



DOCTORATE OF PHILOSOPHY

**Quantum treatment of ultra-low loss electron energy loss
spectroscopy with applications to molecular crystals**

SABRINA YUE WANG

UNIVERSITY OF OXFORD

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ABSTRACT

Continual advancements of experimental hardware for electron energy loss spectroscopy (EELS) - a material characterisation technique grounded in electron scattering - has opened up the avenue for studying vibrational excitations, as energy resolutions are now able to reach down to $\sim 5\text{meV}$. Although optical methods such as Infrared and Raman spectroscopy can be used to study phonon vibrations, EELS paired with scanning transmission electron microscopy (STEM) has the advantage of superior spatial resolution, making it an attractive alternative. An electron beam that is off-sample (aloof mode) reduces the sample beam damage, an attractive technique for better investigations of sensitive, organic molecular crystals such as pharmaceutical products.

In this thesis, the commonly used theoretical derivations of ultra-low loss EELS are reviewed. Their shortcomings are identified, and an improved quantum formalism congruous with molecular crystals is presented. This modified ‘dipole’ theory dominates in magnitude over the current quantum treatment for aloof beam EELS, and is demonstrated to show improved relative intensity predictions for the molecular crystal of β -guanine. It successfully distinguishes between two polymorphs of quinacridone, and reasonably quantifies the relative peak intensities. We also apply our theory to the bulk crystal of boron subphosphide by evaluating its performance over the other theoretical methods. These calculations require material properties determined from first principles using density functional theory, which will be expanded upon in the thesis.

By the end of the thesis, the pros and cons of the different theories have been dissected, and a proof of concept for our quantum 'dipole' theory applied to experimentally acquired spectra for quinacridone lays the foundation for further improvements, which we will also delineate.

DECLARATION OF AUTHORSHIP

This dissertation is submitted to the University of Oxford in accordance with the requirements for award of the degree of Doctorate of Philosophy.

I hereby declare that this dissertation is my own and original work, undertaken during my time at the University of Oxford. I have explicitly acknowledged all external help and collaborators for the relevant parts of the thesis. Any data that have been obtained by others are credited accordingly and have been permitted to be used. Signed:



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For my
Mother & Kevin & Jack

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ACRONYMS

BEC	Born Effective Charge, Section 4.2 .
BZ	Brillouin Zone , Chapter 8 .
COD	Crystallography Open Database, Chapter 9 .
CS	Chemical shift, Chapter 9 .
CSD	Cambridge Structural Database, Chapter 9 .
DFPT	Density functional perturbation theory, Section 3.5 .
DFT	Density Functional Theory, Section 3.5 .
DWF	Debye-Waller factor, Section 5.2 .
EDX	Energy-dispersive X-ray spectroscopy, Section 12.1 .
EELS	Electron energy loss spectroscopy, Chapter 2 .
EFG	Electric field gradient, Section 3.5 .
FTIR	Fourier-transform infrared spectroscopy Section 12.1 .
hBN	Hexagonal boron nitride, Chapter 8 .
HF	Hartree Fock, Section 3.4 .
IFC	Interatomic force matrix, Section 3.2 .
ITC	International Tables for Crystallography, Chapter 10 .

LDA	Local density approximation, Section 3.5 .
MBD*	Many body dispersion, Chapter 9 .
MECV	Mode effective charge vector Section 6.3 .
MP	Monkhorst-Pack , Chapter 8 .
MRD	Mean relative deviation, Chapter 9 .
NMR	Nuclear magnetic resonance , Section 3.5 .
PBE	Perdew-Burke-Ernzerhof, Section 3.5 .
RMSE	Root mean square error, Chapter 9 .
rSCAN	Regularised Strongly Constrained and Appropriately Normed, Chapter 9 .
STEM	Scanning transmission energy microscopy, Chapter 2 .
TEM	Transmission electron microscopy, Chapter 2 .
TS	Tkatchenko-Scheffler, Chapter 9 .
vdW	Van der Waals, Section 3.5 .
XC	Exchange correlation, Section 3.5 .
ZLP	Zero loss peak, Chapter 2 .

LIST OF PUBLICATIONS

The work presented in this thesis has appeared¹ publicly in several formats.

Papers

1. “Benchmarking the *rSCAN* functional’s performance in determining Molecular Crystal properties using density functional theory” in preparation for Physical Chemistry Chemical Physics.
2. “Aloof beam EELS: A multipole approach to the quantum theory of the region of ultra-low energy loss” in preparation for Physical Review B.
3. “OptaDOS version 2.0: New features and applications” in preparation.

Conference Proceedings - Posters and Presentations

1. EMAG 2022: Oral presentation : *Quantum theory of ultra-low loss aloof beam EELS applied to molecular crystals.*
2. Physics by the Lake summer school 2019: Poster presentation : *Theory of Molecular EELS Spectra.*
3. CASTEP workshop 2019: Poster presentation : *Theory of Molecular EELS Spectra.*

¹ Or will appear in the near future.

INTRODUCTION

OVERVIEW AND THESIS OUTLINE

Vibrational spectroscopy plays a central role in the understanding of materials, such as their thermal properties, phase transitions, as well as their interactions with light and sound. Electron energy loss spectroscopy, carried out within the electron microscope, is a common characterisation technique that has recently gained additional capabilities due to advances that have substantially improved energy resolutions down to $\sim 5\text{meV}$ [2,3], thus facilitating phonon mode analyses of the ultra-low energy loss regime.

The most common method in the literature for simulating the electron energy loss spectrum is through solving the classical Poisson equation with the incoming fast electron as an evanescent source. The response of the material is characterised by its dielectric tensor and phonon dispersion. This can be computed from quantum mechanical first principles using density functional theory (DFT), which we will elaborate on throughout this work. There is also a quantum mechanical formalism of the interaction of the electron beam with the specimen, based in Fermi's golden rule of transition probabilities. However, this treatment is not compatible with the aloof beam geometry, and is riddled with ambiguities regarding how charge is distributed in the analytical derivations.

Part I of this thesis introduces relevant experimental techniques used for material characterisation, and theoretical preliminaries including optical spectroscopic methods that are complementary to electron spectroscopy, inelastic electron scattering and fundamentals of DFT. In **Part II** we explore the existing analytical methods of predicting low loss EELS, discuss their limitations, and develop a modified version of the current quantum theory that is compatible with the aloof beam configuration and commensurate with molecular crys-

tals. [Part III](#) contains practical implementations of density functional theory using the *ab Initio* code CASTEP. Focus is put on the parameters required to obtain reliable optimised geometries, and then the phonon and nuclear magnetic resonance properties of a range of molecular crystals, from carboxylic to amino acids. Benchmark tests are performed on these crystals to evaluate the competency of a newly implemented functional, rSCAN. [Part IV](#) brings it all together by assessing the effectiveness of the theories' (discussed in [Part II](#)) abilities to predict relative intensities, as well as distinguish between molecular crystal polymorphs. Specifically, we focus on β -guanine and two polymorphs of quinacridone where experimental aloof beam spectra exist. We also provide theoretical reports of differentiating polymorphs of drugs olanzapine and pyrazinamide. With some adjustments, our modified theory is also applied to the bulk crystal of Boron subphosphide. Finally, [Part V](#) highlights the main conclusions from this work and proposes prospects for future work.

Part I

LITERATURE REVIEW

EXPERIMENTAL SPECTROSCOPY TECHNIQUES

All atoms in matter are continuously vibrating, and they can absorb energy from incoming particles (such as light, electrons, etc) to vibrate further, in accordance with their resonant behaviours. These mechanical vibrational energies, or phonons, are quantised, and can be used to characterise a material and probe its micro and macroscopic properties. This is extremely important in many areas. For example in the pharmaceutical industry, it is crucial to understand the physical properties of a drug in all stages of its development, and vibrational spectroscopy techniques are commonly used for their identification and quantification [4].

2.1 MOLECULAR CRYSTALS

The compounds of interest in such pharmaceutical settings are molecular crystals, which are periodic, ordered solids consisting of molecules on lattice sites. The intermolecular forces are weak, non-covalent bonds. Pharmaceutical companies are very interested in the engineering of molecular solids. A comprehensive understanding of interactions between molecules/ions in a molecular solid is essential in modifying/customising a drug's functionality [5]. There are often various polymorphs for organic and inorganic solid compounds. This means that the solid can exist in different crystalline forms, with the same type and number of atoms involved. Different crystal structures may contain different types of intra and intermolecular bonds. For example, two polymorphs of the medicine carbamazepine (used to treat epilepsy and neurological pain) are shown in Fig. 2.1 [6]. CIF file information are obtained from the Cambridge Structural Database (CSD), where the deposition num-

bers are 1121423 (form II) and 249934 (form IV). Note that the hydrogens are missing on form II, which is a common problem deposited CIF files due to problems in experimental characterisation methods such as X-ray diffraction in detecting light elements (especially hydrogen).

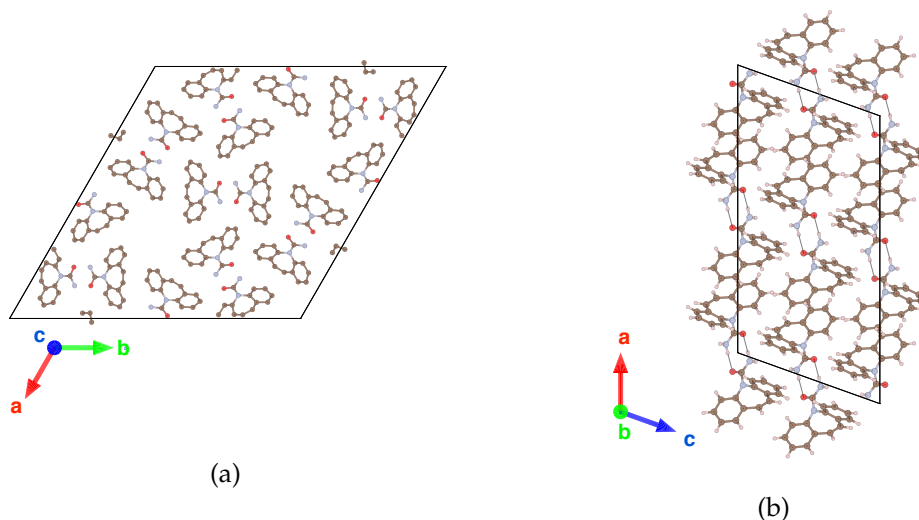


Figure 2.1: Two polymorphs (left) form II and (right) form IV of carbamazepine showing the different unit cell packing formations. The latter shows a layering of the hydrogen-bonded molecules which is not present in the former. Oxygen, Nitrogen, Carbon and Hydrogen are shown in red, blue, brown and white respectively.

Polymorphs can possess a variety of differentiable physical properties, ranging from solubility to melting point. Specifically, in pharmaceuticals, it is very important to distinguish between the different crystal conformations. Not only is this because the polymorph structure is crucial to the purpose and function of the drug, different polymorphs are separately patented [7]. The ability of distinguishing different polymorphs without damaging the samples is very desirable, and is now conceivable with current state of the art electron microscopes. Thus the need for more developments to the theory and interpretation of vibrational EELS data is further endorsed by this potential application.

Currently, popular methods for investigating molecular crystals in industry is by using Raman, IR and INS spectroscopy. Raman and IR spectroscopy experiments are quick and easy to perform, requiring only a beam without the need for careful sample preparations. A lot of research has been done on drugs, such as studying the crystalline structure of indomethacin [8], detecting changes in recrystallizations of ibuprofen [9] and distinguishing between polymorphs of a variety of other pharmaceutical products [10, 11]. Pfizer's Viagra is a drug that is often counterfeited. Raman analysis is important in helping authenticate the product by the unique spectra of its blue dye coating [12].

IR and Raman spectroscopy can only identify vibrational modes which satisfy the requirements of a change in dipole moment and polarizability respectively. This means that the optical techniques are selective and not all modes are active. This problem is not present in INS and X-ray spectroscopy. INS has been successfully demonstrated to capture the lattice dynamics of nanoporous Metal-Organic Frameworks, which are useful in pharmaceuticals due to their absorption capabilities [13, 14]. Another issue to consider is that of beam damage. Since INS and X-ray spectroscopy use impact scattering, it is important to monitor the sample, or perform experiments to study the degradation/damage of the sample over time [15]. This is especially important for biological samples which contain a lot of light elements. Electrons are highly favoured scatterers due to their short wavelength and charge, thus are easily manipulatable and provide more information compared to that of neutrons and light [16]. Sample degradation due to electron beam damage can be dramatically reduced in the aloof beam mode, which further reinforces the advantages of electron microscopy experiments compared to that of the INS and X-ray counterparts.

2.2 TECHNIQUES OVERVIEW

Another noteworthy and complementary technique to EELS is terahertz spectroscopy. This technique uses short pulses of terahertz radiation and can probe the ultra-low loss regimes of the sample. The laser source was costly and cumbersome, which kept its influence on pharmaceutical studies relatively small compared to Raman and IR spectroscopy. Studies mainly focused on the detection of dangerous chemicals and illegal drugs [17]. However, advances in terahertz technology, especially with the development of the quantum cascade laser [18], has renewed interests in vibrational spectroscopy [19]. It has since been used to distinguish between polymorphs of Ranitidine Hydrochloride [20], Carbamazepine and several other drugs [21]. Azuri *et al* [22] calculated the vibrational spectra for 2,4,6-TNT between $30\text{-}100\text{ cm}^{-1}$, which corresponds to vibrational energy values of $< 12\text{meV}$.

2.2 TECHNIQUES OVERVIEW

This section introduces and highlights common experimental techniques for vibrational spectroscopy, as well as some hardware advancements that help uncover information that was previously unattainable.

There are various common methods for probing the vibrational motions of molecules in a material. For example, in infra-red (IR) spectroscopy, IR light interacts with molecular vibrational modes that creates a change in the molecule's dipole moment. The main mechanism is absorption, and this is directly correlated to the power loss by the incident electric field. Hence, one can map out the vibrational spectra of the specimen [23, 24].

In Raman spectroscopy, a strong, monochromatic beam of light in the visible spectrum is used to illuminate a sample. The atoms can transition into several different states in the de-excitation process before they lose all the imparted energy. If a vibrational mode is Raman active, it must be associated

with a change in polarizability. Polarizability is a measure of how the electron cloud surrounding the relevant atoms is deformed (i.e. induced dipole moment) in the presence of an external electric field [23].

Inelastic neutron scattering (INS) is useful in probing bulk samples. The scattering of neutrons allow for much higher momentum transfers compared to using photons in IR and Raman. The momentum resolution allows for proper measurements of phonon dispersion curves. However, building neutron sources for INS is very expensive. It also requires large crystals to be grown and has sub-par spatial resolutions [25].

X-ray spectroscopy involves the electromagnetic interactions between X-rays and the sample's electron cloud. Since the electron cloud is not a single point source, scattering events are not completely in phase and the amplitude heavily depends on the scattering angle (higher angles correspond to lower peak intensities). It is also harder to detect light elements. Despite these disadvantages compared to INS, X-ray spectroscopy is much cheaper to perform and also requires much smaller specimen sizes [26].

Finally, the main method focused in this project is electron energy loss spectroscopy (EELS). EELS is a technique that can probe a material's structural and chemical properties. This was first demonstrated by Hillier and Baker [27] and has now become a standard method. It is measured using the electron microscope, whereby electrons of several tens of keV are focused onto a *thin* sample and then collected on the other side. The electrons inelastically scatter off of the specimen via several different interaction mechanisms, and result in an electron energy loss profile. The plethora of information obtained by the microscope also allows for advanced analyses such as identification/elemental mapping, chemical bonding, and recently, remarkable details of the material's vibrational modes [28].

The samples used in EELS are typically tens of nanometres in thickness. If the sample is too thick, there is a higher likelihood of multiple scattering events. This produces a convoluted signal which is harder to interpret. There are two common types of electron energy loss experiments with similar abbreviations, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). In TEM, electron beams are focused perpendicular to the sample plane and inelastic scattering signals are collected. STEM is very similar, except the electron beam is brought to a *focal point* onto the specimen, and then rastered across the sample. The transmitted signal is thus collected as a function of the electron beam position [29].

Electrons can probe all phonon wave-vectors, couple very strongly with matter, and since they are charged, can be easily focused using lenses [30, 31]. EELS sample sizes are on the order of the mean free path of the beam electrons (typically tens of nanometers in thickness) [32], which are much smaller than those required by INS ($\sim 1\text{mm}^3$) [33]. Electron microscopes have been skilfully engineered to provide higher spatial resolution compared to the other mentioned methods, and chemical/structural analysis at the atomic level. This makes EELS a very attractive technique.

