoparticles are in general much larger systems than the semiconductor systems (from a modelling point of view), one must resort to hybrid methods which treat the constituent systems at different levels of theory to allow for realistic calculations. We discussed existing hybrid methods such as QM/MM and FDTD approaches and proposed the PEOM method as
a computationally cheaper alternative.

**Background Theory**

In Chapter 2, we introduced the concepts with brief derivations and the key equations associated with the state of the art in the theoretical simulation of electronic systems. We began by introducing the notion of polarisation and the dielectric function from which optical absorption spectra may be obtained. We went on to introduce the notion of the wavefunction and the time-independent Schrödinger equation for calculating the ground state properties. Density functional theory (DFT) was introduced within the Kohn-Sham scheme as a density alternative to the wavefunction approach. We then introduced the time-dependent Schrödinger equation for solving the time-evolution of the wavefunction when interacting with an electromagnetic field. Again, several wavefunction alternative methods were also introduced, including time-dependent DFT and the Green’s function-based Bethe-Salpeter equation (BSE) (both within the linear response regime and extended to periodic systems). These methods allow for the direct calculation of the frequency-dependent, linear, macroscopic dielectric function (and, hence, the absorption spectra). Time-dependent frameworks were also introduced which in principle allow for simulations beyond the linear regime. These included the density matrix equations of motion and the time-dependent BSE. The theories discussed in Chapter 2 are the standard approaches to simulating electronic and optical phenomena in electronic systems which may be used, e.g., to treat the ‘primary system’ in the PEOM method.

**The PEOM Method**

The PEOM method was introduced and derived in Chapter 3. We began by stating the fields felt by the coupled primary and secondary systems which are effectively the sum of the externally applied field and the dipole field originating from the coupled system. The dipole moment of the primary system is found by any time-dependent method (e.g. those mentioned in the above paragraph). The dipole moment of the secondary system is described by solving a set of PEOMs which involve parameters fitted from the frequency-dependent polarisability of the secondary system which is assumed to be known. (Note that the primary system may also be treated in the same way, which we refer to as the PEOM-PEOM method.) Chapter 3 concludes with a small test performed on an isolated MNP to demonstrate that the polarisability constructed from the PEOMs reproduces the original polarisability from which the PEOMs were formed.
The SQD-MNP System

In Chapter 4, we applied the PEOM method to a semiconducting quantum dot-metal nanoparticle (SQD-MNP) system. The SQD was treated as a two-level quantum system via density matrix theory while the MNP was modelled within the PEOM framework. We first investigated energy absorption rates (response to a monochromatic wave) in both the weak and strong field regimes and found that the PEOM method produced the same results as the existing rotating wave approximation (RWA) analytical solutions from the literature. We then went on to examine the population dynamics of the SQD in response to a laser pulse when coupled with the MNP. For picosecond pulses, we found good agreement between the PEOM method and existing semi-analytical solutions based on the RWA and an effective field method. However, we showed that these semi-analytical methods become unreliable for femtosecond pulses. Moreover, we showed that the response of the SQD-MNP system depended strongly on the details of the polarisability of the MNP for ultrashort excitation. These details are captured within the PEOM approach but not within the semi-analytical approximations. We then demonstrated that the RWA and effective field approximations may be mimicked by the PEOM method by artificially ‘blurring’ the details of the MNP polarisability by choosing a polarisability that is local in time.

2D Material Composites

In Chapter 5, we investigated the optical absorption spectra of monolayers and bilayers of h-BN and MoS$_2$ as a means of further proof of concept of the PEOM method. We began by describing the atomic configurations of the systems, both of which share the same layered form with hexagonal symmetry. We then calculated the linear response (LR) absorption spectra for each of the systems in both the independent particle (IP) and RPA approximations. In the case of h-BN, we also looked at the BSE response. For the h-BN monolayer, we found little difference between the IP and RPA results, while the BSE showed a strong red-shift and more intense absorption peak as expected due to strong excitonic effects. The bilayer response within IP and RPA was similar to that of the monolayer, while the BSE gave a reduction in magnitude and blue-shift compared with the monolayer. Similar results were obtained for the MoS$_2$ structures and, again, there were only small differences between the IP and RPA calculations, with apparently little interaction between the layers in the bilayer case within these approximations. We expect there to be a significant difference for the BSE calculation (see, e.g., Ref. [14]), which should be investigated further.

We then went on to describe how the PEOM method may be used to simulate the bilayers and discussed two possible approaches. The first approach was similar to that of the SQD-MNP
system as in Chapter 4 where a monolayer is treated (analogously to the SQD) using equations of motion from quantum mechanics in the form of the TD-BSE. The additional monolayer is then treated using the PEOMs which have been fitted from the LR absorption spectrum (we called this method the RT-PEOM method). The second method described both monolayers using the same PEOMs (which we called the PEOM-PEOM method) and we showed that the RT-PEOM and PEOM-PEOM gave the same results for the absorption spectrum of an artificial bilayer of $h$-BN.

Finally, we compared the optical spectra for the bilayers obtained from the standard LR calculations with those from the PEOM-PEOM method for the three different levels of approximation (IP, RPA and BSE). We found that the LR spectra could be qualitatively reproduced by the PEOM-PEOM method: further, the results could be better aligned quantitatively, in terms of peak-strength, by using an effective separation distance, $R_{\text{eff}}$, which depends on the level of approximation used in the $ab\ initio$ simulation and, in terms of peak-position, by including an empirical, rigid energy shift within the PEOMs. In particular, for the LR-BSE spectrum of the $h$-BN bilayer we noticed a peak-shift compared with the monolayer due to the additional screening of the second layer.

**Outlook**

There are further avenues of investigation left open at the conclusion of this thesis in terms of improvement of the PEOM method for both the SQD-MNP system and 2D systems.

For the SQD-MNP system, in the description of the MNP polarisability, we have used the dipole approximation. This has been shown to be sufficient provided the separation distance is relatively large or equally for interacting with short pulses [26]. However, for strong SQD-MNP coupling or for non-spherical MNPs, a multipole description should be preferred [27, 96, 97]. For such cases, the PEOMs should be adapted to accommodate for these higher-order multipole effects. On the other hand, even the multipolar description may not be adequate to treat MNPs with complicated geometries where a full electrodynamical calculation may be necessary [34–37, 98].