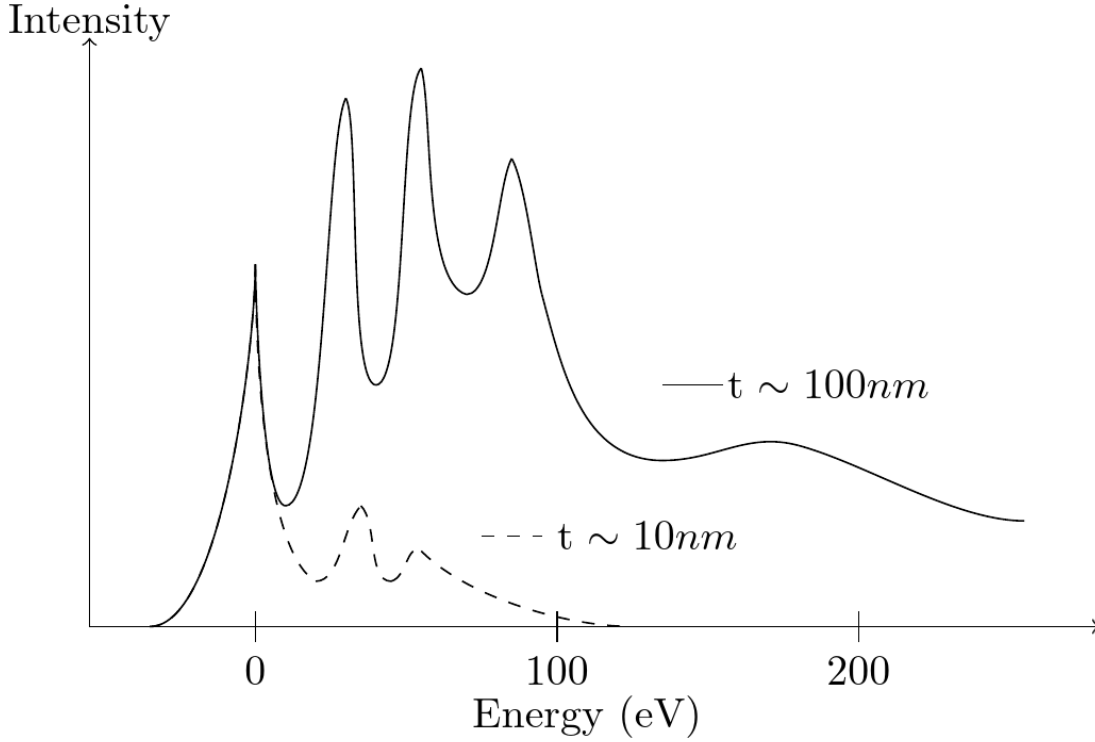


Figure 2.2: Illustration of generic EELS spectra of two samples of different thickness, t .

Figure 2.2 shows a typical EELS spectrum, covering all types of scattering regimes. The zero loss peak (ZLP), represents electrons that are transmitted through the sample without any interactions. This peak is the largest for a thin sample and there is a width associated with the peak due to elastic scattering from nuclei. Hence, it manifests the energy distribution of the electron source. The region just above the ZLP on the order of hundreds of meV is the ultra low-loss region containing vibrational and plasmon excitations, and is the focus of this thesis. Finally, core-excitations make up the high-loss region from tens to hundreds of eV . Notice that the thicker specimen in the figure has more intense signals compared to the ZLP, which corresponds to multiple plasmon scattering events with peaks present at multiples of the plasmon's energy [29]. More detailed explanations of these different scattering phenomena are outlined in Section 3.2.

2.3 HARDWARE ADVANCEMENTS FOR EELS

Traditionally, images captured by the microscope were blurred due to lens aberrations. This is an issue of the hardware/optical system in which light is spread out instead of becoming properly focused. This hurdle was overcome by the development of aberration correctors, which enabled sub-ångström spatial resolution. Batson *et al.* [34] were the first to resolve below 1Å, but required a lot of post processing. They have however paved the way for lower operating voltages and ‘smarter’ instrumentation.

Steady hardware improvements have also allowed STEM to perform better spectroscopically, by becoming cheaper to operate and better resolved compared to the other experimental methods that obtain equivalent information. One can now more easily image/study closely spaced atoms [35], chemical bonding [36], and mapping vibrational modes [37] on the atomic level. As instrumental improvements have become so advanced, current limiting factors to spatial resolution arise from fundamental physics such as beam broadening and delocalisation of the inelastic scattering [38, 39]. This is because electrons can become inelastically scattered even if they are travelling several nanometres away from the sample, thus imposing a basic limit to how well an image can be resolved [40].

The microscope’s *energy* resolution, on the other hand, has also been dramatically improved by new spectrometers [41]. In terms of hardware design, there are two phenomena which limit the performance of a spectrometer. These are the spectrometer’s energy resolution and spectrum-diffraction mixing. The former concerns the aberrations and dispersion (the separation of light into its component wavelengths). Electrons that are collected at high acceptance angles result in focusing effects/problems which deteriorates the energy resolution. The latter phenomenon occurs where there is mixing/-

convolution between the spectral and image information in the microscope. These problems were addressed by Krivanek *et al.* [2,42], who have devised a high energy resolution monochromated EELS-STEM system (HERMES) and recently improved the energy resolution to $\sim 5\text{meV}$ [43]. Typically, fluctuations in the microscope's accelerating voltage can greatly destabilise the electron beam. The HERMES system has multiple components that work together synergistically such that despite these fluctuations, the monochromator still produces very stable electron beams. Monochromators are devices whose primary purpose is to impose limits on the energy distribution of the electron beam [44], but are also important in reducing the full width half maximum and tail of the ZLP so that it does not obscure the spectra [45]. Improvements to the energy resolution have 'revealed' the desired vibrational components in ultra-low loss EELS that were previously hidden. It has also opened up prospects of better quantitative analyses of ionisation edges, band gaps and dielectric function measurements [40].

Valence loss studies have been conducted on materials such as polymorphs of carbon [46] and metal oxides [47]. Nicholls *et al* [48] were able to take advantage of the high spatial and energy resolution in the STEM to test their adapted, general theory of phonon spectroscopy with proper momentum dependence, on inelastic electron scattering experiments involving hexagonal boron nitride (hBN). They were able to demonstrate the fundamental similarities in the physics involving the scattering of electrons, neutrons and X-rays. This generalised method can be extended to other materials and it allows one to scrutinise the individual modes that make up the resulting spectra.

Another active area of research aided by the improvements to energy resolution is in lithium-ion batteries [49]. More specifically, it helps probe the electronic structures and analysis of elemental compositions at a sub-ångström

level. Thus, previously unfeasible experiments such as interface-structure and analyses of light elemental locations are now possible.

2.4 EXPERIMENTAL STUDIES USING ALOOF BEAM EELS

Typically, STEM experiments involving scattering due to impact collisions result in severely degraded samples from the irradiation. This issue is overcome by performing ‘aloof’ mode experiments where the electron beam is placed several nanometres away from the specimen. This set up was experimentally proposed by Cohen *et al* [50] and has become more prevalent due to the hardware improvements discussed above.

Raza *et al* investigated silver nanoparticles confined in silver nitride [51]. They were able to distinguish different types of plasmonic modes induced on the surface depending on the interaction configuration, where the type of mode excited is crucially affected by the impact parameter. A plasmon describes a collective oscillation by plasma, which is often viewed as electrons oscillating about fixed positive nuclei.

Water is omnipresent and central to many fields of science and engineering. However, when it is for example confined on the nanoscale, fundamental understanding of its behaviour is still elusive and typical investigations of structure/bonding are performed with Raman spectroscopy, with a resolution merely on the μm scale. Jokisaari *et al* [52] studied the vibrational spectra of water surrounded by layers of boron nitride using aloof EELS. They demonstrated the ability to study the molecule with better spatial resolution, its interactions with BN solid surface and identifications of isotopes such as D_2O (heavy water). This again, greatly outperforms the information available from IR and Raman means. In cellular biology, isotope labelling is a technique in which atoms in a molecule are replaced by an isotope that is to be

monitored as it progresses through biochemical pathways. One can detect the isotopes using mass spectrometry, but this involves destroying the sample and thus losing spatial resolution. Hachtel *et al* [53] applied aloof beam EELS to study the vibrational modes of L-alanine containing carbon isotopes, and successfully showed a shift in the stretching mode for the carbon-oxygen double bond.

Rez *et al* [54] applied aloof beams to study biogenic guanine crystals and was able to benchmark their findings with IR spectroscopy results. They successfully identified covalently bonded hydrogen, and were able to attribute specific peaks in the EELS spectrum to the structure's eigen-modes of vibration. As the electron beam is moved away from the specimen, intensities of spectral peaks decrease but the signal has been shown to be detectable even at a distance of 100-nm. This work was analysed by Radkte *et al.* [55] using a semi-classical electron energy loss theory. They were able to clearly assign the theoretically predicted and experimentally visualised energy loss peaks due to vibrational modes near the ZLP (ranging from 100-500meV).

Govyadinov *et al* [56] performed a similar type of experiment and theoretical calculation (i.e. same classical electrodynamics approach as Radtke) on hBN. They mapped the phonon excitations at mid-IR frequency ranges and also showed that instead of the bulk phonon modes that are predominantly reported in literature, the main contribution to energy loss in hBN is from phonon-polariton excitations. Polaritons are quanta of energy resulting from interactions between light and dipole transitions of a material [57].

3.1 THEORY OF INFRARED AND RAMAN SPECTROSCOPY

Previously we have introduced the prevalent experimental techniques for studying phonons, the practicalities of the electron microscope and its recent consequential developments. We now turn our attention to the fundamental physics that underpin these methods.

3.1.1 *Scattering cross sections*

Scattering of particles such as neutrons, electrons, and photons allows for the determination of spatial structure and excitation spectrum. The fundamental method of a quantum mechanical description of scattering is as follows. One begins with the relevant Hamiltonian and solve the corresponding time independent Schrödinger equation for the system. For example, an incoming wave scattering off a particle will spread out spherically (Fig. 3.1) the scattered wave will take the form $\psi = f(\theta)\frac{e^{ikr}}{r}$, where $\frac{e^{ikr}}{r}$ denotes the damping of the scattered wave as $r \rightarrow \infty$. The scattering amplitude, f , describes how the system scatters the incoming particle in different directions. In general, f can also depend on $\vec{q}$, the phonon wave-vector (if the object is not perfectly spherically symmetric).

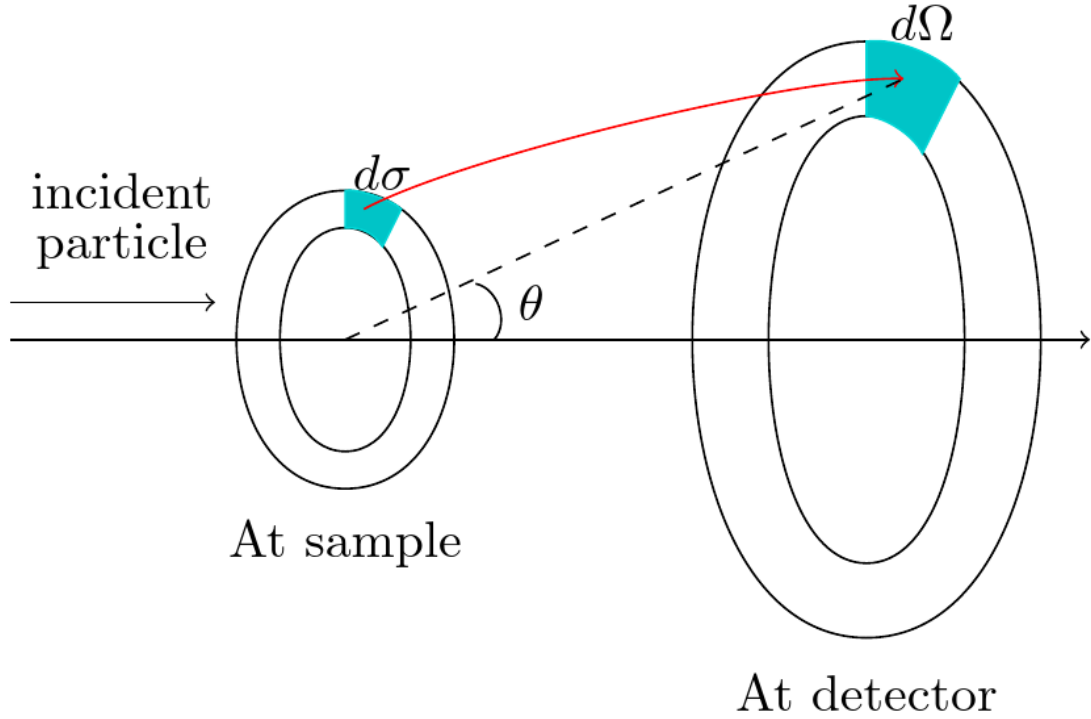


Figure 3.1: Schematic of infinitesimal scattering cross section [58]. σ represents the cross-sectional area in which the incoming particle will scatter off the red dot. Ω represents the solid angle in which the particle from $d\sigma$ will arrive in after scattering.

The differential cross-section is defined as $\frac{d\sigma}{d\Omega}$, and is directly related to the scattering amplitude through

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2. \quad (3.1)$$

The differential cross-section can also be written as the flux of scattered particles in $d\Omega$ over the flux of incoming particles in $d\sigma$ [40, 58], i.e. it is the probability that an incoming particle is scattered.

The expression of interest relating to the inelastically scattered particles is the doubly differential cross-section [59], as it allows for the direct comparison to the experimental measurements,

$$\frac{d^2\sigma}{d\Omega dE} \quad (3.2)$$

where the scattered particles are of energies between E and $E + dE$.

3.1.2 Infrared spectroscopy

IR spectroscopy was previously introduced as one the most common techniques used for characterising a sample based on its spectroscopic signatures. This method relies on the absorption of radiation in the infrared-region. The range of transitions this can induce are rotational, translational and vibrational modes of the target material.

In order for the mode to be IR active, the transition matrix element between the initial and final wavefunctions must be non-zero, i.e. $\langle \phi_{\text{final}} | \hat{\mu} | \phi_{\text{initial}} \rangle$ where $\hat{\mu}$ is the dipole moment operator. Consider the dipole moment of a molecule, which is simply the result of a separation of charge q multiplied by the vector joining them, $\vec{r}$, $\vec{\mu} = q\vec{r}$. The total wavefunction is a product of the electronic, vibrational, rotational and translational functions, i.e. $\phi_{\text{total}} = \phi_E \phi_V \phi_R \phi_T$, as these are separable (independent) terms whose energies sum to the total energy. The electronic and translational components do not participate and thus one can derive the selection rules using the rotational and translational modes. It can then be shown that the matrix element is zero unless the vibrational/rotational mode induces a change in the permanent dipole moment [60].

Group theory can be used to determine which modes cause a change in the dipole moment. A more in depth discussion of the origins of the selection rules using group theory is present in [Appendix E](#). However, the main takeaway is that if the set of wavefunctions $\phi_{\text{initial}}^* \phi_{\text{final}}$ for the two vibrational state levels have the same symmetry transformations as that of the dipole operator, then the dipole transition matrix integral will not vanish. This is equivalent to saying that if a specific mode has a directional dependence (i.e. it trans-

forms the same way as the cartesian x , y , or z), then it is IR active. This is the group-theoretic equivalent of stating that the permanent dipole moment must change in order for the matrix transition element to be non-zero.

The change in dipole moment can be analysed by a Taylor expansion with respect to atomic displacements $\vec{\tau}$, and hence the IR intensity is

$$I_{\text{IR}} \propto |\langle \phi_{\text{final}} | \hat{\mu} | \phi_{\text{initial}} \rangle|^2 \propto \left(\frac{d\mu}{d\tau} \right)^2 \quad (3.3)$$

This is an important relationship that will be revisited later in [Part II](#) when we discuss the quantum treatment of EELS, and how it relates to the theory of IR and Raman spectroscopy. Note that we consider only one phonon excitations since most chemical bond vibrations can be approximated using the simple harmonic oscillator. Any overtones with changes in vibrational numbers greater than one are ignored due to higher derivative of the dipole moment.

3.1.3 Raman spectroscopy

Raman spectroscopy is an inelastic scattering technique. The resulting spectrum consists of a strong excitation peak which matches that of the frequency of the incident light, together with weaker lines shifted from this central frequency on to the left and right at symmetrical positions, called the Stokes and anti-Stokes lines. These are associated with the molecular rotational and vibrational modes and the further the shift in frequency, the higher the energy of the excited mode. Upon scattering, an incident photon of energy $E = h\omega_0$ can be absorbed with a simultaneous emission of a photon of the same (elastic Rayleigh scattering), smaller or larger energy $E_{\text{emit}} = h(\omega_0 \pm \delta\omega)$ [[60](#)]

3.2 ELECTRON SCATTERING AND EELS

If an electric dipole moment can be induced $\vec{\mu}_{\text{induced}}$ in a molecule from an external electric field $\vec{E}$, they are related by the polarisability (tensor) α ,

$$\vec{\mu}_{\text{induced}} = \alpha \vec{E} \quad (3.4)$$

In an isotropic material α will be a purely diagonal matrix of identical terms along the main diagonal. The polarisability transition matrix element is used to determine the selection rules,

$$\langle \phi_{\text{final}} | \hat{\alpha} | \phi_{\text{initial}} \rangle \quad (3.5)$$

and can be evaluated in the same way as that for IR spectroscopy. This is to say that the integral vanishes unless $\phi_{\text{initial}}^* \phi_{\text{final}}$ contains the symmetry elements that that the polarisability tensor transforms according to.

3.2 ELECTRON SCATTERING AND EELS

Scattering of electrons off of a material refers to their interactions through collision, and often results in a transfer of momentum and energy. We can separate the range of interactions into two regimes - elastic and inelastic. Elastic scattering refers to the case where electrons are deflected due to interactions with the heavily charged nucleus. Since electrons are less likely to collide head on with the nucleus, they often scatter at small angles with a small energy transfer. Inelastic scattering, on the other hand, refers to the Coulomb interactions with the specimen's electrons and their excitations to higher quantum numbers [40]. The type of scattering that occurs in EELS is (and hence are of interest to us) inelastic [61].

3.2.1 *Plasmons and single-electron excitations*

An incoming fast electron can interact with the valence electronic charge density, losing energies of tens of eV . The aggregate effect is called the plasma resonance, where rapid oscillations in electronic densities take the form of longitudinal waves. Much like how photons are the discretisation of light waves, plasmons of energy $E = \hbar\omega_p$ are the discretisation of plasma resonance waves, where $\hbar$ is the reduced Planck constant and ω_p is the plasma frequency. It is essential that the valence electrons interact with each other, which is why plasmons are more predominant in metals where the outer shell electrons act like free particles.

Alongside plasmons, there is a competing energy-loss mechanism for the low-loss EELS regime where the incoming electron directly transfers energy to a valence electron. This can cause broadening and shifts to the plasmon peaks [40] in the low loss region of Fig. 2.2.

3.2.2 *Phonon scattering and lattice dynamics*

Moving further down the energy scale, one arrives at the vibrational energies of atoms around their equilibrium positions in a crystal. Incoming fast electrons can interact with such lattice vibrations to produce phonons of energy $k_B T$, where k_B is Boltzmann's constant and T , temperature. Such energies are typically below $0.1eV$ (residing in the meV regions). Phonons make up the ultra low-loss regions of an EELS spectrum (region 1 of Fig. 2.2) and until recently, such fine energy resolution was experimentally unattainable. Phonons provide information on bonding, thermal and dielectric properties of the specimen [28], and are the main type of inelastic scattering concerned in this project.

Now that we've reviewed experimental vibrational spectroscopy, we turn our attention to simulating ultra-low loss EELS spectra from first principles. We begin with the theoretical description of phonons and lattice dynamics. Consider the many-body Schrödinger equation for describing a system of interacting electrons and nuclei at positions and masses $\vec{r}_i, m$ and $\vec{R}_I, M_I$ respectively [62], and apply the adiabatic approximation [63], whereby the electronic and nuclear motion are uncoupled. We focus on the nuclear equation,

$$\left(-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \vec{R}_I^2} + U(\vec{R}) \right) \phi(\vec{R}) = \epsilon \phi(\vec{R}). \quad (3.6)$$

where ϵ is the eigenvalue for eigenstate ϕ . $U(\vec{R})$ is the Born-Oppenheimer potential energy surface and represents the ground state energy of a system of fixed nuclei and interacting electrons. It is the energy corresponding to the Hamiltonian including electronic kinetic energy, and all interactions involving nuclei and electrons.

At the ground state, the system is in equilibrium, which requires zero net force on all nuclei,

$$\vec{F}_I = -\frac{\partial E(\vec{R})}{\partial \vec{R}_I} = 0. \quad (3.7)$$

In order to obtain the desired modes of vibrations, harmonic approximation is employed whereby the energy of the periodic crystal is expanded to second order [64],

$$E(\{\Delta\tau\}) = E^0 + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left(\frac{\partial^2 E}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right) \Delta(\tau_{\kappa\alpha}^a) \Delta(\tau_{\kappa'\beta}^b) + \dots \quad (3.8)$$

where $\Delta\tau_{\kappa\alpha}^a$ denotes a displacement of atom κ along the α direction in cell a . The cell refer to the fact that computationally, calculations on a supercell several times larger than the unit cell that the atoms reside in are required, in

order to completely capture the periodic nature of the phonon modes [65].

The second derivatives of energy, $C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right)$ make up the interatomic force constant matrix (IFC). The desired phonon modes are the solutions to the eigenvalue problem in reciprocal space through a fourier transform,

$$\sum_{\kappa'\beta} D_{\kappa\alpha,\kappa'\beta}(\vec{q}) U_{m,\kappa'\beta}(\vec{q}) = \omega_{m\vec{q}}^2 U_{m,\kappa\alpha}(\vec{q}) \quad (3.9)$$

where $\vec{q}$ is the phonon vector corresponding to the eigenfrequency at mode m , $\omega_{m\vec{q}}$ and the dynamical matrix,

$$D_{\kappa\alpha,\kappa'\alpha'}(\vec{q}) = \frac{1}{\sqrt{m_\kappa m_{\kappa'}}} \sum_b \tilde{C}_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\vec{q} \cdot \vec{R}_b} \quad (3.10)$$

is the mass normalised fourier transform of the IFC matrix. For a primitive unit cell containing N atoms (labelled κ with mass m_κ), this is a $3N \times 3N$ hermitian matrix for each wavevector. Solving the eigenvalue equation yields $3N$ phonon branches, and the phonon dispersion curve is the relationship between the frequency of these branches with respect to the wavevectors. When multiple types of atoms are involved, curves at higher frequencies correspond to optical modes, where adjacent atoms move in opposition, while lower frequency curves correspond to acoustic modes, where atoms move in unison. Acoustic vibrations are long in wavelength and thus have much higher penetration depth compared to the optical phonons, which are more localized [66]. Figure 3.2 shows the phonon dispersion of NaCl along the high symmetry path $\Gamma \rightarrow R$ in reciprocal space. At these high symmetry k-points, the number of distinct eigen-modes is reduced due to degeneracy and the curves converge to produce a less convoluted graph, convenient for experimental comparisons. This convergence of dispersion curves can be easily seen in for example near the Γ point of Fig. 3.2.

An important aspect regarding all theoretical considerations is that thermal effects at non-zero temperature are neglected in the harmonic approximation [64]. The inclusion of thermal and other anharmonic effects can help better predict physical properties such as vibrational frequencies, thermal conductivity [67] and band gaps [68], but the harmonic approximation is often sufficiently adequate to probe the vibrational modes of interest. This also justifies neglecting terms higher than first order derivatives in the expansion of intrinsic and induced dipole moments in the derivation of IR, Raman and ultra-low loss EELS.

3.2.3 *Low loss EELS*

One can divide the literature study of low loss EELS in terms of classical and quantum treatment of the electron source and the target. Ritchie [69] was the first to derive a general energy loss in which everything was considered classical. Retardation effects were neglected, i.e. the electron-sample interaction was treated as instantaneous. If the incident electron speed is a substantial fraction of that of light, retardation effects become prominent [70]. As a result, the range of interaction increases and energy modes become red-shifted [71]. As for the target specimen, Enchenique *et al* [72] derived a general quantum mechanical expression for the energy loss of electrons interacting through direct impact with spherical and planar sample geometries. It was then shown by Ritchie and Howie [73] that the quantum and classical interpretations of EELS converge to the same result if one is able to collect all the inelastically scattered signals. Further effort has been put into both the classical and quantum treatment of interactions between collective effects (plasmons) and optical phonons with the incident electron beam. These are again theoretical circumstances where electrons have direct collisions with the target [70,74–76], thus

focus is placed on interactions with the nuclear rather than electronic subsystems.

In the aloof beam mode, long-range dipole interactions dominate [77]. [Part II](#) delves into the details of both the current semi-classical and quantum treatments used in literature. In [Chapter 6](#), we provide a new, analytically derived method of calculating aloof beam EELS and also review how it fits in with the concurrent theoretical landscape of the quantum dipole formalism in [Section 6.6](#).

3.2.4 LO-TO splitting

There are two different types of optical phonons modes: transverse (TO) and longitudinal (LO). In the former (latter) mode, the poly-atom motions are perpendicular (parallel) to the direction of phonon propagation (i.e. $\vec{q}$ vector). The two modes are degenerate (have the same frequency) as predicted by symmetry considerations. However, LO-TO splitting occurs near the Brillouin zone centre, where degeneracy is broken between the LO and TO modes [78]. As the atoms move, dipoles are created due to charge displacement and hence an induced electric field, $\vec{E}$. For LO modes, the induced field is parallel to the propagation vector and hence the two can interact, $\vec{q} \cdot \vec{E} \neq 0$, to produce a restoring force and hence shift the LO frequencies upwards [79]. At $\vec{q} = \vec{0}$, the dielectric response of the material is important in determining the splitting. This will alter the final electron energy loss and thus, it's important to take this phenomenon into account when considering the sensitive, ultra low energy phonon excitations.

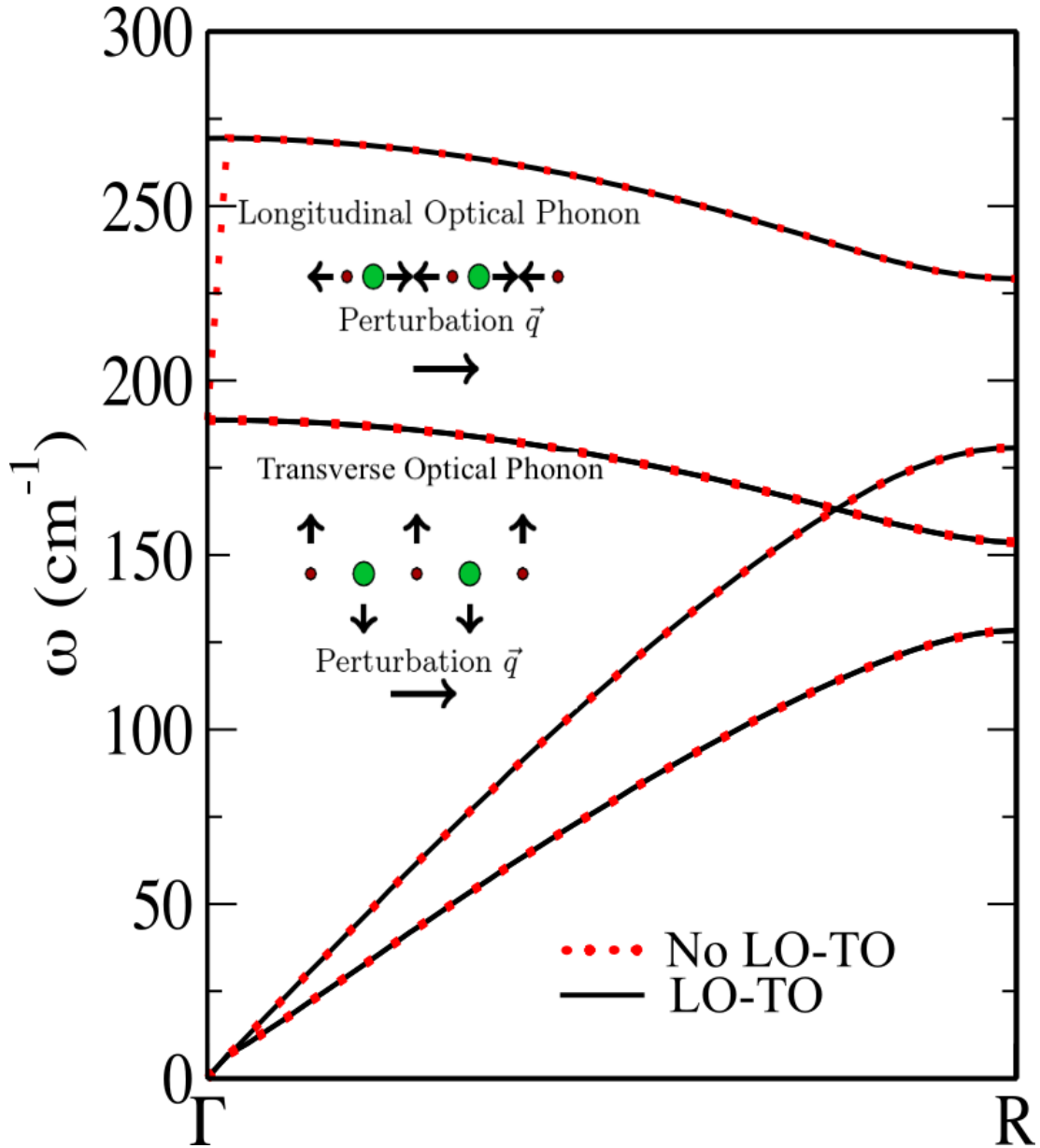


Figure 3.2: Phonon dispersion curve along a high symmetry path $\Gamma \rightarrow R$ for cubic NaCl. The optical modes converge at the Γ point when LO-TO splitting is turned off, as depicted by the red dotted line. As depicted pictorially, the LO-mode energies are upshifted (top band) as they couple with the perturbing $\vec{q}$ wavevector compared to the TO modes (second band).

More specifically, the LO-TO splitting phenomenon is described by a 'non-analytic' contribution to the force constant matrices due to these long-ranged electrostatic interactions. At the non-analytic Γ point, there is no single limit to the value of the force constant matrix which means that in a general polar material, this contribution is dependent on the direction in which one

approaches the Γ point. Imagine an anisotropic material undergoing a long wavelength optical phonon mode. The positive charges and negative charges move out of phase from each other, creating a macroscopic oscillating electric field. The strength of this field is heavily dependent on the viewing direction.

3.3 THE MANY-BODY PROBLEM

In attempting to accurately and quantitatively describe the behaviour of any material at the subatomic level, one will inevitably be faced with the many body problem [80]. All quantum systems are governed by the Schrödinger equation,

$$H |\psi\rangle = E |\psi\rangle \quad (3.11)$$

with a hamiltonian H energy E . The Hamiltonian can be generally written as

$$H = -\frac{\hbar^2}{2m_j} \sum_j \nabla_j^2 - \frac{\hbar^2}{2m_l} \sum_l \nabla_l^2 - \frac{1}{4\pi\epsilon_0} \left[\frac{1}{2} \sum_{j,l} \frac{Z_l e^2}{|\vec{r}_j - \vec{R}_l|} + \frac{1}{2} \sum_{l,l'} \frac{Z_l Z_{l'} e^2}{|\vec{R}_l - \vec{R}_{l'}|} + \frac{1}{2} \sum_{j,j'} \frac{e^2}{|\vec{r}_j - \vec{r}_{j'}|} \right], \quad (3.12)$$

where the index j, j' and l, l' run over the electrons (with mass m_j) and nuclei (with mass m_l) respectively. One commonly adopts the Born Oppenheimer approximation, which separates the nuclear and electronic wavefunctions, by fixing the nuclear positions as the ionic mass is much larger than that of the electron. Thus one can ignore the second and fourth term in Eq. (3.12), dropping the terms only dependent on nuclear coordinates to form the many-electron hamiltonian. In a system of N electrons, the wavefunction is dependent on the $3N$ translational degrees of freedom defined by the electrons' positions. We would need M^{3N} many numbers to describe the discretised wavefunction on a grid of M points. For a simple compound such as graphene, with two atoms per unit cell, if we wanted to use a 3D grid of 10^3 points, it will need to store

3.4 HARTREE-FOCK APPROXIMATION

on the order of 10^{18} numbers, which is an incredible, unfeasible amount of information. Solving the total interacting hamiltonian is only possible for very small systems, and approximations must be made to tackle the exponential scaling problem.

3.4 HARTREE-FOCK APPROXIMATION

An early approach to tackling the many-electron problem is the Hartree-Fock (HF) method [81, 82]. Here, the Hamiltonian of a system of N interacting electrons in $3N$ -dimensions is rewritten as a series of N 3D single-electron Hamiltonians (with single electron wavefunctions ϕ_i) [83]

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_n(\vec{r}) + V_H(\vec{r}) \right] \phi_i(\vec{r}) + \int d\vec{r}' V_X(\vec{r}, \vec{r}') \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (3.13)$$

where $V_n(\vec{r})$ is the electron-nuclear Coulomb repulsion. The electron is also subject to two more potential terms. The former Hartree potential, $V_H(\vec{r})$, arises from the mean field approximation, is the averaged potential contribution due to the rest of the electrons. It is formally the solution to Poisson's equation

$$V_H(\vec{r}) = \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (3.14)$$

where $n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$ is the averaged charge density. However, V_H is not enough to fully account for the electron-electron interactions. Thus, the Fock exchange non-local potential $V_X(\vec{r}, \vec{r}')$ is needed. The V_H potential and electronic charge density depends on the single-electron wavefunctions, which is what Eq. (3.13) attempts to solve for. This can be solved through a self-consistent method, which requires a guesstimate for the initial wavefunction, solving the corresponding Schrödinger equations and iteratively obtain a new set of solutions until convergence is achieved. The HF method allows for the

total wavefunction of N electrons to be written as a Slater determinant [82,84]

$$\psi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \dots & \phi_N(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \dots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_N) & \phi_2(\vec{r}_N) & \dots & \phi_N(\vec{r}_N) \end{vmatrix} \quad (3.15)$$

which satisfies fermionic anti-symmetry requirements upon exchange. The only term that is not included so far is the non-classical electron-electron correlation stemming from the Coulomb interaction that is not captured in the V_H and V_X potentials. The insufficiency of electron correlation included in the Hartree-Fock mean field approach leads to failure to perform well in areas such as describing complexes of D block elements [85] and thermochemistry [86].

3.5 DENSITY FUNCTIONAL THEORY

3.5.1 Hartree Fock and Kohn-Sham equations

The HF method using Slater determinants is not enough to capture the desired exact interacting system. This chapter introduces the framework which rigorously connects the single-particle electron densities to the full many-body one, density functional theory (DFT).