Further, in all the literature discussed in this thesis regarding optics in SQD-MNP systems, the SQD has been modelled as a 2-level system as shown in Chapter 4. However, to describe phenomena such as electromagnetically induced transparency or second harmonic generation in the hybrid system, a 2-level description will not suffice and 3-level models have been used. For example, in Refs. [22, 99] pump-probe experiments were simulated in a similar way to as outlined in Chapter 4 but with two incident electric fields (the pump and the probe field) and where the SQD has three instead of two energy levels, resulting in a $3 \times 3$ density matrix. The external fields are monochromatic and equations similar to those of Section 4.2.1 (though much more
involved) are obtained within the RWA. These simulations may be equally performed within the PEOM method in exactly the same fashion as shown in Fig. 4.2 but where the general master equation for the $3 \times 3$ density matrix (see Eq. (2.56)) are evolved with the PEOMs. The effect of ultrafast pulse excitation within this system may also easily be investigated within the PEOM method as, beyond the RWA, the short pulse will excite multiple transitions within the multi-level system, coupled with the fully-described MNP polarisability.

Now, in the $h$-BN bilayer system, we noticed a peak-shift in the absorption spectrum with respect to the monolayer due to the additional screening of the second layer. Though we approximated this effect empirically (see Fig. 5.15), this screening effect cannot be inherently described within the PEOMs. It is also worth noting that the PEOM method is based on a macroscopic field and takes as input the macroscopic dielectric function. Of course, e.g. in TDDFT calculations, the macroscopic dielectric function is obtained via an average over the microscopic contributions. Therefore, the PEOM approach does not take into account any microscopic fluctuations or effects from local inhomogeneities which may be important for some systems. In such cases, one may wish to modify the PEOMs to include, e.g., a spatial dependence.

Other quantum mechanical phenomena cannot be replicated within the PEOM, such as wavefunction overlap if the constituent parts are brought very close together, or quantum tunnelling. However, these are exotic processes: more realistically for systems of interest, one may be interested in the role of interlayer excitons in TMD heterostructures which have been shown to influence the spectroscopic properties as described, e.g., in Refs. [100, 101]. The formation of electron-hole pairs shared between the constituent monolayers can clearly not be described by the PEOM method. In Ref. [101], the quantum-electrostatic heterostructure (QEH) model (a semiclassical, hybrid method to yield the dielectric function of heterostructures as discussed in Section 1.2) was combined with an effective Hamiltonian to describe such effects. In this sense, the QEH model is an improvement over the PEOM method. However, it is a static model while the PEOM method is time-dependent and may be used, e.g., to investigate non-linear phenomena such as second harmonic generation in these heterostructures as shown experimentally in Refs. [102, 103].

Now, compared to ab initio LR approaches, we have shown that the coupling between the monolayers in the PEOM method can be modified depending on the choice of $R_{\text{eff}}$ which determines the coupling strength. While we have previously described this as a disadvantage from an ab initio point of view, it may be seen as a way to simulate effects such as in Ref. [104] where it was shown that there is negligible interlayer coupling in mechanically stacked hetero-junctions of MoS$_2$ and WSe$_2$ monolayers but that a van der Waals interaction is induced when the system is subject to heating, thus changing the spectroscopic properties. Moreover, the PEOMs can be easily modified to include dissipative effects, e.g., from heating, in the dynamics.
by incorporating a stochastic process as described in Refs. [74, 105].

Finally, though we have presently modelled 2D bilayer systems using the PEOM method as a proof of concept, we note that the original intention was to model semiconductor-metal nanoparticle systems which are currently out of reach of the state-of-the-art \textit{ab initio} approaches (as discussed in the introduction to the thesis). Therefore, the next step in this work should be to simulate experiments such as in Refs. [10–12, 106, 107] where metal nanoparticles have been shown to enhance the optical properties of MoS$_2$ monolayers. As a starting point, in the PEOM method, one would require an effective polarisability to describe the array of nanoparticles such as in Ref. [108].
Appendix A

The Projected Equations of Motion Method

A.1 Generalisation to Anisotropic Media

In the case of anisotropic media, the effective fields in Eq. (3.1) become

\[ E_{PS}(t) = E_{EXT}(t) + \frac{3\hat{n}(p_{SS}(t) \cdot \hat{n}) - p_{SS}(t)}{R^3}, \]  
\[ E_{SS}(t) = E_{EXT}(t) + \frac{3\hat{n}(p_{PS}(t) \cdot \hat{n}) - p_{PS}(t)}{R^3}, \]

and the polarisability of the secondary system now becomes a tensor (see Eq. (2.6)),

\[ \alpha_{SS} = \begin{pmatrix} \alpha^{(xx)} & \alpha^{(xy)} & \alpha^{(xz)} \\ \alpha^{(yx)} & \alpha^{(yy)} & \alpha^{(yz)} \\ \alpha^{(zx)} & \alpha^{(zy)} & \alpha^{(zz)} \end{pmatrix}. \]

The theory then proceeds as in Section 3.2 except in how \( p_{SS}(t) \) is expanded: we expand the \( i \)-th vector component \( (i = x, y, z) \) as (see Eq. (2.7))

\[ p^{(i)}_{SS}(t) = \sum_{j=x,y,z} N_{ij} \sum_{k=1} c_{ik}^{(ij)} \text{Re} \left[ s_{k}^{(ij)}(t) \right], \]

where the functions \( s_{k}^{(ij)}(t) \) are found from the differential equations

\[ s_{k}^{(ij)} = - \left( \gamma_{k}^{(ij)} + \omega_{k}^{(ij)} \right) s_{k}^{(ij)} + iE_{SS}^{(i)}(t), \]
for $i, j = x, y, z$ and $k = 1, \ldots, N_{ij}$ and the parameters are found by fitting each component of the $\alpha$ tensor to

\[
\alpha_{ij}^{(ij)}(\omega) = \sum_{k=1}^{N_{ij}} c_k^{(ij)} \left[ \frac{1}{(\omega_k^{(ij)} - \omega) - i\gamma_k^{(ij)}} + \frac{1}{(\omega_k^{(ij)} + \omega) + i\gamma_k^{(ij)}} \right],
\]

for $i, j = x, y, z$. 

\hspace{1cm} (A.6)
Appendix B

Semiconducting Quantum Dot-Metal Nanoparticle Hybrid

B.1 Density Matrix Equations of Motion for Isolated SQD

It is common to model the SQD as a simple 2-level system with ground state, $|1\rangle$ with energy $\hbar \omega_1$, and excited state, $|2\rangle$ with energy $\hbar \omega_2$. We describe the dynamics of the system under interaction with the field, $E(t)$, by means of the density matrix equations of motion (see Section 2.3.2). In particular, we choose the form with phenomenological damping as given in Ref. [39], i.e.

$$\dot{\rho} = i[H, \rho] - \Gamma \circ \left(\rho - \rho^{eq}\right),$$

where $\rho$ is the 2 x 2 density matrix, $H$ is the system Hamiltonian matrix and $\Gamma$ and $\rho^{eq}$ describes the damping (e.g., $\rho_{11}$ decays to $\rho_{11}^{eq}$ at a rate of $\Gamma_{11}$). By choosing

$$\rho^{eq} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix},$$

and

$$\Gamma = \begin{pmatrix} \Gamma_{11} & \Gamma_{21} \\ \Gamma_{21} & \Gamma_{11} \end{pmatrix},$$

the system naturally decays to the ground state.