A powerful theorem that underpins DFT is the seminal theorem by Hohenberg and Kohn [87], which states that the ground state energy E_g is a functional of only the electron charge density, $n(\vec{r})$,

$$E_g = F[n(\vec{r})]. \quad (3.16)$$

This is only a function of $\vec{r}$, as opposed to the total wavefunction, $\psi(\vec{r}_1, \dots, \vec{r}_N)$, a function of the coordinates of all the electrons. The theorem proves the existence of a universal functional for all quantum systems, but its exact form is unknown. The most widely used method to construct this functional is given by the Kohn Sham scheme [88], which expands Eq. (3.16) as

$$E = \int d\vec{r} n(\vec{r}) V_n(\vec{r}) - \sum_i \int d\vec{r} \phi_i^*(\vec{r}) \frac{\hbar^2}{2m_e} \nabla^2 \phi_i(\vec{r}) + \frac{1}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{XC}[n(\vec{r})] \quad (3.17)$$

The first three terms are the familiar electron nuclear external potential, single electron kinetic and Hartree energies discussed earlier, which come from independent single electron Hamiltonians. Everything else unaccounted for in the Coulomb interaction is lumped together to form last term, called the exchange-correlation ((XC)) energy, $E_{XC}[n(\vec{r})]$. One can impose that the solutions ϕ_i form an orthonormal set, as well as the Hohenberg-Kohn variational principle,

$$\left. \frac{\delta F[n]}{\delta n} \right|_{n=n_0} = 0 \quad (3.18)$$

which formally establishes that the ground state density n_0 minimises the total energy. This finally leads to the Kohn-Sham equations,

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_n(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (3.19)$$

where $V_{XC}(\vec{r}) = \left. \frac{\delta E_{XC}[n(\vec{r})]}{\delta n} \right|_{n(\vec{r})}$ is the exchange correlation potential. There is an immense amount of work dedicated to formulating accurate and general correlation functionals. The simplest approximation of this functional is the local density approximation (LDA) [87], where the electron's XC energy depends only on the local density of a homogeneous electron gas. This method

works well for systems with slow density variations, but its inadequacies such as the lack of treatment for self-interaction often causes overbinding.

The large body of work put into constructing XC functionals [89] can be summarised as Jacob's Ladder [90], where consecutive rungs depict increasing complexity. Each rung leading further up the ladder builds on top of that of the lower rungs, but we will restrict ourselves to the first three. The lowest rung consists of the LDA approximation. The functionals populating the second rung is governed by the generalised gradient approximation, where E_{XC} depends on the both the charge density and its gradient, $\nabla\rho(\vec{r})$. This leads to notable improvements over LDA, and a very successful GGA is the Perdew-Burke-Ernzerhof (PBE) functional [91,92], which will be featured extensively in Part III and Part IV. The laplacian of the density naturally follows in the third meta-GGAs rung, but can also contain other local properties such as the orbital kinetic energy $|\nabla\psi|^2$ for wavefunction ψ used in rSCAN [93]. This ladder is depicted in Fig. 3.3

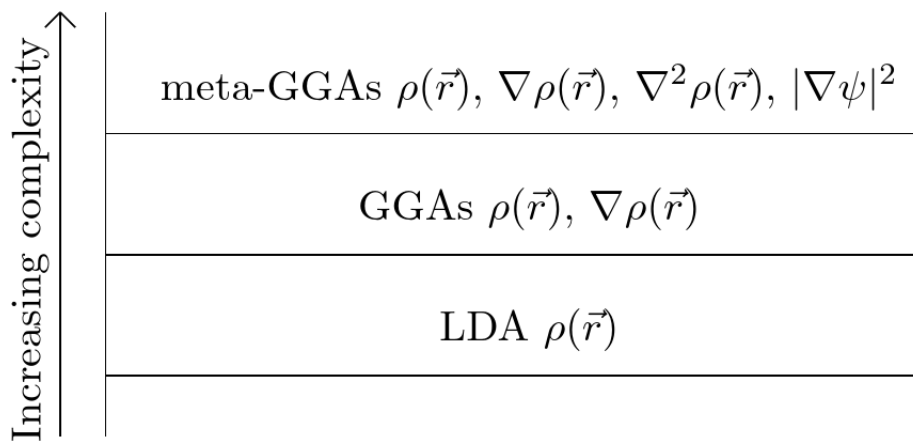


Figure 3.3: Schematic of the first three rungs of Jacobs ladder, where with increasing complexity, more derivatives of the charge density is added to the exchange correlation energy functional.

The Hartree and XC potentials in the KS Hamiltonian depends on $\rho(\vec{r})$, which in turn depends on the wavefunctions $\phi_i(\vec{r})$. Therefore in practice, this circular dependence means that the KS equations must be solved self-

consistently. An initial guesstimate of $n(\vec{r})$ is made such that the relevant potentials can be computed. This is then used to solve Eq. (3.19) to produce a new charge density. If the difference between the old and new charge densities does not fall within the tolerance threshold, the procedure is repeated, otherwise it stops and the ground state is effectively attained.

All-electron wavefunctions have high oscillatory behaviours near the core. This is because core electrons are highly localised, and thus valence states must also oscillate quickly in order to fulfil the mutually orthogonal condition of the eigenstates. This behaviour gives it a high kinetic energy near the core, and balances out some of the Coulomb repulsion, making valence electrons less tightly bound. This is difficult to reproduce with a small number of Fourier components using a plane-wave basis set. However, only the valence charge density which participates in chemical bonding is desirable. Thus, it is common to use pseudopotentials, which replaces the oscillatory core region with a slower varying function and is identical to the all-electron wavefunction outside of some radius, R_c [94] (see schematic in Fig. 3.4). The number of Fourier components required to build an accurate pseudopotential determines its hardness. The earliest forms are called norm-conserving pseudopotentials [94], which has a fitting requirement that the squared amplitude integrals of the pseudopotential must equal to that of the full wavefunction. Vanderbilt [95] later suggested for this condition to be relaxed, leading to a dramatic reduction of cut-off energy needed, leading to the era of ultrasoft pseudopotentials.

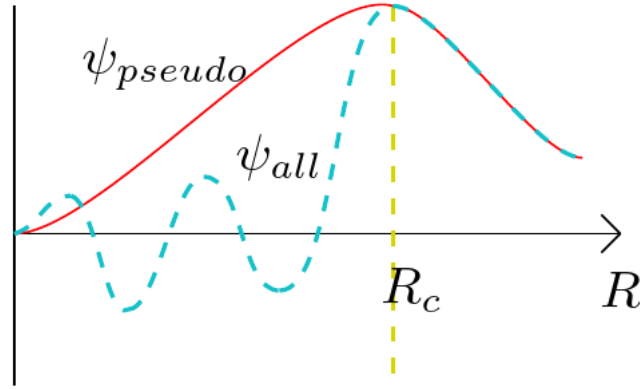


Figure 3.4: Schematic of a generic pseudopotential wavefunction compared to the all-electron wavefunction. The two match for $R > R_c$.

DFT is essential for calculating material properties we require in later chapters, such as nuclear magnetic resonance (NMR) and vibrational spectroscopy parameters.

3.5.2 Vibrational spectroscopy

The objective is to construct the dynamical matrix Eq. (3.10) by calculating the second derivatives of total energy. This can be achieved numerically through either finite displacement or linear perturbation (density functional perturbation theory (DFPT)). The former uses the central-difference finite difference method to calculate the IFC matrix,

$$\left(\frac{\partial^2 E}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b} \right) \approx \frac{F_{\kappa\alpha}^+ - F_{\kappa\alpha}^-}{2u} \quad (3.20)$$

where τ is the displacement of atom κ' along direction α or β by a small distance of $\pm u$. This method is general and works for any system, but is only valid for a Γ -point perturbation $\vec{q} = \vec{0}$. This is because in Eq. (3.10), the IFC matrix requires contributions of interactions from atoms from all other primitive unit cells. However, the forces between atoms are short-ranged so

one can decide a "cut-off" radius such that interactions outside this range is effectively zero. Thus a phonon with wavevector not at the Γ point (i.e. non-commensurate with the unit cell) cannot be computed with finite difference unless one creates a supercell large enough to construct a reasonable IFC matrix. This naturally leads to high computational costs, where sampling a $\vec{q}$ -grid of $n_1 \times n_2 \times n_3$ requires supercells of exactly that size. A widely used procedure to reduce this cost by orders of magnitude is the non-diagonal supercell method [96]. This technique uses less primitive cells (by capitalising on having non-zero diagonal elements in the supercell construction matrix) that are mathematically equivalent to the maximum $n_1 \times n_2 \times n_3$ supercell are constructed.

The perturbative method, on the other hand, is an analytical method that solves the Sternheimer equation [97], given by

$$(\hat{H}^{KS} - \epsilon_m) |\phi_m^1\rangle = -P_{\text{unocc}} v^1 |\phi_m^0\rangle \quad (3.21)$$

for the first order Kohn-Sham orbitals $|\phi_m^1\rangle$ at phonon mode m , which is the linear response to a perturbation such as an electric field or atomic displacements. ϵ_m is the energy of the unperturbed KS state $|\phi_m^0\rangle$, P_{unocc} is the projector onto the unoccupied states and v^1 is the first order change in KS potential [64]. This has to be solved using the self-consistency method because the first order potential depends on the first order charge density. DFPT, if implemented, is powerful as it can compute the system response at an arbitrary wave-vector. However, the numerical implementation is more problematic. Additional terms are required when coupled with the widely used ultra-soft pseudo-potentials in order to quench issues arising with orbital orthogonality and norm conservation requirements [62].

3.5.3 *Dispersion corrections*

We are primarily focusing on molecular crystals, which make up the majority of pharmaceutical products. These are usually organic, hydrogen bonded with non-negligible van der Waals (vdW) effects [98]. These are long range interactions and is not considered by many XC functionals (which mainly consider local effects) [99]. As a workaround, there are common dispersion corrections terms (pairwise/beyond-pairwise long-range interactions) that are added to the DFT exchange correlation energy.

Intermolecular bonding will alter electron density distributions and hence bond lengths restoring forces on displaced atoms. It is particularly challenging to treat vdW dispersions for molecular crystals and this is compounded by the fact that crystal polymorphs often occur in very small energy ranges, making them difficult to order [100]. However, there has been a lot of theoretical and experimental work put into studying vdW forces in specific systems such as solid benzene, thus greatly improving the confidence of the DFT results [101, 102].

Due to the challenging nature to reliably describe these effects and the importance of chemical bonding in ultra low-loss EELS, it is important during simulations to consider the relative weight of the errors that dispersion corrections introduce, and to compare the outcomes of different dispersion correction schemes for the system in question.

Part II

THEORY OF ULTRA-LOW LOSS EELS

SEMI-CLASSICAL THEORY

A semi-classical theory is often used in literature [55, 103, 104] to simulate ultra-low loss EELS spectra in the aloof beam mode. Here, from a macroscopic viewpoint, the thin sample is assumed to be a linear, continuous medium, and is treated as a dielectric slab characterised by the dielectric tensor $\epsilon(\vec{k}, \omega)$; whereby $\vec{k}$ is the momentum exchange/scattering vector and ω the frequency corresponding to the energy-loss. It is important to understand how the approximations used in the derivation affect the outcome and validity. That being so, we can then appropriately simulate the spectrum for the β -guanine molecular crystal, for which there are aloof beam ultra-low loss EELS experimental results in literature [54].

The electron beam in high-voltage (S)TEM require a relativistic treatment as the electrons with energies around 200keV correspond to $\gamma \sim 2.1$ or $\frac{v}{c} \sim 0.88$, where retardation effects are not insignificant as the electrons are comparable to the speed of light in the medium. This relativistic treatment requires solving the full Maxwell's equations and lead to radiative energy losses such as Cherenkov radiation and has been considered by Gardian *et al.* [105]. Because we are considering the aloof beam, ultra-low energy loss regime, we will use the non-retarded approximation in the derivation of the energy loss, whereby the delay in the electron-sample interaction signal is neglected. This is because not only does will the electron beam not impact the sample (thus no radiation effects in the local vicinity of the swift electrons), the electron beam operates at a much lower energy around 30-60 keV [54, 106, 107]. A quick back of the envelope calculation for a 60 keV electron beam gives a $\frac{v}{c} \sim 0.48$, and for an example molecular crystal we've calculated in section 11.1, the electronic

4.1 ELECTRON PASSING THROUGH HOMOGENEOUS MEDIA

dielectric tensor ϵ^∞ has the property $\frac{1}{3}\text{Tr}(\epsilon^\infty) \sim 3.24$, which gives a speed of light in the medium at $\frac{v}{c} = \frac{1}{\sqrt{\epsilon^\infty}} \sim 0.56$.

More importantly, a relativistic treatment is needed when the imaginary part of the dielectric function becomes very close to zero [103, 108–110]. As one will see in part IV, this is not the case for the molecular crystal dielectric tensors at the vibrational modes under consideration. We thus consider the non-retarded, classical dielectric formalism in this chapter, effectively treating the speed of light as $c \rightarrow \infty$. As an electron moves through a medium, it can be treated as an evanescent wave source which induces an electric field. This induced field then acts to push back and slows down the original electron. In the following sections we explore the classical dielectric formalism in obtaining the electron's energy loss.

4.1 ELECTRON PASSING THROUGH HOMOGENEOUS MEDIA

Here, we follow the dielectric formalism by Ritchie [69] where he considers the interaction between fast electron beam and electrons residing in a metallic medium characterised by the dielectric tensor $\epsilon(\vec{k}, \omega)$ where the frequency ω and momentum vector $\vec{k}$ are electromagnetic perturbations. The dielectric tensor describes the macroscopic proportionality relationship between the displacement electric field that results in an insulator from an externally applied electric field. Several other authors have used the dielectric approach before, such as Fermi [111] and Kramers [112] when considering how much stopping power a material has against incoming fast charged particles. However these methods considered only the frequency dependence of ϵ , neglecting $\vec{k}$ from the perturbation.

We will first flesh out Ritchie's derivation of the electron's energy loss as it passes through the medium and then adapt the theory in section 4.2 to

the case of aloof beam EELS by introducing a new flat surface at an impact parameter/grazing distance.

The convention used for the Fourier and inverse Fourier transforms in future derivations between the $(x, t) \leftrightarrow (k, \omega)$ domains are (for real space function $f(t)$ or $f(x)$)

$$\begin{aligned} f(t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \hat{f}(\omega) \exp i\omega t \leftrightarrow \hat{f}(\omega) = \int_{-\infty}^{\infty} dt f(t) \exp(-i\omega t) \\ f(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \hat{f}(k) \exp ikx \leftrightarrow \hat{f}(k) = \int_{-\infty}^{\infty} dx f(x) \exp(-ikx) \end{aligned} \quad (4.1)$$

Consider an electron as a point charge with velocity $\vec{v}$ traveling in a straight line along the x-axis (and set $y = z = 0$ without loss of generality). Its charge density is given by $\rho(\vec{r}, t) = -e\delta(\vec{r} - \vec{v}t)$ with position vector $\vec{r}$. It is subject to Poisson's equation such that the electric potential $\psi(\vec{r}, t)$ satisfies [69] (Note that Ritchie uses gaussian units whereas this thesis uses SI units to explain the difference in factors of 4π)

$$\epsilon_0 \epsilon(\vec{k}, \omega) \nabla^2 \psi(\vec{r}, t) = e\delta(\vec{r} - \vec{v}t) \quad (4.2)$$

where $\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}$ where $\hat{x}, \hat{y}, \hat{z}$ are the coordinate system unit vectors. Using the property that

$$\mathcal{F}\left(\frac{df(t)}{dt}\right)(\omega) = i\omega \mathcal{F}(f(t))(\omega) \quad (4.3)$$

where $\mathcal{F}$ denotes the fourier transform, we transform equation 4.2 into

$$\mathcal{F}[\epsilon_0 \epsilon(\vec{k}, \omega) \nabla^2 \psi(\vec{r}, t)] = \int dt \int d\vec{r} e \delta(\vec{r} - \vec{v}t) \exp(-i(\vec{k} \cdot \vec{r} + \omega t)) \quad (4.4)$$

$$\begin{aligned} -\epsilon_0 k^2 \epsilon(\vec{k}, \omega) \psi(\vec{k}, \omega) &= e \int dt \int dx \int dy \int dz \delta(x - vt) \delta(y = 0) \delta(z = 0) \\ &\quad \times \exp(-i(k_x x + \omega t)) \exp(-ik_y y) \exp(-ik_z z) \end{aligned} \quad (4.5)$$

$$= e \int dt \int dx \delta(x - vt) \exp(-i(k_x x + \omega t)) \quad (4.6)$$

$$= e \int dt \exp(it(k_x v + \omega)) \quad (4.7)$$

$$= -(2\pi) e \delta(k_x v + \omega) \quad (4.8)$$

$$\rightarrow \psi(\vec{k}, \omega) = -\frac{2\pi e}{\epsilon_0 \epsilon(\vec{k}, \omega) k^2} \delta(k_x v + \omega), \quad (4.9)$$

Finally for completeness, we let $k_x v = \vec{k} \cdot \vec{v}$ and also explicitly state the frequency and momentum dependence of the dielectric tensor, $\epsilon(\omega, \vec{k})$.

$$\psi(\vec{k}, \omega) = -\frac{2\pi e \delta(\vec{k} \cdot \vec{v} + \omega)}{\epsilon_0 \epsilon(\omega, \vec{k}) k^2} \quad (4.10)$$

4.2 ELECTRON GRAZING HOMOGENEOUS FLAT SURFACES

Equipped with the electron's electric potential $\psi(\vec{k}, \omega)$, we now consider the aloof beam setup in Fig. 4.1 and derive the electron energy loss spectrum.

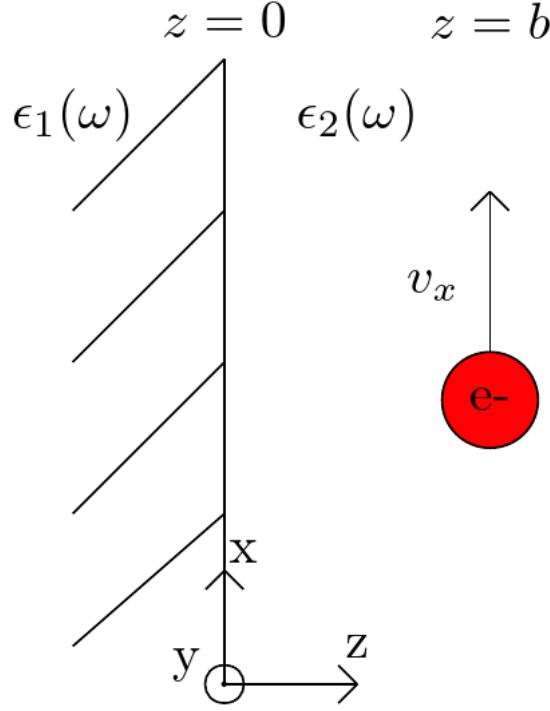


Figure 4.1: Geometry of aloof beam setup where a fast incident electron is grazing the dielectric medium at an impact parameter of b .

There are several authors who have considered this setup and published the analytical energy loss in a general manner [104, 109, 113, 114]. Here we follow a similar setup to that of Batson [113, 114], flesh out all of the details and arrive at an analytical loss equation pertaining to the geometry of Fig. 4.1.

We have encountered how to obtain the electron's electric potential in the previous section. Thus with the coordinates of this setup, $\vec{v} = \begin{bmatrix} v_x \\ 0 \\ 0 \end{bmatrix}$ and we can modify Eq. (4.10) to become ¹

$$\psi(\omega, \vec{k}) = -\frac{2\pi e}{\epsilon_0 \epsilon(\omega, \vec{k})} \frac{1}{k_{\perp}^2 + \frac{\omega^2}{v^2}} \frac{\delta(k_x + \frac{\omega}{v})}{v} \quad (4.11)$$

where $k_{\perp}^2 = k_y^2 + k_z^2$ is the momentum transfer perpendicular to the electron motion.

¹ using the property $\delta(ax) = \frac{\delta(x)}{|a|}$ and $k_x = \frac{\omega}{v}$.

As there is a change in the medium at the surface $z = 0$ separating the two dielectrics, we must consider surface excitations in addition to the bulk modes encapsulated in Eq. (4.11). The potential along the z -direction should have a decaying form, and we can obtain the form of this decay by considering that at the surface, one must obey the homogeneous Laplace's equation $\nabla^2\psi = \frac{1}{\psi_x} \frac{d^2\psi_x}{dx^2} + \frac{1}{\psi_y} \frac{d^2\psi_y}{dy^2} + \frac{1}{\psi_z} \frac{d^2\psi_z}{dz^2} = 0$ (as we are considering energy losses outside the volume containing the fast electron charge density source). Assuming the total wavefunction is separable and of the form $\psi = \psi_x(x)\psi_y(y)\psi_z(z)$, we arrive at the three equations $\frac{1}{\psi_i} \frac{d^2\psi_i}{di^2} = j^2$ for $i = x, y, z$ and constants $j = \xi, \sigma, \beta$ where $\xi^2 + \sigma^2 + \beta^2 = 0$. Intuitively, the potential should decay along the z -axis as it hits the surface, whilst along the x and y -directions in free space we have oscillatory behaviours such that $\xi = ik_x, \sigma = ik_y$. Consequently, we have $\beta = \sqrt{k_x^2 + k_y^2}$ for the surface solution of the form

$$\psi(z) \propto e^{\pm\beta z} \quad (4.12)$$

As the full solution to the potential is a function of the z -coordinate, we take the fourier transform of the bulk solution (Eq. (4.11)) with respect to k_z in order to pull out this z -dependence. For an electron located at $z = b$,

$$\begin{aligned} \psi(\omega, k_x, k_y, z) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi(\omega, \vec{k}) \exp(ik_z(z-b)) dk_z \\ &= -\frac{1}{2\pi} \int_{-\infty}^{\infty} dk_z \frac{2\pi e}{v\epsilon_0\epsilon} \frac{1}{k_z^2 + k_y^2 + \frac{\omega^2}{v^2}} \delta(k_x + \frac{\omega}{v}) \exp(ik_z(z-b)) \end{aligned} \quad (4.13)$$

where k_x is replaced by $-\frac{\omega}{v}$. The fourier transform gives (see Appendix D.1 for derivation)

$$\int_{-\infty}^{\infty} \frac{e^{ik_z|z-b|}}{k_x^2 + k_y^2 + k_z^2} dk_z = \frac{\pi \exp(-\sqrt{k_x^2 + k_y^2}|z-b|)}{\sqrt{k_x^2 + k_y^2}} \quad (4.14)$$

Thus we've extracted the z -dependence of the electron's electric potential of Eq. (4.10) to get

$$\psi(\omega, k_x, k_y, z) = \frac{e}{v\epsilon_0\epsilon} \delta(k_x + \frac{\omega}{v}) \frac{\pi \exp(-\sqrt{k_x^2 + k_y^2})|z - b|}{\sqrt{k_x^2 + k_y^2}} \quad (4.15)$$

$$= \frac{2\pi e}{v\epsilon} \delta(k_x + \frac{\omega}{v}) \frac{\exp(-\sqrt{k_x^2 + k_y^2})|z - b|}{2\sqrt{k_x^2 + k_y^2}} \quad (4.16)$$

$$= \frac{V_k}{\epsilon} H(z - b) \quad (4.17)$$

where we've defined

$$V_k = \frac{2\pi e \delta(k_x + \frac{\omega}{v})}{v\epsilon_0} \quad (4.18)$$

and

$$H(z - b) = \frac{\exp(-\sqrt{k_x^2 + k_y^2})|z - b|}{2\sqrt{k_x^2 + k_y^2}} = \frac{\exp(-\beta|z - b|)}{2\beta} \quad (4.19)$$

which matches that by Batson [115], which describes a one-dimensional scattering function.

Finally, the full solution on the fast electron side is a linear combination of the bulk and surface solutions from Eq. (4.17) and 4.12 is

$$\psi(z, \omega, \vec{k}) = A \frac{V_k}{\epsilon} H(z - b) + B \exp(-\beta z) \quad (4.20)$$

for constants A and B . We assume that the electron is traveling in vacuum, so that for the side $z > 0$, $\epsilon = \epsilon_0 = 1$, the permittivity of free space.

On the specimen side, we have to incorporate the dielectric tensor, which relates the displacement field $\vec{D}$ that is set up in a material due to an external electric field $\vec{E}$ such that $\vec{D} = \epsilon \vec{E}$

$$\epsilon = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} \quad (4.21)$$

and solve Poisson's equation (no source) whereby the wavefunction is again written as the fourier transform (to get z-dependence)

$$\begin{aligned} \psi(\vec{r}, t) &= \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} d\omega \int dk_x dk_y \psi(z, \omega, \vec{k}) e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} \\ &\rightarrow \nabla \cdot \bar{\epsilon} \nabla (\psi(z, \omega, \vec{k}) e^{i(\vec{k}_{xy} \cdot \vec{\rho} + \omega t)}) = 0 \end{aligned} \quad (4.22)$$

where $\vec{k}_{xy} = \begin{bmatrix} k_x \\ k_y \\ 0 \end{bmatrix}$ and $\vec{\rho} = \begin{bmatrix} x \\ y \\ 0 \end{bmatrix}$. Also, let $\epsilon_{\rho\rho} = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} \\ \epsilon_{yx} & \epsilon_{yy} \end{bmatrix}$ and $\epsilon_{\rho z} = \begin{bmatrix} \epsilon_{xz} \\ \epsilon_{yz} \end{bmatrix}$.

Thus we solve

$$\nabla \cdot \bar{\epsilon} \left(\begin{bmatrix} 0 \\ 0 \\ \frac{d\psi}{dz} \end{bmatrix} e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} + i\psi \begin{bmatrix} k_x \\ k_y \\ 0 \end{bmatrix} e^{i(\vec{k} \cdot \vec{\rho} - \omega t)} \right) \quad (4.23)$$

$$\begin{aligned} &= e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} \nabla \cdot \begin{bmatrix} \epsilon_{xz} \frac{d\psi}{dz} \\ \epsilon_{yz} \frac{d\psi}{dz} \\ \epsilon_{zz} \frac{d\psi}{dz} \end{bmatrix} + i \begin{bmatrix} k_x \\ k_y \\ 0 \end{bmatrix} \cdot \bar{\epsilon} \begin{bmatrix} 0 \\ 0 \\ \frac{d\psi}{dz} \end{bmatrix} e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} \\ &+ i \begin{bmatrix} 0 \\ 0 \\ \frac{d\psi}{dz} \end{bmatrix} \bar{\epsilon} \begin{bmatrix} k_x \\ k_y \\ 0 \end{bmatrix} e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} - \psi \vec{k} \cdot \bar{\epsilon} \vec{k} e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} \\ &= e^{i(\vec{k} \cdot \vec{\rho} + \omega t)} \left[\epsilon_{zz} \frac{d^2\psi}{dz^2} + 2i\epsilon_{\rho z} \vec{k} \frac{d\psi}{dz} - \vec{k} \cdot \epsilon_{\rho\rho} \cdot \vec{k} \psi \right] = 0 \end{aligned} \quad (4.24)$$

The solutions to Eq. (4.24) are of the form $\phi = Ce^{\gamma z}$ for a constant C and $\gamma = \frac{1}{2\epsilon_{zz}} \left(2i\vec{k} \cdot \epsilon_{\rho z} \pm \sqrt{-4(\vec{k} \cdot \epsilon_{\rho z})^2 + 4\epsilon_{zz}(\vec{k} \cdot \epsilon_{\rho\rho} \vec{k})} \right)$. Assuming the dielectric tensor is diagonal and of the form

$$\epsilon(\omega) = \begin{bmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{bmatrix} \quad (4.25)$$

such that we are operating in a coordinate system where polarisation is linear along the direction of the applied field, this simplifies γ to

$$\begin{aligned} \gamma &= \frac{1}{\epsilon_{zz}} \sqrt{\epsilon_{zz} \begin{bmatrix} k_x & k_y \end{bmatrix} \begin{bmatrix} \epsilon_{xx} & 0 \\ 0 & \epsilon_{yy} \end{bmatrix} \begin{bmatrix} k_x \\ k_y \end{bmatrix}} \\ &= \frac{1}{\epsilon_{zz}} \sqrt{\epsilon_{zz}(k_x^2 \epsilon_{xx} + k_y^2 \epsilon_{yy})} \end{aligned} \quad (4.26)$$

since $\epsilon_{\rho z} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$. The full solution on the $z < 0$ specimen side should also be a combination of bulk and surface modes. Thus the solutions to the electric potential in the xy -plane are

$$\psi(z > 0) = \frac{V_k}{\epsilon_{vacuum}} H_1(z - b) + B \exp(-\beta z) \quad (4.27)$$

$$\psi(z < 0) = C \frac{V_k}{\epsilon_{dielectric}} H_2(z - b) + D \exp(\gamma z) \quad (4.28)$$

with constants B, C and D . $\epsilon_{vacuum} = 1$, $H_1(z - b)$ and $H_2(z - b)$ are of the form

$$H_n(z - b) = \frac{1}{2\chi_n} \exp(-\chi_n(z - b)) \quad (4.29)$$

where $\chi_1 = \beta$ on the vacuum side and $\chi_2 = \gamma$ on the specimen side. The constants are found by imposing the boundary conditions where ψ and its derivative $\epsilon \frac{\partial \psi}{\partial z}$ are continuous $z = 0$, and ψ must be finite at $\pm\infty$.

The former condition gives

$$\begin{aligned} H_1(z) &= \frac{1}{2\beta} \exp(-\beta z) \\ H_2(z) &= \frac{1}{2\gamma} \exp(-\gamma z) \end{aligned} \quad (4.30)$$

and the latter gives

$$B = -\frac{\gamma}{\beta} \epsilon_{dielectric} D \quad (4.31)$$

$$1 = C \frac{\exp(-\gamma|b|)}{\exp(-\beta|b|)} \quad (4.32)$$

Putting together Eq. (4.18), Eq. (4.26), Eq. (4.28), Eq. (4.30), Eq. (4.31) and Eq. (4.32) we arrive at

$$D = \frac{1}{2} V_k \exp(-\beta|b|) \frac{1}{\gamma \epsilon_{\text{dielectric}}} \left[\frac{\sqrt{\epsilon_{zz}(k_x^2 \epsilon_{xx} + k_y^2 \epsilon_{yy}) / \beta - 1}}{\sqrt{\epsilon_{zz}(k_x^2 \epsilon_{xx} + k_y^2 \epsilon_{yy}) / \beta + 1}} \right] \quad (4.33)$$

Since γ is really the reciprocal vector along the z-direction, it will just bring out the ϵ_{zz} component of the dielectric tensor such that $\gamma \cdot \epsilon_{\text{dielectric}} = \sqrt{\epsilon_{zz}(k_x^2 \epsilon_{xx} + k_y^2 \epsilon_{yy})}$. We retrieved in the square brackets in Eq. (4.33) what Radtke *et al.* [55] defined as the polarisability,

$$\alpha(\omega, k_x, k_y) = \frac{\sqrt{\epsilon_{zz}(k_x^2 \epsilon_{xx} + k_y^2 \epsilon_{yy}) / \beta - 1}}{\sqrt{\epsilon_{zz}(k_x^2 \epsilon_{xx} + k_y^2 \epsilon_{yy}) / \beta + 1}} \quad (4.34)$$

The polarisability describes the response of a solid to an applied electric potential [65]. In the presence of such a field, the electron clouds will distort and as a result of this distortion, a compound which is originally non-polar can attain a dipole moment. Next, we would like to calculate the energy loss probability per unit path length of the electron, which is derived from the electric potential of the induced electric field in the medium and can be written as

$$\begin{aligned} E_{\text{loss}} &= -\frac{dW}{dx} = -eE_{r=vt} = -\frac{e}{v} \vec{v} \cdot \vec{E}_{r=vt} \\ &= -\frac{e}{v} \frac{d \text{ Potential}}{dt} = -\frac{e}{v} \frac{d\psi_{\text{ind}}}{dt} \end{aligned} \quad (4.35)$$

where W is the work done by the electron or energy absorbed by the medium. The probabilistic energy loss (per unit energy) is thus

$$L(\omega, b) = -\frac{e}{v} \frac{1}{\hbar \omega} \int_{-\infty}^{\infty} \frac{d\psi_{\text{ind}}}{dt} dx \quad (4.36)$$

The induced potential refers to the decaying solution along the z-direction (Eq. (4.12)), $\psi_{\text{ind}} = B \exp(-\beta z)$ and B is given by Eq. (4.31) and Eq. (4.33).