The system Hamiltonian may be split into a non-interacting part, $\hat{H}_0$, and the part describing the interaction with the field, $\hat{V}(t)$,

$$\hat{H} = \hat{H}_0 + \hat{V}(t).$$
The interaction Hamiltonian is given in the dipole approximation, i.e.,

$$\hat{V}(t) = -\hat{\mu} \cdot \mathbf{E}(t) ,$$  \hspace{1cm} (B.5)

where $\hat{\mu}$ is the dipole moment operator, $\hat{\mu} = -e\mathbf{r}$. From Eq. (2.42) its matrix elements are

$$\mu_{mn} = \langle \psi_m | \mathbf{r} | \psi_n \rangle ,$$  \hspace{1cm} (B.6)

where $\{\psi_n\}$ are the (orthonormal) eigenfunctions of the TISE with corresponding eigenenergies, $\{\hbar \omega_n\}$, i.e.

$$\hat{H}_0 \psi_n = \hbar \omega_n \psi_n .$$  \hspace{1cm} (B.7)

It is clear from Eq. (B.6) that the transition dipole moment matrix is anti-diagonal and Hermitian and its elements are, in general, vectors. Hence,

$$\mu = \begin{pmatrix} 0 & \mu_{12} \\ \mu_{21} & 0 \end{pmatrix} .$$  \hspace{1cm} (B.8)

Moreover, its elements are necessarily real so $\mu_{12} = \mu_{21}^*$. We also assume that the SQD is isotropic so that $\mu_{21} = (\mu_{21}, \mu_{21}, \mu_{21})^T$. Hence, if we write the field as $\mathbf{E}(t) = E(t)\hat{e}$, where $\hat{e}$ is the unit vector in the direction of the field, then

$$\mu_{21} \cdot \mathbf{E}(t) = \mu_{21} E(t) ,$$  \hspace{1cm} (B.9)

and from Eqs. (B.5) and (B.8) the matrix representation of the interaction Hamiltonian is

$$\mathbf{V} = - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \mu_{21} E(t) .$$  \hspace{1cm} (B.10)

Similarly, the elements of the non-interacting Hamiltonian matrix are

$$H_{0,mn} = \langle \psi_m | \hat{H}_0 | \psi_n \rangle ,$$  \hspace{1cm} (B.11)

and from Eqs. (2.24) and (B.7) and using that the $\{\psi_n\}$ are orthonormal, it is easy to show that

$$H_{0,mn} = \hbar \omega_n \delta_{mn} ,$$  \hspace{1cm} (B.12)

and hence

$$\mathbf{H}_0 = \begin{pmatrix} \omega_1 & 0 \\ 0 & \omega_2 \end{pmatrix} .$$  \hspace{1cm} (B.13)
From Eqs. (B.4), (B.10) and (B.13), the total Hamiltonian matrix is

\[
H = \begin{pmatrix}
\omega_1 & -\mu_{21} E(t) \\
-\mu_{21} E(t) & \omega_2
\end{pmatrix},
\]

(B.14)

Therefore, substituting Eqs. (B.2), (B.3) and (B.14) into Eq. (B.1) gives the following equations of motion for the density matrix elements,

\[
\dot{\Delta} = -4\mu_{21} E(t) \text{Im} [\rho_{21}] - \Gamma_{11}(\Delta - 1),
\]

(B.15a)

\[
\rho_{21} = -(\Gamma_{21} + i\omega_0) \rho_{21} + i\mu_{21} E(t) \Delta,
\]

(B.15b)

where we have used the relation \( \rho_{12} = \rho_{21}^* \) (see Eq. (2.47)) and defined the population difference as

\[
\Delta = \rho_{11} - \rho_{22},
\]

(B.16)

and the energy difference as

\[
\omega_0 = \omega_2 - \omega_1.
\]

(B.17)

### B.2 RWA Steady-State Solution for Isolated SQD

Depending on the form of the external field, the EOMs in Eq. (B.15) may be solved analytically. In particular, if it has a plane-wave form, e.g.,

\[
E(t) = E_0 \cos(\omega_L t),
\]

(B.18)

then the steady-state solution may be obtained within the rotating wave approximation (RWA). In Eq. (B.18), \( E_0 \) is the amplitude of the field and \( \omega_L \) is the frequency. Now, according to [109], if the SQD is treated as a dielectric sphere of dielectric constant, \( \epsilon_S \), then the field is screened by a factor,

\[
\epsilon_{\text{effS}} = \frac{2 + \epsilon_S}{3}.
\]

(B.19)

In the literature, this screening is often absorbed into the dipole matrix element, though some argue that the screening should be explicitly included in the external field. We follow the former procedure, and introduce the screened dipole matrix element,

\[
\tilde{\mu}_{21} = \frac{\mu}{\epsilon_{\text{effS}}},
\]

(B.20)

where \( \mu \) is the bare dipole matrix element.

In the RWA, we assume that the laser frequency is very close to the energy gap of the system,
i.e. $\omega_L \approx \omega_0$. In this case, any terms in the dynamics oscillating ‘quickly’ at frequencies much greater than $\omega_0$ (e.g. at $\omega_0 + \omega_L$) may be neglected, while the ‘slowly’ oscillating terms (e.g. at $\omega_0 - \omega_L$) are retained. We thus write $\rho_{21}$ as composed of a slowly oscillating term, $\tilde{\rho}_{21}$, and the quickly oscillating part, $e^{-i\omega_L t}$, i.e.

$$\rho_{21} = \tilde{\rho}_{21}e^{-i\omega_L t}. \quad (B.21)$$

By slowly oscillating, here, we mean that $\tilde{\rho}_{21}$ is assumed to vary on a much larger timescale than $2\pi/\omega_L$. Using the exponential form of the cosine function, substituting Eqs. (B.18) and (B.21) into Eq. (B.15b) under the RWA and rearranging yields

$$\dot{\tilde{\rho}}_{21} = -[\Gamma_{21} + i(\omega_0 - \omega_L)]\tilde{\rho}_{21} + i\frac{\tilde{\rho}_{21}E_0}{2}\Delta. \quad (B.22)$$

Taking the steady-state conditions where the slowly varying part of $\rho_{21}$ and the population difference, $\Delta$, remain constant in time, i.e.,

$$\dot{\tilde{\rho}}_{21} = 0, \quad (B.23a)$$

$$\dot{\Delta} = 0, \quad (B.23b)$$

gives the following set of equations from Eqs. (B.15a) and (B.22)

$$\tilde{\rho}_{21}^{s.s.} = \frac{-\Omega_0\Delta^{s.s.}}{(\omega_L - \omega_0) + i\Gamma_{21}}, \quad (B.24a)$$

$$(1 - \Delta^{s.s.})\Gamma_{11} = 4\Omega_0\text{Im}[\tilde{\rho}_{21}^{s.s.}], \quad (B.24b)$$

where we have defined the Rabi frequency,

$$\Omega_0 = \frac{\tilde{\rho}_{21}E_0}{2}. \quad (B.25)$$

Eq. (B.24) can be solved algebraically to obtain analytical expressions for the steady-state values of $\tilde{\rho}_{21}$ and $\Delta$ by considering the real and imaginary parts of $\tilde{\rho}_{21}^{s.s.}$ separately.

### B.3 Effective Field for Coupled SQD-MNP System

We now wish to see how the SQD dynamics are modified when the coupled to the MNP as described in Section 4.1. In this section, we derive an approximate formula for the field
experienced by the SQD when coupled to an MNP under the following pulsed external field,

\[ E_{\text{EXT}}(t) = f(t)E_0 \cos(\omega_L t) \]
\[ = f(t) \frac{E_0}{2} (e^{i\omega_L t} + e^{-i\omega_L t}) , \]

where \( f(t) \) is a slowly-varying temporal pulse envelope. From Eq. (4.1a), the field experienced by the SQD is

\[ E_{\text{SQD}} = E_{\text{EXT}} + g \frac{p_{\text{MNP}}}{R^3} . \]

Now, as discussed in the previous section, the screening of the SQD is incorporated into a screened dipole matrix element, \( \tilde{\mu}_{21} \) so that the density matrix EOMs in Eq. (B.15) become

\[ \dot{\Delta} = -4i \tilde{\mu}_{21} E_{\text{SQD}}(t) \text{Im} [\rho_{21}] - \Gamma_{11} (\Delta - 1) , \]
\[ \rho_{21} = - (\Gamma_{21} + i\omega_0) \rho_{21} + i\tilde{\mu}_{21} E_{\text{SQD}}(t) \Delta . \]

In the frequency domain,

\[ p_{\text{MNP}}(\omega) = \alpha_{\text{MNP}}(\omega) E_{\text{MNP}}(\omega) , \]

where \( \alpha_{\text{MNP}}(\omega) \) is the polarisability of the MNP and

\[ E_{\text{MNP}} = E_{\text{EXT}} + g \frac{p_{\text{SQD}}}{R^3} . \]

Substituting Eq. (B.31) into Eq. (B.30) gives

\[ p_{\text{MNP}}(\omega) = \alpha_{\text{MNP}}(\omega) \left[ E_{\text{EXT}}(\omega) + g \frac{p_{\text{SQD}}(\omega)}{R^3} \right] , \]

which, when substituted into Eq. (B.28) upon rearranging gives

\[ E_{\text{SQD}}(\omega) = E_{\text{EXT}}(\omega) + \frac{g}{R^3} \alpha_{\text{MNP}}(\omega) E_{\text{EXT}}(\omega) + \frac{g^2}{R^6} \alpha_{\text{MNP}}(\omega) p_{\text{SQD}}(\omega) . \]

We define the Fourier transform (FT) and the inverse Fourier transform respectively by

\[ \text{FT} [g(t)](\omega) = \int_{-\infty}^{\infty} g(t)e^{i\omega t} dt , \]
\[ \text{FT}^{-1} [g(w)](t) = \int_{-\infty}^{\infty} g(w)e^{-i\omega t} d\omega . \]
APPENDIX B. SEMICONDUCTING QUANTUM DOT-METAL NANOPARTICLE HYBRID

Taking the FT of the external field from Eq. (B.27) gives

\[
\text{FT} \left[ E_{\text{EXT}}(t) \right] (\omega) = \frac{E_0 f(t)}{2} \int_{-\infty}^{\infty} \left( e^{i\omega_L t} e^{-i\omega t} \right) e^{i\omega t} dt \quad (B.35)
\]

\[
= \frac{E_0 f(t)}{2} \int_{-\infty}^{\infty} \left( e^{i(\omega+\omega_L)t} + e^{i(\omega-\omega_L)t} \right) dt \quad (B.36)
\]

\[
= \frac{E_0 f(t)}{2} \left[ \delta(\omega + \omega_L) + \delta(\omega - \omega_L) \right] , \quad (B.37)
\]

where we have assumed that the slowly-varying envelope, \( f(t) \), varies on a much larger timescale than \( 2\pi/\omega_L \), allowing us to separate it outside the integral. Hence,

\[
\text{FT}^{-1} [\alpha_{\text{MNP}}(\omega) E_{\text{EXT}}(\omega)] (t) = \frac{E_0 f(t)}{2} \int_{-\infty}^{\infty} \alpha_{\text{MNP}}(\omega) \left[ \delta(\omega + \omega_L) + \delta(\omega - \omega_L) \right] e^{-i\omega t} d\omega \quad (B.38)
\]

\[
= \frac{E_0 f(t)}{2} \left[ \alpha_{\text{MNP}}(\omega_L)e^{-i\omega_L t} + \alpha_{\text{MNP}}(-\omega_L)e^{i\omega_L t} \right] . \quad (B.39)
\]

By the properties of the polarisability, it can be shown that (see e.g. Ref. [39])

\[
\alpha_{\text{MNP}}(-\omega_L) = \alpha_{\text{MNP}}^*(\omega_L) , \quad (B.40)
\]

and so Eq. (B.37) becomes

\[
\text{FT}^{-1} [\alpha_{\text{MNP}}(\omega) E_{\text{EXT}}(\omega)] (t) = \frac{E_0 f(t)}{2} \left[ \alpha_{\text{MNP}}(\omega_L)e^{-i\omega_L t} + \alpha_{\text{MNP}}^*(\omega_L)e^{i\omega_L t} \right] . \quad (B.41)
\]

Now, from the dipole operator matrix, Eq. (B.8), and using Eq. (2.53), it is easy to show that

\[
P^\text{SQD} = \text{tr} (\rho \hat{\rho}_{21}) \quad (B.42)
\]

\[
= \bar{\rho}_{21} (\rho_{21} + \rho^*_{21}) . \quad (B.43)
\]