Putting this together we arrive at

$$\begin{aligned}
\psi_{\text{ind}}(\omega, \vec{k}_{\perp}, z) &= B \exp(-\beta z) \\
&= -\frac{\pi e \delta(k_x + \frac{\omega}{v}) \exp(-\beta b) \alpha}{v \beta} \exp(-\beta z) \\
&= -\frac{\pi e \delta(k_x + \frac{\omega}{v}) \exp(-\sqrt{k_y^2 + \frac{\omega^2}{v^2}} b) \alpha(\omega, k_x, k_y)}{v \sqrt{k_y^2 + \frac{\omega^2}{v^2}}} \exp(-\sqrt{k_y^2 + \frac{\omega^2}{v^2}} z) \quad (4.37)
\end{aligned}$$

We need to express ψ_{ind} as a function of time and space through an inverse fourier transform. This is so that we can perform the time derivative and integrate over the electron path. Finally, without loss of generality let $y = 0$, we can evaluate the analytical energy loss and use the property of the polarisability $\alpha^*(\omega, \vec{k}) = \alpha(-\omega, -\vec{k})$,

$$\begin{aligned}
L(\omega, b) &= -\frac{e}{\hbar \omega v} \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx d\omega dk_x dk_y \\
&\quad \frac{d}{dt} \left[\exp(i(k_x \cdot x + \omega t)) \psi_{\text{ind}}(z = b, \omega, k_x, k_y) \right] \\
&= -\frac{e}{\hbar \omega v} \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx d\omega dk_x dk_y \\
&\quad \frac{d}{dt} \left[\exp(i(k_x \cdot x + \omega t)) \times \left(-\frac{\pi e}{v \epsilon_0 \beta} \exp(-\beta b) \exp(-\beta z) \alpha(\omega, k_x, k_y) \right. \right. \\
&\quad \left. \left. \times \delta(k_x + \frac{\omega}{v}) \right) \Big|_{z=b} \right] \\
&= \frac{\pi e}{\epsilon_0 v^2} \frac{e}{\hbar \omega} \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx d\omega dk_x dk_y \\
&\quad i\omega \frac{1}{\beta} \exp(i(k_x \cdot x + \omega t)) \exp(-2b\beta) \alpha(\omega, k_x, k_y) \delta(k_x + \frac{\omega}{v})
\end{aligned}$$

$$\begin{aligned}
 &= \frac{\pi i e^2}{\epsilon_0 \hbar (2\pi)^3 v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx d\omega dk_y \\
 &\quad \frac{1}{((\frac{\omega}{v})^2 + k_y^2)^{1/2}} \exp\left(-2b\sqrt{(\frac{\omega}{v})^2 + k_y^2}\right) \alpha\left(\omega, \frac{\omega}{v}, k_y\right) \exp\left(it\left(\frac{-\omega}{v}v + \omega\right)\right) \\
 &= \frac{\pi i e^2}{\epsilon_0 \hbar (2\pi)^3 v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx d\omega dk_y \\
 &\quad \frac{1}{\sqrt{(\frac{\omega}{v})^2 + k_y^2}} \exp\left(-2b\sqrt{(\frac{\omega}{v})^2 + k_y^2}\right) \alpha\left(\omega, \frac{\omega}{v}, k_y\right) \\
 &= \frac{\pi i e^2}{\epsilon_0 \hbar (2\pi)^3 v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} dx d\omega dk_y \\
 &\quad \frac{1}{\sqrt{(\frac{\omega}{v})^2 + k_y^2}} \exp\left(-2b\sqrt{(\frac{\omega}{v})^2 + k_y^2}\right) \left(\alpha\left(\omega, \frac{\omega}{v}, k_y\right) - \alpha^*(\omega, \vec{k})\right) \\
 &= -\frac{2\pi e^2}{\epsilon_0 \hbar (2\pi)^3 v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} dx d\omega dk_y \\
 &\quad \frac{1}{\sqrt{(\frac{\omega}{v})^2 + k_y^2}} \exp\left(-2b\sqrt{(\frac{\omega}{v})^2 + k_y^2}\right) \text{Im}(\alpha(\omega, \frac{\omega}{v}, k_y)) \tag{4.38}
 \end{aligned}$$

Finally, we arrive at the energy loss probability per unit electron path per unit angular frequency, which will be comparable to experimental energy loss spectra. This gives

$$\begin{aligned}
 \frac{d^2 L(\omega, b)}{dx d\omega} &= -\frac{2\pi e^2}{(2\pi)^3 v^2 \epsilon_0 \hbar} \int_{-\infty}^{\infty} \text{Im}(\alpha(\omega, \frac{\omega}{v}, k_y)) \frac{e^{-2b\sqrt{(\frac{\omega}{v})^2 + k_y^2}}}{\sqrt{k_y^2 + \frac{\omega^2}{v^2}}} dk_y \\
 &= -\frac{e^2}{(2\pi)^2 v^2 \epsilon_0 \hbar} \int_{-\infty}^{\infty} \text{Im}(\alpha(\omega, \frac{\omega}{v}, k_y)) \frac{e^{-2b\sqrt{(\frac{\omega}{v})^2 + k_y^2}}}{\sqrt{k_y^2 + \frac{\omega^2}{v^2}}} dk_y \tag{4.39}
 \end{aligned}$$

which matches that quoted by Radtke *et al.* [55], who considered a similar setup geometry ².

The derivation of the probabilistic energy loss we have so far explored is that of a classical dielectric formalism. However, this procedure is referred to as the semi-classical theory as we need to employ quantum mechanical calculations to obtain the non-trivial, material specific dielectric permittivity

² Several authors in literature quote different combinations of π as part of the global coefficients and this is noted in [Appendix A](#).

tensor ϵ and hence the polarisability α . This is delineated in the subsequent section.

4.2.1 *Low-frequency dielectric tensor*

The material's dielectric tensor is the major component in determining the energy loss spectrum. It is dependent on parameters such as frequency of the applied field and temperature [116]. We neglect temperature and other thermodynamic effects, focusing only on the frequency dependence. In order to simulate the dielectric tensor for different molecular crystals in future sections, this section discusses in more detail how ϵ can be analytically expressed in terms of the material specific characteristics.

Contributions to the frequency dependence of ϵ arise from different types of polarisation mechanisms in the material. These can include the polarisation contributions from [117, 118]

- bulk mobile space charges; which separate under the applied field to create an interfacial polarisation.
- Permanent electric dipoles; whereby material with permanent intrinsic dipoles will rotate upon the introduction of an external field.
- ions; which occur when positive and negative ions in an ionic crystal are displaced and induces a dipole moment.
- Electrons cloud displacement relative to their respective nuclei.

Fig. 4.2 shows the frequency dependence of a generic dielectric tensor. We will ignore the temperature dependence of the dielectric constant as simulations are calculated at 0K. At different frequency ranges, the different mechanisms mentioned previously dominate based on their characteristic relaxation times.

As dipoles are heavier than ions, which are in turn heavier than electrons, the dominant process at very low frequencies come from dipole contributions. As the applied field frequency increases, it will eventually match the processes of nuclei and electronic resonances. Simultaneously, as the period of the oscillatory field becomes lower than the relaxation time of the heavier mechanisms, the real part of the dielectric tensor is reduced. This is because the electric field energy is not completely imparted into changing the polarisation, and is instead being fed into the imaginary components (which are associated with energy dissipation). As frequency continues to increase, dipolar rotations and ionic motions can no longer follow the rapid oscillations of the electric field, dropping off successively and only the electron cloud is able to keep up. Eventually, permittivity becomes a constant as all of the above mechanisms lose their response. Notationally, as the applied frequency $\omega \rightarrow 0$, if enough time is allowed to pass for the system to reach equilibrium and achieve maximum polarisation, the resulting dielectric constant is the static dielectric tensor ϵ_s . Similarly as $\omega \rightarrow \infty$, ϵ_∞ is referred to as the high frequency dielectric tensor.

The general complex dielectric tensor can be written as [117]

$$\epsilon(\omega) = \epsilon_\infty + \int_0^\infty g(t) \exp(i\omega t) dt \quad (4.40)$$

where $g(t)$ describes the decay in the displacement field of the dielectric upon the removal of the external electric field. An early model of this dynamic dielectric property is the Debye equations, which give the form of $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ for the case of noninteracting dipoles by assuming that $g(t)$ is exponential decay function [117].

$$\epsilon_1(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\eta^2} \quad (4.41)$$

$$\epsilon_2(\omega) = \frac{(\epsilon_s - \epsilon_\infty)\omega\eta}{1 + \omega^2\eta^2} \quad (4.42)$$

where η is the relaxation time of the material. For a consistency check, as $\omega \rightarrow \infty(0)$, the real part approaches $\epsilon_\infty(\epsilon_s)$ and imaginary part approaches zero, so that the permittivity is real and constant.

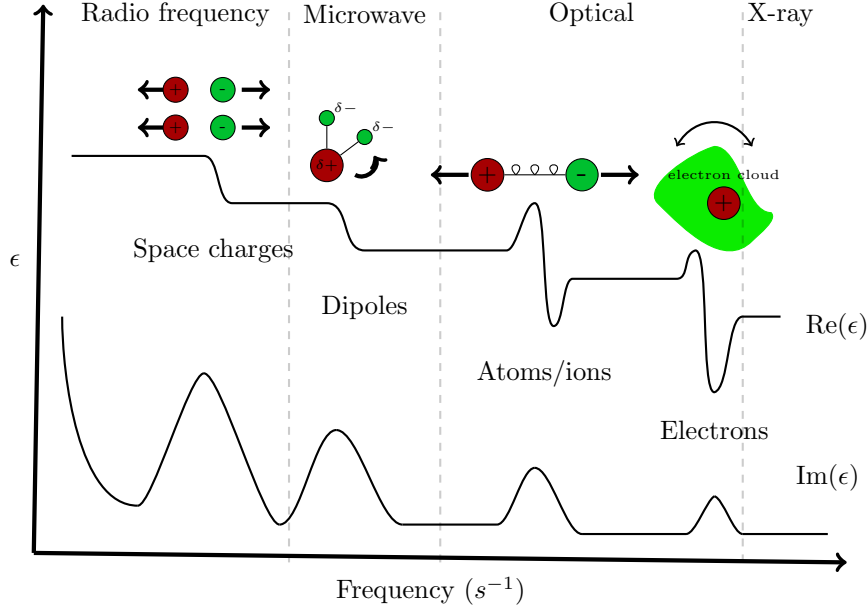


Figure 4.2: Qualitative depiction of the real and imaginary parts of a generic dielectric tensor. The atomic and electronic polarisation resonant effects are shown at frequency ranges from IR towards UV, whereas the relaxation effect such as rotational polarisation occur at frequencies below IR. These processes drop out consecutively as frequency increases.

The dielectric materials we will consider (molecular crystals) are not as straightforward. These are insulators and we want to investigate their phonon properties due atomic displacements and hence we are interested in the low frequency range (and thus low momentum $\vec{k} \rightarrow \vec{0}$ impact range). These interactions are calculated using DFT. For our materials of interest, $\epsilon(\omega)$ is the sum of the electronic and ionic contributions to polarisation, expressed as [62,65]

$$\epsilon_{i,j}(\omega) = \epsilon_{i,j}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,i,j}}{\omega_m^2 - \omega^2} \quad (4.43)$$

where $\epsilon_{i,j}^\infty$ is the electronic contribution along cartesian coordinates i and j . Ω_0 is the unit cell volume and ω_m is the frequency of mode m . $S_{m,i,j}$ is the mode-oscillator strength defined by

$$S_{m,i,j} = \left(\sum_{\kappa,i'} Z_{\kappa,i,i'}^* u_{\kappa,m,i'}(\vec{k}=0) \right) \left(\sum_{\kappa',j'} Z_{\kappa,j,j'}^* u_{\kappa',m,j'}(\vec{k}=0) \right) \quad (4.44)$$

where $u_{\kappa,m,i'}(\vec{k}=0)$ is the eigendisplacement of atom κ at zero momentum transfer $\vec{k}=0$ and satisfies the mass normalisation constraint (for atom κ with mass m_κ)

$$\sum_{\kappa,j} m_\kappa u_{p,\kappa,j}^* u_{q,\kappa,j} = \delta_{pq}. \quad (4.45)$$

$Z_{\kappa,i,j}^*$ is the Born effective charge (BEC), which describes how the polarisation per unit cell, P changes along some direction i when displacing an atom κ by τ along the direction j when no external electric field is present, i.e.

$$Z_{\kappa,i,j}^* = \Omega_0 \frac{\partial P_i}{\partial \tau_{\kappa,j}} \Big|_{\vec{k}=\vec{0}} \quad (4.46)$$

$\left(\sum_{\kappa,i'} Z_{\kappa,i,i'}^* u_{\kappa,m,i'}(\vec{k}=0) \right)$ is often referred to as the mode effective charge vector. When evaluating the low frequency dielectric tensor, there are two phenomena arising from the interactions between ionic motions and electric fields which are captured in the mode oscillator strength tensor. The first is simply that the electric field imparts a force on the ions giving rise to phonon modes. The second phenomenon is the fact that there is an (macroscopic) electric field associated with these atomic displacements, and there is a directional dependency on how $\vec{k}$ approaches $\vec{0}$. This is the origin of LO-TO splitting. At exactly $\vec{k} = \vec{0}$ the longitudinal optical (LO) and transverse optical (TO) phonon modes should be degenerate. However, the macroscopic electric field set up due to the atomic displacements, this interacts with the LO and TO modes differently and lifts the degeneracy. This is succinctly summarised

in the Lyddane-Sachs-Teller relationship [119], which relates the LO and TO frequencies via

$$\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_{static}}{\epsilon_{\infty}} \quad (4.47)$$

As this effect changes the dynamical matrix, which in turn affects the eigenfrequencies and eigenvectors, it is therefore important to include LO-TO splitting in our numerical simulations of phonon properties later in [Part IV](#).

4.2.2 *Summary*

So far we have discussed obtaining ultra-low loss EELS for the aloof beam configuration via the classical dielectric formalism. This theory is described as semi-classical because a quantum mechanical treatment (DFT) is required to obtain the material's dielectric response.

[Eq. \(4.39\)](#) is re-examined numerically in [Part IV](#), where comparisons between this semi-classical result is carried out against both literature experiments, as well as the analogous fully quantum mechanical models for ultra-low loss aloof beam EELS in the subsequent chapters.

There is extensive research in literature on the interaction of fast charged particles with solids and a quantum description can be used to investigate interactions at energy ranges from phonons to plasmons and core level excitations. A good review is given by FJG De Abajo [38]. The scattering of particles, such as electrons and photons, is used to probe the spatial information and excitation spectra of many-body systems. The former depends on both elastic and inelastic scattering whilst the latter hinges on inelastic scattering. As delineated in Section 3.1, the quantity of interest in the former case is the differential cross section, $\frac{d\sigma}{d\Omega}$, whilst the latter is the DDCS, $\frac{d^2\sigma}{d\Omega dE}$. The DDCS is the subject of interest of this chapter as we outline the quantum approach of the electron-sample interaction for phonon excitations.

The general expression of the DDCS for neutron and X-ray scattering at all energies was derived by Leon von Hove [120]. This theory has since been modified by R.J. Nicholls *et al.* [48] to work for inelastically scattered electrons in EELS. Their work also shows that fundamentally, the physics of EELS, INS and X-ray spectroscopy share many commonalities. In the following sections we go through the formalism to understand its assumptions and shortcomings, in order to later adapt it for aloof beam EELS.

We will follow the same formalism by Sinha [121] to analytically derive the EELS double differential cross section used by Nicholls *et al.* [48]. Details of some ambiguities and shortcomings of the theory will be discussed alongside the derivation. The main overarching issue as we will see, is how to analytically divide up the material's charge distribution. This is later addressed in the modified dipole theory in section Section 6.1 and Section 6.3.

5.1 THE DOUBLE DIFFERENTIAL CROSS SECTION & DYNAMIC STRUCTURE FACTOR

A monochromatic beam of particles with current density along the (without loss of generality) z-direction $(\vec{j}_0)_z$ illuminates a target with N scatterers. Each incoming particle from the beam will not interact with the entire target but an effective area, $d^2\sigma$. Thus the total number of interactions per second resulting in a scattered beam is $Nd^2\sigma(\vec{j}_0)_z$. This scattered beam per second along the unit vector $\hat{r}$ into a solid angle of $d\Omega$, with energies in the range of E_1 and $E_1 + dE_1$ along reciprocal vector $\vec{k}_1$ can be written in terms of the current density of scattered particles $\vec{j}_1(\vec{r}, \vec{k}_1, E_1)$ as $[\vec{j}_1(\vec{r}, \vec{k}_1, E_1) \cdot \hat{r}]r^2d\Omega dE_1$. Putting these together, we can write [122]

$$\frac{d^2\sigma}{d\Omega dE_1} = \frac{1}{N} \frac{[\vec{j}_1(\vec{r}, \vec{k}_1, E_1) \cdot \hat{r}]r^2}{\vec{j}_0|_z} \quad (5.1)$$

where the DDCS, $\frac{d^2\sigma}{d\Omega dE_1}$ can be understood as the ratio of the flux of the scattered to incident beam. If a quantum mechanical treatment this scattering process is used to determine Eq. (5.1), one must consider the Hamiltonian of the interaction between the free, fast moving particle and sample, $\langle n_i, k_i | H_{int} | n_f, k_f \rangle$ where $n_i, k_i (n_f, k_f)$ denote the initial (final) states of the system and fast electron respectively. This requires the knowledge of the total wavefunction, which is non-trivial to solve. However, one can derive an analytical expression for the DDCS using appropriate assumptions. Firstly, we assume that there is no interaction between the particles and system before and after scattering, so that their joint state is separable, i.e. $|n_i, \vec{k}_i\rangle = |n_i\rangle |\vec{k}_i\rangle$. Secondly, we employ the first order Born approximation, which assumes that the incoming and scattered wave-function is a plane-wave because the scattering potential/interaction Hamiltonian is weak enough to cause negligible

change in the wavefunction. This allows us to treat the system and scatterer separately.

5.1.1 Spectral intensities for impact scattering EELS

Equipped with the aforementioned approximations and letting the incident beam current density $j_0|_z = \frac{N_0}{V} \frac{\hbar k_0}{m}$ (all variables have their usual meaning), the DDCS for EELS can be written as

$$\frac{d^2\sigma}{d\Omega dE_1} = \frac{k_1}{k_0} \frac{m^2 V^2}{N \hbar^4 (2\pi)^2} \sum_{n_0, n_1} P_{n_0} |\langle n_1, \vec{k}_1 | H_{\text{int}} | n_0, \vec{k}_0 \rangle|^2 \delta(E_{n_0} + E_0 - E_{n_1} - E_1) \quad (5.2)$$

where P_{n_0} is the probability that the initial system state is $|n_0\rangle$. As the particles scattered transition from states $|\vec{k}_0\rangle$ to $|\vec{k}_1\rangle$ (with energies E_0 and E_1 respectively), they induce transitions of the material system from states $|n_0\rangle$ to $|n_1\rangle$ with energies E_{n_0} and E_{n_1} respectively. V is a volume term stemming from integration and for further comments and a more in depth derivation of Eq. (5.2) see [Appendix B.1](#).

The perturbing potential or interaction Hamiltonian H_{int} is the Coulomb interaction between the fast electron and the total charge density of the material, ρ_{total} , which is often approximated as a sum of point charges

$$\begin{aligned} H_{\text{int}} &= -\frac{e}{4\pi\epsilon_0} \int \frac{\rho_{\text{total}}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' \\ &\approx -\frac{e}{4\pi\epsilon_0} \sum_i \frac{Z_i e}{|\vec{r} - \vec{r}_i|} \end{aligned} \quad (5.3)$$

with e the electron's charge, Z_i is the charge of particle i and ϵ_0 the vacuum permittivity. Using this point density approximation as a foundation, Van Hove's [120] seminal paper described for a non-relativistic scattering event,

with interaction potential and momentum transfer of $\hbar\vec{k}$, the DDCS expression of Eq. (5.2) is equivalently written as (see Appendix B.2 for algebraic details)

$$\frac{d^2\sigma}{d\Omega dE} = AS(\vec{k}, \omega) \quad (5.4)$$

The term $A = \frac{m^2 e^2}{N \hbar^4 \epsilon_0^2 4\pi^2} \frac{k_1}{k_0} \frac{1}{|\vec{k}|^4}$ for electron scattering describes the type of particle-particle interaction (i.e. Coulomb interaction for EELS). $S(\vec{k}, \omega)$ is the structure factor, an object that describes how the material responds to the scattering event and it is not dependent on the scattered particle nor interaction potential. Thus at a specific momentum transfer, the energy loss during the inelastic scattering event is entirely encapsulated in the structure factor, making it the object of interest in comparisons to experimental EELS intensities. Hove also establishes the correspondence between the structure factor and the space time correlation function. This relationship is expressed as [121]

$$S(\vec{k}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \rho(\vec{k}, 0) \rho^+(\vec{k}, t) \rangle \quad (5.5)$$

which suggests that it is sufficient to compute the (charge) density-density correlation of the material in order to compute the EELS intensity spectrum.

Using this formalism, Sinha studied the case of inelastic X-ray scattering for a Bravais lattice of identical atoms, with one atom per unit cell. Here, one only need consider the charge density of the electron cloud in the construction of the interaction Hamiltonian, because the nuclei are much heavier than the electron cloud so they radiate and scatter much less. Furthermore, the photon energies used in X-ray crystallography (typically 4 – 30keV [123]) are not enough energy or high enough frequency to penetrate to the nucleus, thus effectively shielded by its electron cloud.

In EELS, the beam of fast electrons can scatter off from both the electron cloud and the nucleus and thus we must take both into consideration. Thus

for a general, non-Bravais lattice, we approximate the total charge density as a sum of nuclear and electronic point charges over all unit cells labelled l (with positions $\vec{R}_l$), each containing atoms labeled i with nuclear charge Z_i and positions $\vec{R}_i$ relative to the unit cell origin. The associated electrons of atom i are labeled j . The fourier transform of this in reciprocal space becomes

$$\rho(\vec{k})_{total} = \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} [-e \sum_i \sum_l \sum_{j(i)} \delta(\vec{r} - \vec{R}_i - \vec{R}_l - \vec{R}_j) + Z_i e \sum_i \sum_l \delta(\vec{r} - \vec{R}_l - \vec{R}_i)] \quad (5.6)$$

$$= e \sum_i e^{-i\vec{k}\cdot\vec{R}_i} \sum_l [\sum_{j(i)} -e^{-i\vec{q}\cdot(\vec{R}_i)} e^{-i\vec{k}\cdot(\vec{R}_l)} + Z_i e^{-i\vec{k}\cdot\vec{R}_l}] \quad (5.7)$$

$$= e \sum_i e^{-i\vec{k}\cdot\vec{R}_i} \sum_l e^{-i\vec{k}\cdot\vec{R}_l} [Z_i - f_i(\vec{k})] \quad (5.8)$$

where $f_i(\vec{q})$ can be identified as the X-ray atomic form factor for atom i , as it is equivalent to the fourier transform of the electronic charge density (point charges i) for atom i in unit cell l ,

$$f_i(\vec{k}) = e \sum_{j(i)} \int d\vec{r} \delta(\vec{r} - \vec{R}_i - \vec{R}_l - \vec{R}_j) e^{-i\vec{k}\cdot\vec{r}} \quad (5.9)$$

We can add time dependence to the charge density $\rho(\vec{q}, t)$ by adding a time-dependent displacement term $u_i(t)$ to the atomic equilibrium positions, i.e. $\vec{R}_i \rightarrow \vec{R}_i + \vec{u}_i(t)$. Inserting this time-dependence [Eq. \(5.8\)](#) into the structure factor ([Eq. \(5.5\)](#)) gives

$$S(\vec{k}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \rho(\vec{k}, 0) \rho^+(\vec{k}, t) \rangle \quad (5.10)$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} e^2 \sum_i e^{-i\vec{k}\cdot\vec{R}_i} \sum_{i'} e^{i\vec{k}\cdot\vec{R}_{i'}} \sum_{ll'} e^{-i\vec{k}\cdot(\vec{l}-\vec{l}')} [Z_i - f_i(\vec{k})] [Z_{i'} - f_{i'}(\vec{k})]^* \langle e^{-i\vec{k}\cdot\vec{u}_{li}(0)} e^{i\vec{k}\cdot(\vec{u}_{l'i'}(t))} \rangle \quad (5.11)$$

The displacement of atoms about their equilibrium position, $\vec{u}_i$ is caused by lattice vibrations. Thus we can introduce phonons by replacing $\vec{u}_{l,i}(0)$ and $\vec{u}_{l',i'}(t)$ with the phonon displacement operator [124],

$$\vec{u}_{l,i}(t) = \left(\frac{\hbar}{2m_i N} \right)^{1/2} \sum_s \omega_s^{-1/2} [\vec{e}_{d,s} a_s e^{i\vec{q} \cdot \vec{l}} e^{-i\omega_s t} + \vec{e}_{d,s}^* a_s^\dagger e^{-i\vec{q} \cdot \vec{l}} e^{i\omega_s t}] \quad (5.12)$$

where a_s and $a_s^\dagger$ are the annihilation and creation operators of the phonon mode s respectively. Mode s is actually the double index q, j (q the wavevector of the mode. j is the polarisation index spanning $j = 1, 2, 3$ the three dimensions that vibrational motion can occur). ω_s , $\vec{e}_{i,s}$ and m_i are the mode frequency, polarisation vector and atomic mass respectively. The thermal average of the product of the exponential operators in Eq. (5.11) can be expanded to (letting operator $A = \vec{k} \cdot \vec{u}_{l,i}(0)$ and $B = \vec{k} \cdot \vec{u}_{l',i'}(t)$) using the Campbell-Baker-Hausdorff series [125]

$$\exp(A) \exp(B) = \exp\left(A + B + \frac{1}{2}[A, B] + \frac{1}{12}[A, [A, B]] - \frac{1}{12}[B, [A, B]] + \dots\right) \quad (5.13)$$

where $[A, B]$ is the commutator between the operators. From Eq. (5.12), one can deduce that the commutator of $[A, B]$ in this case are scalars because they are commutators of the combinations of a and $a^\dagger$ operators. Thus the commutators $[A, [A, B]]$, $[B, [A, B]]$ and all subsequent terms vanish and thus only the first three terms in expansion of Eq. (5.13) remain. Since phonon displacements are generally very small, we perform a Taylor expansion to first order on the thermal average quantity in Eq. (5.11) to finally arrive at

$$\langle e^{-i\vec{k} \cdot \vec{u}_{l,i}(0)} e^{i\vec{k} \cdot \vec{u}_{l',i'}(t)} \rangle \approx e^{-2W_i} \left(1 + \sum_{\alpha, \beta} k_\alpha k_\beta \langle \vec{u}_{l,i,\alpha} \vec{u}_{l',i',\beta}(t) \rangle \right). \quad (5.14)$$

The exponential e^{-2W_i} is the Debye-Waller factor (DWF) [126],

$$e^{-2W_i} = e^{-\frac{1}{2}\langle[\vec{k}\cdot\vec{u}_{i,l}(0)]^2\rangle} e^{-\frac{1}{2}\langle[\vec{k}\cdot\vec{u}_{i,l}(t)]^2\rangle}. \quad (5.15)$$

which is a damping term arising from the thermal motion and disorder in the material. It is the averaged mean squared amplitude of the atomic displacements as shown in Eq. (5.15). The two exponentials are equal as we are considering the average displacement of the vibrational motion, and hence the DWF is only temperature dependent and the time dependence can be ignored.

Inserting Eq. (5.14) and Eq. (5.12) into the structure factor (see full derivation in Appendix D.2) results in

$$\begin{aligned} S(\vec{k}, \omega) \propto & \left| \sum_i e^{-i\vec{k}\cdot\vec{R}_i} (Z_i - f_i(\vec{k})) \right|^2 e^{-2W_i} \\ & \times \left(\delta(\omega) \sum_{\vec{G}} \delta(\vec{k} - \vec{G}) + \frac{\hbar}{2Nm_i\omega_{q,j}} \sum_{q,j} |\vec{k} \cdot \vec{e}_i(\vec{q}, j)|^2 [\langle n_{q,j} \rangle \delta(\omega + \omega_q) \right. \\ & \left. \times \sum_{\vec{G}} \delta(\vec{k} + \vec{q} - \vec{G}) + \langle n_{q,j} + 1 \rangle \delta(\omega - \omega_q) \times \sum_{\vec{G}} \delta(\vec{k} - \vec{q} - \vec{G})] \right) \end{aligned} \quad (5.16)$$

for reciprocal lattice vectors $\vec{G}$. The first term corresponds to elastic scattering as there is no energy change/no particle creation nor annihilation, and simply depends on the X-ray form factor of the material. The second and third terms correspond to the one-phonon creation and annihilation process respectively quantified by the eigenvalues they contain, which are $\langle n_{q,j} \rangle$ and $\langle n_{q,j} + 1 \rangle$. We are only interested in the phonon creation term (i.e. the latter term), which participates in the energy loss process and hence in EELS detection. Thus we have considered the quantum impact scattering formalism, with the expression for ultra-low loss EELS matching that reported by Nicholls *et al.* [48].

5.2 SHORTCOMING OF IMPACT SCATTERING THEORY

The total DDCS for the quantum impact scattering case including global factors is thus (combining [Eq. \(5.4\)](#) and [Eq. \(5.16\)](#))

$$\begin{aligned} \frac{d^2\sigma}{dE d\Omega} = & \frac{m^2 e^4}{N \hbar^4 \epsilon_0^2 4 \pi^2} \frac{k_1}{k_0} \frac{1}{|\vec{k}|^4} \frac{V^3}{(2\pi)^6} \sum_{q,j} \left| \sum_i e^{-i\vec{k} \cdot \vec{R}_i} (Z_i - f_i(\vec{k})) e^{-W_i(\vec{k} \cdot \vec{e}_i(\vec{q}, j))} \right|^2 \\ & \times \frac{\hbar}{2N m_i \omega_{q,j}} \delta(\omega - \omega_{q,j}) \langle n_{q,j} + 1 \rangle \sum_{\vec{G}} \delta(\vec{k} - \vec{q} - \vec{G}) \end{aligned} \quad (5.17)$$

In the original Hamiltonian, Z_i is just the charge of the bare nucleus. However, practically this is manually altered to include the effects of static charge transfer (bonding) and thus nuclear screening. This issue, together with the numerical implementation and discussion of the DWF and atomic form factors in [Eq. \(5.17\)](#) is examined in detail in [Chapter 10](#).

5.2 SHORTCOMING OF IMPACT SCATTERING THEORY

The impact scattering derivation is also not directly applicable in the aloof beam context due to the incongruity between the two setups. There is a difference in the nature of the charge density experienced by the fast electron upon direct collision with vs passing by the sample at some impact parameter. In the former case, it is reasonable to approximate individual charges in the sample as point charges as we have in the previous section. In the latter case, the method of simplifying the continuous total charge distribution ρ_{total} should be reconsidered.

Furthermore, we also highlight the issue of charge partitioning. Recall that in the electron-sample interaction Hamiltonian [Eq. \(5.3\)](#), the total system charge density is approximated by the sum of point charges. Once the structure factor/energy loss spectrum is derived, each atom's nuclear charge Z_i is manually tweaked to mimic charge transfer by writing it as the bare nuclear charge $Z_{i,0}$ plus a change δZ . The choice for the charge transfer δZ can range

from static partitioning methods such as Mulliken or Hirshfield analysis, to containing dynamics such as using Born effective charges. However, these methods are all simply dividing up and assigning the point charges on the ions, as visualised in Fig. 5.1(a). Ideally, proper considerations of the effects of molecular bonding and the continuity of charge transfer inside the molecule are desired (visualised in Fig. 5.1(b)).

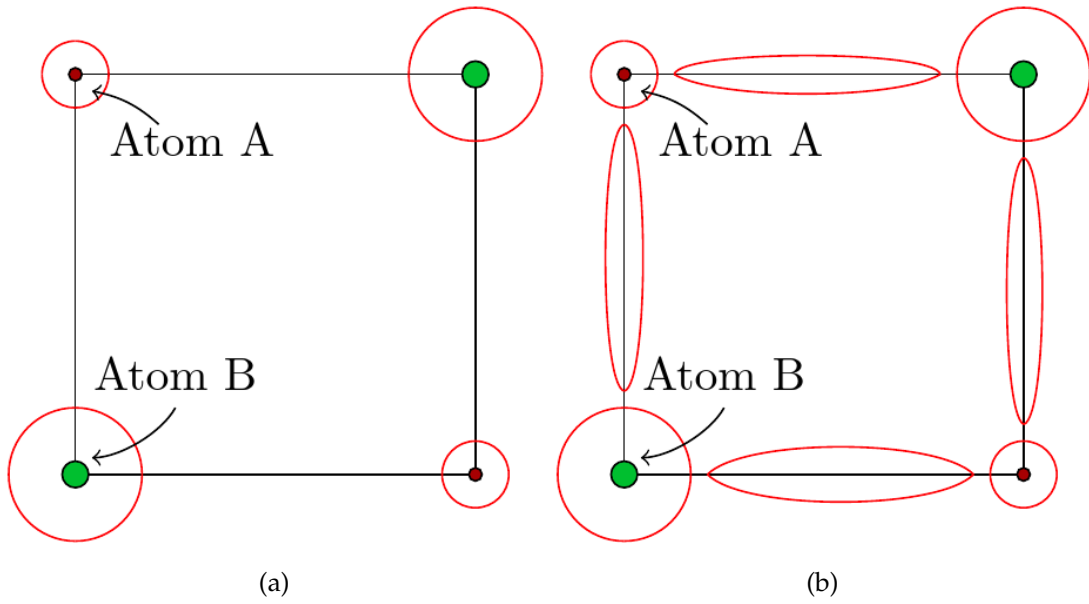


Figure 5.1: Simplified diagram of atoms in a square lattice. (a) Current method of charge partitioning in quantum impact scattering theory, where each atom is assigned a point charge value depending on charge partitioning analysis used (e.g. Mulliken, Hirshfeld, Born). The size of the red circles denote the magnitude of the assigned charge (b) Ideal method of charge partitioning to include bonding.

Recall that as mentioned in Section 3.2.3, the quantum approach is equivalent to the classical approach if all the scattered particles are collected at all angles. However, this is again through analytically dividing/simplifying the target charge distribution as point charges and summing over the discretised Coulomb interaction with the fast electron.

This formalism of deriving the generalised energy loss probability function starting from Fermi's rule was shown by Ritchie and Howie [73] to be equivalent to the classical derivation in the case when all collection angles are

5.2 SHORTCOMING OF IMPACT SCATTERING THEORY

included. However recall that in the electron-sample interacting Hamiltonian, analytical charge separation is simplified to point charges.

In the following chapter, we aim to address these issues by re-examining the electron-sample interaction potential in the context of ultra-low loss aloof beam EELS for molecular crystals.

QUANTUM ALOOF BEAM SCATTERING THEORY

Recall that we want an alternative method of dividing up charge when considering aloof beam EELS. In this section, the electronic term of the total charge density in the interacting Hamiltonian is revisited.

6.1 MULTIPOLE EXPANSION OF CHARGE DISTRIBUTION

Instead of assuming point charges (as was done in (Eq. (5.3))), we write

$$H_{int} = \frac{-e}{4\pi\epsilon_0} \int \frac{\rho_{total}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \quad (6.1)$$

$$= -e \left[\frac{1}{4\pi\epsilon_0} \sum_{i=1} \frac{Z_i e}{|\vec{r} - \vec{r}_i|} + \frac{1}{4\pi\epsilon_0} \int \frac{\rho_e(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \right] \quad (6.2)$$

where we still retain the discrete ionic lattice Coulomb charges. Consider the case of an aloof beam EELS setup visualised in Fig. 6.1 for a molecular crystal. In a real experiment, the distance between the fast electron to the sample (typically on the order of magnitude of $\sim 10 - 100nm$ [54, 107]) is much larger than the molecular size $\tilde{1}nm$. Thus with the electron being far away enough, in lieu of treating individual electron as point charges, we consider performing the conventional multiple expansion of the charge distribution around each molecule separately. This is then summed over all the unit cells.