As in Eq. (B.21), we separate \( \rho_{21} \) into its quickly and slowly oscillating components. Again, since \( \bar{\rho}_{21} \) varies on a much longer timescale than \( 2\pi/\omega_L \), we can, separate the slowly-varying part outside of the integrals when using the FT:

\[
\text{FT} [\rho_{21}(t)] (\omega) = \bar{\rho}_{21} \int_{-\infty}^{\infty} e^{-i\omega_L t} e^{i\omega t} dt \quad (B.44)
\]

\[
= \bar{\rho}_{21} \delta(\omega - \omega_L) , \quad (B.45)
\]

and, similarly,

\[
\text{FT} [\rho^*_{21}(t)] (\omega) = \bar{\rho}^*_{21} \delta(\omega + \omega_L) . \quad (B.46)
\]
Substituting Eqs. (B.45) and (B.46) into Eq. (B.43) gives

\[ p_{\text{SQD}}(\omega) = \bar{\mu}_{21} (\bar{\rho}_{21} \delta(\omega - \omega_L) + \bar{p}_{21}^* \delta(\omega + \omega_L)) , \] (B.47)

and, hence,

\[ \text{FT}^{-1} [\alpha_{\text{MNP}}(\omega)p_{\text{SQD}}(\omega)](t) = \bar{\mu}_{21} \int_{-\infty}^{\infty} \alpha_{\text{MNP}}(\omega) [\bar{\rho}_{21} \delta(\omega - \omega_L) + \bar{p}_{21}^* \delta(\omega + \omega_L)] e^{-i\omega t} d\omega , \] (B.48)

\[ = \bar{\mu}_{21} [\alpha_{\text{MNP}}(\omega_L)\bar{\rho}_{21} e^{-i\omega_L t} + \alpha_{\text{MNP}}^*(\omega_L)\bar{p}_{21}^* e^{i\omega_L t}] . \] (B.49)

Finally, using Eqs. (B.27), (B.41) and (B.49) we see by taking the inverse FT of Eq. (B.33) and with some rearranging that

\[ E_{\text{SQD}}(t) = \left\{ \frac{E_0 f(t)}{2} \left( 1 + \frac{g}{R^3} \alpha_{\text{MNP}}(\omega_L) \right) + \frac{g^2 \bar{\mu}_{21}}{R^6} \alpha_{\text{MNP}}(\omega_L) \bar{p}_{21}(t) \right\} e^{-i\omega_L t} + \text{c.c.} , \] (B.50)

which is valid provided both \( \bar{\rho}_{21} \) and the pulse envelope, \( f(t) \), vary on a much larger timescale than \( 2\pi/\omega_L \). We call this approximation the effective field method.

### B.4 RWA and Steady-State Solution for SQD-MNP System

In the previous section we derived an approximation for the effective field experienced by the SQD, \( E_{\text{SQD}} \), when coupled to an MNP as given in Eq. (B.50). We seek the steady-state solution to the density matrix EOMs in Eq. (B.29). Substituting Eq. (B.50) in to Eq. (B.29), invoking the RWA and rearranging gives

\[ \hat{\Delta} = 4 \text{Im} [(f(t)\Omega_{\text{eff}} + G\bar{\rho}_{21}) \hat{\rho}_{12}] + \Gamma_{11} (1 - \Delta) , \] (B.51a)

\[ \dot{\bar{\rho}}_{21} = [i(\omega_L - \omega + G\Delta) - \Gamma_{21}] \bar{\rho}_{21} + if(t)\Omega_{\text{eff}} \Delta , \] (B.51b)

where we have introduced

\[ \Omega_{\text{eff}} = \Omega_0 \left( 1 + \frac{g}{R^3} \alpha_{\text{MNP}}(\omega_L) \right) , \] (B.52)

\[ G = \frac{g^2 \bar{\mu}_{21}^2}{R^6} \alpha_{\text{MNP}}(\omega_L) . \] (B.53)

As in Appendix B.2, for the steady-state solution the external field shall be a monochromatic field, which is equivalent to taking the pulse envelope to be \( f(t) = 1 \). By setting \( f(t) = 1 \) in Eq. (B.51b) and taking the steady-state condition, \( \dot{\bar{\rho}}_{21} = 0 \), we arrive at the following coupled
APPENDIX B. SEMICONDUCTING QUANTUM DOT-METAL NANOPARTICLE HYBRID

equations,

\[ \rho_{21}^{s.s.} = \frac{-(\Omega_R + i\Omega_I)\Delta^{s.s.}}{(\omega_L - \omega_0 + G_R \Delta^{s.s.}) + i(\Gamma_{21} + G_I \Delta^{s.s.})}, \]

\[ (1 - \Delta^{s.s.})\Gamma_{11} = 4\Omega_R \text{Im} [\rho_{21}] - 4\Omega_I \text{Re} [\rho_{21}] - 4G_I |\rho_{21}|^2, \]

where we have written \( \Omega_{\text{eff}} = \Omega_R + i\Omega_I \) and \( G = G_R + iG_I \). Upon substituting Eq. (B.54a) into Eq. (B.54b) and rearranging, we get the following cubic equation

\[ a(\Delta^{s.s.})^3 + b(\Delta^{s.s.})^2 + c\Delta^{s.s.} + d = 0, \]

where the coefficients are

\[ a = |G|^2, \]

\[ b = 2G_I \Gamma_{21} + 2(\omega_L - \omega_0)G_R |G|^2, \]

\[ c = 4|\Omega_{\text{eff}}|^2 \frac{\Gamma_{21}}{\Gamma_{11}} + \Gamma_{21}^2 + (\omega_L - \omega_0)^2 - 2(G_I \Gamma_{21} + (\omega_L - \omega_0)G_R), \]

\[ d = -\left( \Gamma_{21}^2 + (\omega_L - \omega_0)^2 \right). \]

The nature of the roots of Eq. (B.55) are determined by the discriminant, \( \zeta \), given by

\[ \zeta = 18abcd - 4b^2d + b^2c^2 - 4ac^3 - 27a^2d^2. \]

In particular, if \( d \geq 0 \) then there are 3 real roots and if \( d < 0 \) there are 2 nonreal complex conjugate roots and 1 real root. Since \( \Delta \) is the population difference (which is a measurable observable), we require the root to be real. Hence, in the first case there may be three possible values of \( \Delta^{s.s.} \), but in reality there can only be one (which may be found, e.g., by the numerical solutions to Eq. (B.51)). This issue is discussed in detail in REF. B.5

### B.5 Time-Derivative of \( p_{\text{MNP}}(t) \)

From Eq. (4.24), we have that

\[ p_{\text{MNP}}(t) = \sum_{k=1}^{N} c_k \text{Re} [s_k(t)]. \]

and so it follows that

\[ \frac{d}{dt} p_{\text{MNP}}(t) = \sum_{k=1}^{N} c_k \text{Re} [\dot{s}_k(t)]. \]
APPENDIX B. SEMICONDUCTING QUANTUM DOT-METAL NANOPARTICLE HYBRID

Substituting Eq. (4.25) into Eq. (B.59) gives

$$\frac{d}{dt}p_{MNP}(t) = \sum_{k=1}^{N} c_k \text{Re} \left[ - (\gamma_k + i\omega_k) s_k(t) + iE_{MNP}(t) \right], \quad \text{(B.60)}$$

and using the fact the $E_{MNP}(t)$ is real-valued, we arrive at

$$\frac{d}{dt} = \sum_{k=1}^{N} c_k \left( \omega_k \text{Im} [s_k(t)] - \gamma_k \text{Re} [s_k(t)] \right). \quad \text{(B.61)}$$

### B.6 Energy Absorption Rate for MNP in the RWA

From Eq. (4.12), Eq. (4.15) and Eq. (4.14), the energy absorption rate for the MNP is defined as

$$Q_{MNP} = \frac{1}{\delta T} \int_{T}^{T+\delta T} \left( \frac{d}{dt}p_{MNP}(t) \right) \left( E_{MNP}(t) - \frac{4\pi}{3} P_{MNP}(t) \right) dt, \quad \text{(B.62)}$$

where we have cancelled out the volume integral as the quantities of interest here have no spatial dependence. From Eq. (4.7) and Eq. (4.1b), we have

$$p_{MNP}(\omega) = \alpha_{MNP}(\omega) \left( E_{\text{EXT}}(\omega) + \frac{g}{R^3} \rho_{\text{SQD}}(\omega) \right), \quad \text{(B.63)}$$

and then from Eq. (B.41) and Eq. (B.49), we see by taking the inverse Fourier transform of Eq. (B.63) and rearranging that

$$p_{MNP}(t) = \mathcal{F}^{-1} \left[ \alpha_{MNP}(\omega) E_{\text{EXT}}(\omega) + \frac{g}{R^3} \alpha_{MNP}(\omega) \rho_{\text{SQD}}(\omega) \right](t) \quad \text{(B.64)}$$

$$= E_{MNP} \alpha_{MNP}(\omega_L) e^{-i\omega_L t} + \text{c.c.}, \quad \text{(B.65)}$$

where we have defined

$$E_{MNP} = \frac{E_0}{2} + \frac{g_2}{R^3} \rho_{21}. \quad \text{(B.66)}$$

Taking the time derivative of Eq. (B.65) gives

$$\frac{d}{dt}p_{MNP}(t) = -i\omega_L E_{MNP} \alpha_{MNP}(\omega_L) e^{-i\omega_L t} + \text{c.c.} \quad \text{(B.67)}$$

Hence,

$$\left( \frac{d}{dt}p_{MNP}(t) \right) E_{MNP}(t) = (-i\omega_L E_{MNP} \alpha_{MNP}(\omega_L) e^{-i\omega_L t} + \text{c.c.}) \left( E_{MNP} e^{-i\omega_L t} + \text{c.c.} \right) \quad \text{(B.68)}$$

$$= -i\omega_L E_{MNP} E_{MNP}^{\ast} \left( \alpha_{MNP}(\omega_L)^* - \alpha_{MNP}(\omega_L) \right) \quad \text{(B.69)}$$

$$= 2\omega_L \text{Im} [\alpha_{MNP}(\omega_L)] |E_{MNP}|^2, \quad \text{(B.70)}$$
where we have invoked the RWA in the second line. Similarly,

\[
\left( \frac{d}{dt} p_{\text{MNP}}(t) \right) p_{\text{MNP}}(t) = (-i \omega_L \tilde{E}_{\text{MNP}}(\omega_L)e^{-i \omega_L t} + c.c.) \left( \tilde{E}_{\text{MNP}}(\omega_L)e^{-i \omega_L t} + c.c. \right) \tag{B.71}
\]

\[
= -i \omega_L |E_{\text{MNP}}|^2 |\alpha_{\text{MNP}}(\omega_L)|^2 \tag{B.72}
\]

\[
= 0, \tag{B.73}
\]

where we have, again, used the RWA in the second line. Therefore, substituting Eqs. (B.70) and (B.73) into Eq. (B.62) gives

\[
Q_{\text{MNP}} = 2 \omega_L \text{Im} \left[ \alpha_{\text{MNP}}(\omega_L) \right] |\tilde{E}_{\text{MNP}}|^2. \tag{B.74}
\]

In going from Eq. (B.62) to Eq. (B.74), we have used the fact that $\rho_{21}$ varies on a much longer timescale than $2\pi/\omega_L$ and since $\delta T = 2\pi/\omega_L$ (from Eq. (4.16)), the integrand is effectively constant over the limits of the integral, and then $1/\delta T \int_T^{T+\delta T} dt = 1$.

### B.7 Effective Field Limitations

With the pulsed external field,

\[
E_{\text{EXT}}(t) = \frac{E_0}{2} f(t) \left( e^{-i \omega_L t} + c.c. \right), \tag{B.75}
\]

and by writing the SQD dipole in its positive and negative frequency contributions as

\[
p_{\text{SQD}}(t) = \tilde{\mu}_{21} \left( \rho_{21} e^{-i \omega_L t} + c.c. \right), \tag{B.76}
\]

it is easy to show from Eq. (4.1b) that the field felt by the MNP is given by

\[
E_{\text{MNP}}(t) = \tilde{E}_{\text{MNP}}(t) e^{i \omega_L t} + c.c., \tag{B.77}
\]

where

\[
\tilde{E}_{\text{MNP}}(t) = \frac{E_0}{2} f(t) + \frac{g \tilde{\mu}_{21}}{R^3} \rho_{21}(t). \tag{B.78}
\]

Now, in the effective field method, it is easy to show that the dipole moment of the MNP is given by (see Eq. (B.65))

\[
p_{\text{eff}}^{\text{MNP}}(t) = \tilde{E}_{\text{MNP}}(t) \alpha(\omega_L) e^{-i \omega_L t} + c.c. \tag{B.79}
\]
In general, however, the dipole moment is found from
\begin{equation}
 p_{MNP}(t) = \int_{0}^{\infty} \alpha(t - t')E_{MNP}(t')dt' 
 = \int_{0}^{\infty} \alpha(t - t')E_{MNP}(t')e^{-\omega_L t'}dt' + c.c. 
\end{equation}

Now, if we choose the response function to be local in time such that its frequency representation is \textit{constant} \((\alpha(\omega) = \alpha(\omega_L))\), i.e.
\begin{equation}
 \alpha(t - t') = \alpha(\omega_L)\delta(t - t') \ , 
\end{equation}
then substituting the above into Eq. (B.81) gives
\begin{equation}
 p_{MNP}(t) = E_{MNP}(t)\alpha(\omega_L)e^{-\omega_L t} + c.c. 
\end{equation}

Therefore, by comparing Eq. (B.83) with Eq. (B.79), we have shown by choosing \(\alpha(\omega)\) to take its constant value at \(\omega_L\) everywhere \((\alpha(\omega) = \alpha(\omega_L))\), then the effective field method can be recovered by the PEOM method.
Appendix C

Fourth-Order Runge-Kutta Method for Solving First-Order ODEs

Suppose we have a first-order differential equation of the form

\[ \dot{y} = f(t, y) , \quad (C.1) \]

where \( y \equiv y(t) \), and we want to approximate the solution over some interval \( t \in [a, b] \) (\( b > a \)). We begin by splitting the interval into \( N + 1 \) equally-spaced points, \( \{t_0, t_1, \ldots, t_N\} \) with \( t_0 = a \) and \( t_N = b \), such that

\[ t_n = a + nh , \quad n = 0, 1, \ldots, N , \quad (C.2) \]

where \( h \) is the spacing, or step-size, given by

\[ h = \frac{b - a}{N} . \quad (C.3) \]

Provided \( y(t_0) = y(a) \) (the initial condition) is known, the fourth-order Runge-Kutta method approximates \( \{y(t_1), y(t_2), \ldots, y(t_N)\} \) using the following algorithm: [75]
For \( n = 0,1,\ldots,N-1 \),

\[
\begin{align*}
  k_1 &= h \, f(t_n, y_n) , \\
  k_2 &= h \, f(t_n + \frac{1}{2}h, y_n + \frac{1}{2}k_1) , \\
  k_3 &= h \, f(t_n + \frac{1}{2}h, y_n + \frac{1}{2}k_2) , \\
  k_4 &= h \, f(t_n + h, y_n + k_3) ; \\
  y_{n+1} &= y_n + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) ; \\
  t_{n+1} &= t_n + h .
\end{align*}
\]

where we have defined

\[
y_n \equiv y(t_n) .
\]
Appendix D

Algorithms

D.1 Least-Squares Fitting Algorithm (MATLAB)

```matlab
1  global s
2
3  % Number of fitting functions
4  %
5  s = 12;
6
7  % Limits on parameters for fitting algorithm (units in eV)
8  %
9  min_omega_k = -3;
10  max_omega_k = 50;
11  min_gamma_k = 0;
12  max_gamma_k = 10;
13  min_c_k = -10;
14  max_c_k = Inf;
15
16  % Range over which to fit (units in eV)
17  % If fit_range = [0,0], use entire range available
18  fit_range = [0,10];
19
20  % Required number of points to use in fit. If fit_points = 0 or is
21    % less
22  % than the data available, use all available points
```
fit_points = 0;

% File containing the frequency-dependent polarisability, $\alpha(\omega)$, to be fitted

% File format:
%  Column 1: $\omega$ (eV) (Must start from 0eV)
%  Column 2: Imag[$\alpha(\omega)$]
%  Column 3: Real[$\alpha(\omega)$]

infile = 'alpha.dat';

% Output file containing the fitted parameters saved as <input_file>.fit_params
% Output file also saved as a MATLAB binary file for easy import back to MATLAB

[pathstr,name,ext] = fileparts(infile);
param_outfile = {[name,ext],'.fit_params'};

% Importing input file

fid = fopen(infile);
A = textscan(fid,'%f%f%f','%CommentStyle','#');
imag_col=2;
real_col=3;
fclose(fid);

if fit_range(1)==fit_range(2)
    fit_range = [min(omega_orig),max(omega_orig)];
end

omega_orig = A{1};
alpha_orig = (A{real_col} + 1i*A{imag_col});
end

% Selecting data from required fit range
%
fit_range_id = omega_orig >= fit_range(1) & omega_orig <= fit_range(2);
omega_in = omega_orig(fit_range_id);
alpha_in = alpha_orig(fit_range_id);

if fit_points ~= 0
    N = size(omega_in,1);
    fit_points = min(N,fit_points);
    new_range = 1:floor(N/fit_points):N;
    omega_in = omega_in(new_range);
    alpha_in = alpha_in(new_range);
end

N = size(omega_in,1);

% Fitting algorithm requires a minimum value of data points
%
fprintf( '%s
%i
n ' , 'Number of points fitted = ',N)
if 3*s > 2*N
    error( ['3s>2N so fit not possible. Either decrease s or ',
            'increase the resolution of the input.
'] )
end

% We assume the input file has zomega starting at 0. To fit, we want the
% reflection about the y axis which should obey the properties of the
% polarisability:
%
Imag\alpha(\omega<0) = -Imag\alpha(\omega>0)
Real\alpha(\omega<0) = Real\alpha(\omega>0)

omega = zeros(2*N,1);
\%\$alpha = \texttt{zeros}(2*N,1)\; ;$

\texttt{omega}(N+1:2*N) = \texttt{omega}\_\texttt{in}\; ; \quad \% \\texttt{omega} > 0$

\texttt{omega}(1:N) = -\texttt{omega}\_\texttt{in}(N:-1:1)\; ; \quad \% \\texttt{omega} < 0$

\texttt{alpha}(N+1:2*N) = \texttt{alpha}\_\texttt{in}\; ;$

\texttt{alpha}(1:N) = \texttt{conj}(\texttt{alpha}\_\texttt{in}(N:-1:1))\; ;$

\% \textit{Set up for the least squares procedure}$

\texttt{v0} = \texttt{zeros}(3*s, 1)\; ;$

\texttt{v0}(1:s) = [1:s] \times \texttt{max}(\texttt{omega})/(s+1)\; ;$

\texttt{v0}(s+1:2*s) = 0.025 \times \texttt{max}(\texttt{omega})/s\; ;$

\texttt{v0}(2*s+1:3*s) = 1.0\; ;$

\% \textit{Lower bounds}$

\texttt{lb} = \texttt{zeros}(3*s, 1)\; ;$

\texttt{lb}(1:s) = \texttt{min}\_\texttt{omega} \_k\; ;$

\texttt{lb}(s+1:2*s) = \texttt{min}\_\texttt{gamma} \_k\; ;$

\texttt{lb}(2*s+1:3*s) = \texttt{min}\_\texttt{c} \_k\; ;$

\% \textit{Upper bounds}$

\texttt{ub} = \texttt{zeros}(3*s, 1)\; ;$

\texttt{ub}(1:s) = \texttt{max}\_\texttt{omega} \_k\; ;$

\texttt{ub}(s+1:2*s) = \texttt{max}\_\texttt{gamma} \_k\; ;$

\texttt{ub}(2*s+1:3*s) = \texttt{max}\_\texttt{c} \_k\; ;$

\% \textit{We use the trust–region–reflective least squares algorithm}$

\texttt{opts} = \texttt{optimset}(’\texttt{Algorithm’},’\texttt{trust–region–reflective’},’\texttt{Display’},’\texttt{Off’});$

\% \textit{We use MATLAB’s \texttt{lsqcurvefit} to perform a least–squares fit of the}
% input \( \alpha(\omega) \) to the fitting functions to obtain the parameters.

% We fit the real and imaginary parts separately by means of the function realimag.m as the chosen algorithm is not designed for complex functions.

[fitted_parameters, resnorm] = lsqcurvefit (@fitting_function, v0, omega, ... 

realimag(alpha), lb, ub, 

opts);

omega_k = fitted_parameters(1:s);
gamma_k = fitted_parameters(s+1:2*s);
c_k = fitted_parameters(2*s+1:3*s);

% This is the approximate \( \alpha(\omega) \) from the found parameters

alpha_approx = lorentz(fitted_parameters, omega_orig);

% Estimated percentage error:

pe = 100*max(abs(abs(alpha_approx(fit_range_id))) - ... 

abs(alpha_orig(fit_range_id))) / ... 

max(abs(alpha_orig(fit_range_id)));

% Saving the parameters to the output files

fid = fopen(param_outfile, 'w');
fprintf(fid, '%s
', '#

Input file: ', infile);
fprintf(fid, '%s%fs\n', '#_Fitted_over_the_range: ', ...) 

fit_range(1), ': ', fit_range(2), ' eV');
fprintf(fid, '%s%fs\n', '#_Estimated_percentage_error: ', ') 

pe, '%

fprintf(fid, '%s ', '#');
fprintf(fid, '%n\n', 'n_k');
fprintf(fid, '%d\n', s);
fprintf(fid, '\n%fs\n', 'omega_k');
fprintf(fid, '%fs\n', 'omega_k');
fprintf(fid, '\n%s\n', 'gamma_k');
fprintf(fid, '%f\n', gamma_k);
fprintf(fid, '\n%s\n', 'c_k');
fprintf(fid, '%f\n', c_k);
fclose(fid);

save(param_outfile_mat, 'gamma_k', 'c_k', 'omega_k', 's')

function f = fitting_function(parameters, omega)

global s

omega_k = parameters(1:s);
gamma_k = parameters(s+1:2*s);
c_k = parameters(2*s+1:3*s);

f_tmp = 0.0;
for k = 1:s
    f_tmp = f_tmp + c_k(k)*(1.0./(omega_k(k) - omega - gamma_k(k)*1j) + ... 1.0./(omega_k(k) + omega + gamma_k(k)*1j));
end

f = realimag(f_tmp);

function y_out = realimag(y_in)

% This function decomposes a complex variable into a vector containing
% alternations of the real and imaginary parts

y_out = zeros(2*length(y_in),1);
jj = 0;
for ii = 1:length(y_in)
    jj = jj + 1;
    y_out(jj) = real(y_in(ii));
D.2 Runge-Kutta Solution to Isolated PEOM

```matlab
% Multiply by ha2ev to convert units from Hartree to eV
ha2ev = 27.2113834;
% Multiply by fs_to_au to convert units from femtoseconds to atomic units
fs_to_au = 41.3413745758;

load('../Curve_Fitting/MATLAB/alpha.dat.fit.params.mat')

% Output file
% File format:
% Column 1: Time (fs)
% Column 2: Applied field (atomic units)
% Column 3: Dipole moment (atomic units)

outfile = 'output.dat';
```

```matlab
global step
global E0
global step_id
global start_delta_id
global s
global c_k
global gamma_k
global omega_k

% Read MATLAB file generated by the least-squares procedure
```
30 \%
31 \text{max}_T = 80;
32
33 \% \text{Runge–Kutta timestep (fs)}
34 \%
35 \text{step} = 0.001;
36
37 \% \text{Output to file at check intervals (fs)}
38 \%
39 \text{checkt} = 0.001;
40 \text{checkt} = \text{round}(\text{checkt}/\text{step});
41
42 \% \text{Amplitude of applied field (atomic units)}
43 \%
44 \text{E0} = 0.0001;
45
46 \% \text{Number of steps in Runge–Kutta}
47 \%
48 \text{N} = \text{round}(\text{max}_T/\text{step});
49
50 \% \text{Convert parameters to atomic units}
51 \%
52 c_k = c_k/\text{ha2ev};
53 \text{gamma}_k = \text{gamma}_k/\text{ha2ev};
54 \text{omega}_k = \text{omega}_k/\text{ha2ev};
55 \text{step} = \text{step}*\text{fs_to_au};
56
57 \% \text{Timing (output percentage complete every so often)}
58 \%
59 \text{every\_percent} = 5;
60 \text{checkp} = \text{N}*\text{every\_percent}/100;
61
62 \% \text{The start time for the delta function is equal to the first output time}
63 \%
64 \text{start\_delta\_id} = \text{checkt};
% Initial values

\[
t = 0;
p = 0;
s_k = \text{zeros}(s,1);
\]

% Setting up output file

\[
fid = \text{fopen}(\text{outfile},'w');
\]

\[
\text{fprintf}(fid, '%15s%15s%20s
', '#t (fs)','Field (a.u.)','Dipole Moment (a.u.)');
\]

\[
\text{fprintf}(fid, '%.9e%.9e%.9e
', 0, 0, 0);
\]

% Iteratively solve the PEOMs using the Runge–Kutta method and output to file

\[
\text{for step_id} = 1:N
\begin{align*}
[t, s_k] &= \text{rk4_step('peom',} t, s_k)\
p &= \text{sum}(c_k.*\text{real}(s_k));
\end{align*}
\]

\[
\text{if mod(step_id,checkp) == 0}
\begin{align*}
\text{fprintf('%.2f%.s
', step_id/checkp*every_percent, '}\%');
\end{align*}
\]

\[
\text{if mod(step_id,checkt) == 0;}
\begin{align*}
\text{fprintf(fid, '%.9e%.9e%.9e\n', t/fs_to_au, eext(t), p);
\end{align*}
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
\text{fclose(fid);}
\]

\[
\text{function [t, y] = rk4_step(func,} t_n, y_n)\]

\[
\text{global step}
\]

\[
k1 = \text{step} * \text{feval(func,} t_n, y_n);\]

\[
k2 = \text{step} * \text{feval(func,} t_n+0.5*}\text{step,} y_n+0.5*k1);\]

\[
k3 = \text{step} * \text{feval(func,} t_n+0.5*}\text{step,} y_n+0.5*k2);\]
7 k4 = step * feval(func, t_n+step, y_n+k3);
8
9 y = y_n + 1/6 * (k1 +2*k2 + 2*k3 + k4);
10 t = t_n + step;

1 function y = eext(t)
2
3 global E0
4 global start_delta_id
5 global step_id
6
7 if step_id == start_delta_id
8     y = E0;
9 else
10     y = 0;
11 end
Bibliography