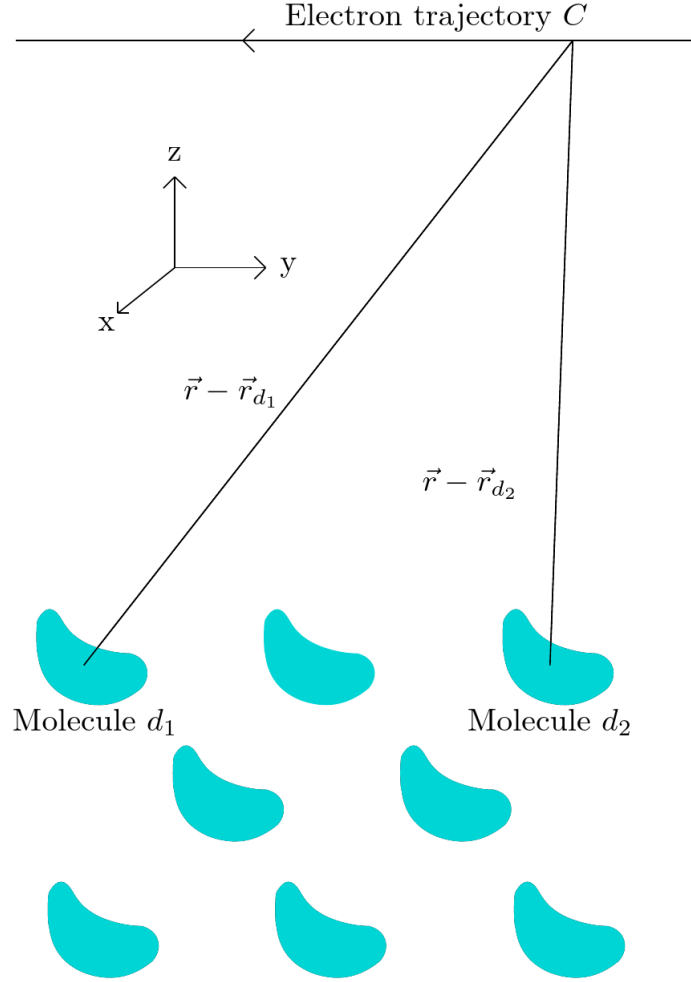


Figure 6.1: Visual representation the alouf beam setup, whereby molecules in a molecular crystal are represented by a charge distribution d_i . The incoming fast electron is far away and traveling along trajectory C .

Consider the geometry between one molecule in the molecular crystal and the fast electron in the alouf setup, shown in Fig. 6.2. As the electron is sufficiently far away ($\vec{r} \gg \vec{R}$), the multipole expansion performed on this generic total charge distribution ρ_{total} gives an electric potential $V(\vec{r})$ of [127]

$$\begin{aligned}
 V(\vec{r}) &= \frac{1}{4\pi\epsilon_0} \int \frac{\rho_{\text{total}}}{|\vec{r} - \vec{R}|} d^3r \\
 &\approx \frac{1}{4\pi\epsilon_0} \left[\frac{q_{\text{total}}}{r} + \frac{\mu \cdot \vec{r}}{r^3} + \sum_j \frac{\vec{r} \cdot Q_{ij} \cdot \vec{r}}{r^5} + \dots \right]
 \end{aligned} \tag{6.3}$$

where q_{total} , $\vec{\mu}$ and Q_{ij} are the total charge, dipole moment and quadrupole moment of the charge distribution respectively. These are the multipole moments and are defined either as integrals of the charge distribution for a continuous system or a summation for a discretised group of charges q_k .

$$\begin{aligned} q_{\text{total}} &= \int \rho(\vec{r}) d^3r \text{ or } \sum_k q_k \\ \vec{\mu} &= \int \vec{r} \rho(\vec{r}) d^3r \text{ or } \sum_k \vec{r}_k q_k \\ Q_{i,j} &= \int (3r_i r_j - r^2 \delta_{i,j}) \rho(\vec{r}) d^3r \text{ or } \sum_k (3r_{i,k} r_{j,k} - r_k^2 \delta_{i,j}) q_k \end{aligned} \quad (6.4)$$

As argued previously, at sufficiently large distances away $\vec{r} \gg \vec{R}$, the dominant term in the electrostatic potential is the leading non-vanishing term. The electric multipole moments have explicit dependence on the choice of the origin, except for the first non-vanishing moment [128]. For example, if we translate the origin by a vector $\vec{r}_a$, the total charge q_{mol} will stay the same whilst the higher order multipole terms change, e.g. $\mu \rightarrow \int (\vec{r} - \vec{r}_a) \rho(\vec{r} - \vec{r}_a) d^3r \neq \int \vec{r} \rho(\vec{r}) d^3r$. In the case where there is no net charge ($q_{\text{mol}} = 0$), a translation of the origin will not change the first, non-vanishing moments, which is the dipole moment. In that case, $\int \vec{r}_a \rho(\vec{r} - \vec{r}_a) d^3r = 0$.

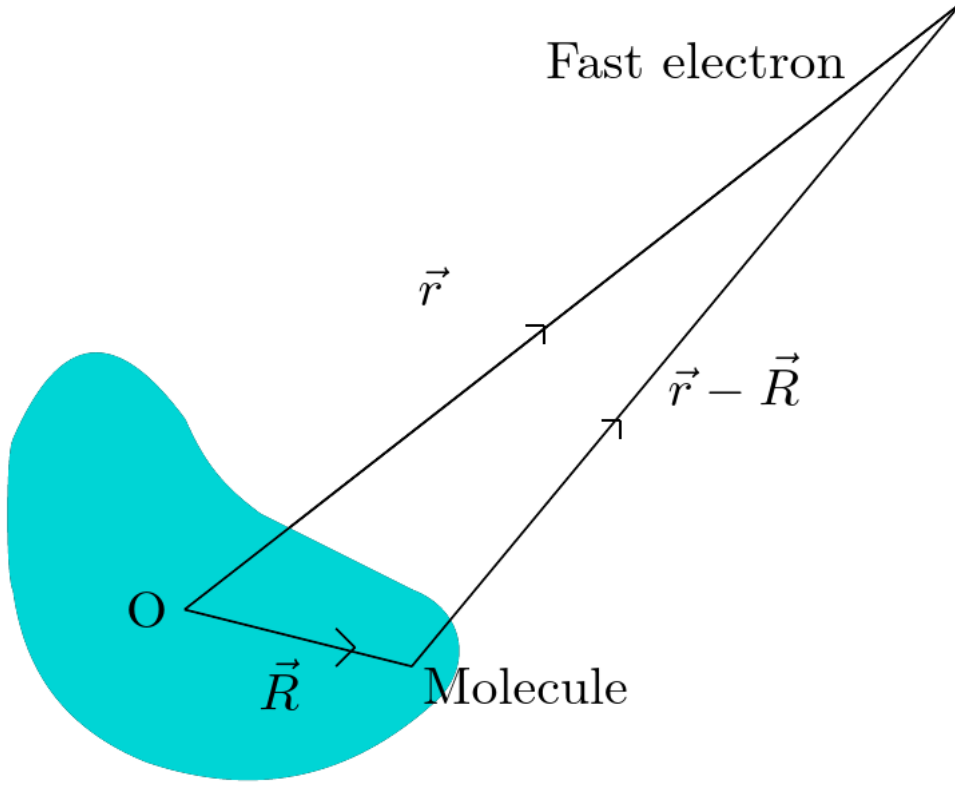


Figure 6.2: Multipole expansion of charge density around a generic molecule/charge distribution (centered at the origin, O).

In the molecular crystals of interest, we consider neutral molecules which means we have a vanishing first multipole moment where the point charges sum to zero. This can be viewed as bunching the charges at the centre and thus we assume that these molecules can be represented as point dipoles, with dipole moments that are origin independent.

Revisiting [Fig. 6.1](#), the interaction Hamiltonian obtained via the multipole expansion of the charge density cut off at the dipole term gives

$$H_{int} = \frac{-e}{4\pi\epsilon_0} \int \frac{\rho_{total}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \quad (6.5)$$

$$= -e \left[\frac{1}{4\pi\epsilon_0} \sum_{i=1} \frac{Z_i e}{|\vec{r} - \vec{r}_i|} + \frac{1}{4\pi\epsilon_0} \int \frac{\rho_e(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \right] \quad (6.6)$$

$$\approx -\frac{e}{4\pi\epsilon_0} \sum_d \left[\sum_{i=1} \frac{Z_i e}{|\vec{r} - \vec{r}_d|} - \sum_{j(i)} \frac{e}{|\vec{r} - \vec{r}_d|} + \frac{\vec{\mu}_d \cdot (\vec{r} - \vec{r}_d)}{|\vec{r} - \vec{r}_d|^2} \right] \quad (6.7)$$

for the sum over all dipoles d and their constituent atoms i , each with electrons indexed j .

We would now like to compute the double differential cross section using this modified interaction Hamiltonian. Recall that in [Section 5.1.1](#), the transition probability obtained via Fermi's golden rule can be related to the structure factor in the impact scattering formalism. We will now show this is also the case using the dipole moment expansion.

6.2 RELATING TRANSITION PROBABILITY WITH STRUCTURE FACTOR

Using [Eq. \(6.7\)](#), the matrix element can be written as

$$|\langle n_0, \vec{k}_0 | H_{int} | n_1, \vec{k}_1 \rangle|^2 = \frac{e^2}{(4\pi\epsilon_0)^2} |\langle n_0, \vec{k}_0 | \sum_d \frac{\vec{\mu}_d \cdot \widehat{(\vec{r} - \vec{r}_d)}}{|\vec{r} - \vec{r}_d|^2} | n_1, \vec{k}_1 \rangle|^2 \quad (6.8)$$

$$= \frac{e^2}{(4\pi\epsilon_0 V)^2} |\langle n_0 | \int d\vec{r} \sum_d e^{-i(\vec{k}_0 - \vec{k}_1) \cdot \vec{r}} \frac{\vec{\mu}_d \cdot \widehat{(\vec{r} - \vec{r}_d)}}{|\vec{r} - \vec{r}_d|^2} | n_1 \rangle|^2 \quad (6.9)$$

$$= \frac{e^2}{(4\pi\epsilon_0 V)^2} |\langle n_0 | \int d\vec{r} \sum_d e^{-i\vec{k} \cdot \vec{r}_d} e^{-i\vec{k} \cdot (\vec{r} - \vec{r}_d)} \frac{\vec{\mu}_d \cdot \widehat{(\vec{r} - \vec{r}_d)}}{|\vec{r} - \vec{r}_d|^2} | n_1 \rangle|^2 \quad (6.10)$$

$$= \frac{e^2}{(4\pi\epsilon_0 V)^2} |\langle n_0 | \sum_d e^{-i\vec{k} \cdot \vec{r}_d} \int d\vec{R} e^{-i\vec{k} \cdot \vec{R}} \frac{\vec{\mu}_d \cdot \widehat{\vec{R}}}{|\vec{R}|^2} | n_1 \rangle|^2 \quad (6.11)$$

$$= \frac{e^2}{(\epsilon_0 V)^2} |\langle n_0 | \sum_d e^{-i\vec{k} \cdot \vec{r}_d} \frac{(i\vec{\mu}_d \cdot \vec{k})}{k^2} | n_1 \rangle|^2 \quad (6.12)$$

where in [Eq. \(6.9\)](#) the electron's state is replaced with plane wave illumination. $\vec{k} = \vec{k}_0 - \vec{k}_1$ is the change in momentum, V is a volume term that arises through normalisation of the plane waves. Dipole d has position vector $\vec{r}_d$. The fourier transform evaluation from [Eq. \(6.11\)](#) to [Eq. \(6.12\)](#) is discussed in [Appendix D.4](#). In order to establish the relationship between the matrix element and structure factor, we need to express the dipole's charge density

in fourier space. A point dipole positioned at $\vec{r}_0$ has a charge density of [127] (derivation using Gauss' law discussed in [Appendix D.5](#))

$$\rho_d(\vec{r}) = -\vec{\mu} \cdot \nabla \delta(\vec{r} - \vec{r}_0) \quad (6.13)$$

such that the total dipole charge density summed over all molecules is given by

$$\rho(\vec{r}) = -\sum_d \vec{\mu}_d \cdot \nabla \delta(\vec{r} - \vec{r}_d) \quad (6.14)$$

The fourier transform of the total dipole charge density in the crystal is thus

$$\hat{\rho}_d(\vec{k}) = \int d\vec{r} \hat{\rho}(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} \quad (6.15)$$

$$= -\int d\vec{r} \sum_d \vec{\mu}_d \cdot \nabla \delta(\vec{r} - \vec{r}_d) e^{-i\vec{k} \cdot \vec{r}} \quad (6.16)$$

$$= \sum_d i(\vec{\mu}_d \cdot \vec{k}) e^{-i\vec{k} \cdot \vec{r}_d} \quad (6.17)$$

Using Eq. (5.2), Eq. (6.12), Eq. (6.17) and the relationships $\delta(E_{n_0} - E_{n_1} + \hbar\omega) = \frac{1}{2\pi\hbar} \int dt e^{-i\omega t} e^{i(E_{n_1} - E_{n_0})t/\hbar}$, $\sum_{n_1} |n_1\rangle \langle n_1| = 1$ and $e^{-iE_{n_i}t/\hbar} |n_i\rangle = e^{-iHt/\hbar} |n_i\rangle$, we can show that

$$\frac{d^2\sigma}{d\Omega dE_1} = \frac{1}{N} \frac{N_0 \sum_{n_0, n_1} P_{n_0} \frac{2\pi}{\hbar} |\langle n_1, \vec{k}_1 | H_{\text{dipole int}} | n_0, \vec{k}_0 \rangle|^2 \delta(E_{n_0} - E_{n_1} + \hbar\omega) \frac{V}{(2\pi)^3} \frac{mk_1}{\hbar^2}}{\frac{N_0}{V} \frac{\hbar k_0}{m}} \quad (6.18)$$

$$= \frac{m^2 V^2}{N \hbar^4 (2\pi)^2} \frac{k_1}{k_0} \sum_{n_0, n_1} P_{n_0} \frac{e^2}{(\epsilon_0 V)^2} |\langle n_0 | \sum_b e^{-i\vec{k} \cdot \vec{r}_l} \sum_d e^{-i\vec{k} \cdot \vec{r}_D} \frac{(i\vec{\mu}_d \cdot \vec{k})}{k^2} | n_1 \rangle|^2 \delta(E_{n_0} - E_{n_1} + \hbar\omega) \quad (6.19)$$

$$= \frac{m^2 e^2}{N \hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \sum_{n_0, n_1} P_{n_0} |\langle n_0 | \sum_b e^{-i\vec{k} \cdot \vec{r}_l} \sum_d e^{-i\vec{k} \cdot \vec{r}_D} \frac{(i\vec{\mu}_d \cdot \vec{k})}{k^2} | n_1 \rangle|^2 \delta(E_{n_0} - E_{n_1} + \hbar\omega) \quad (6.20)$$

$$= \frac{m^2 e^2}{(2\pi)^2 N \hbar^4 \epsilon_0^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar} \frac{1}{k^4} \int dt e^{-i\omega t} \sum_{n_0, n_1} P_{n_0} \langle n_0 | e^{iE_{n_0}t/\hbar} \sum_b e^{-i\vec{k} \cdot \vec{r}_l} \sum_d e^{-i\vec{k} \cdot \vec{r}_D} \times (i\vec{\mu}_d \cdot \vec{k}) | n_1 \rangle \langle n_1 | \sum_{b'} e^{i\vec{k} \cdot \vec{b}'} \sum_{d'} e^{i\vec{k} \cdot \vec{r}_{D'}} (-i\vec{\mu}_{d'} \cdot (-\vec{k})) e^{-iE_{n_0}t/\hbar} | n_0 \rangle \quad (6.21)$$

$$= \frac{m^2 e^2}{N \hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar} \frac{1}{k^4} \int dt e^{-i\omega t} \sum_{n_0} \langle n_0 | P_{n_0} \sum_b e^{-i\vec{k} \cdot \vec{r}_l} \sum_d e^{-i\vec{k} \cdot \vec{r}_D} (i\vec{\mu}_d \cdot \vec{k}) \times e^{iHt/\hbar} \sum_{b'} e^{i\vec{k} \cdot \vec{b}'} \sum_{d'} e^{i\vec{k} \cdot \vec{r}_{D'}} (-i\vec{\mu}_{d'} \cdot (-\vec{k})) e^{-iHt/\hbar} | n_0 \rangle \quad (6.22)$$

$$= \frac{m^2 e^2}{N \hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar} \frac{1}{k^4} \int dt e^{-i\omega t} \sum_{n_0} \langle n_0 | P_{n_0} \hat{\rho}_{d, \vec{k}} e^{iHt/\hbar} \hat{\rho}_{d, -\vec{k}} e^{-iHt/\hbar} | n_0 \rangle \quad (6.23)$$

$$= \frac{m^2 e^2}{N \hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar k^4} \int dt e^{-i\omega t} \sum_{n_0} P_{n_0} \langle n_0 | \hat{\rho}_d(\vec{k}, 0) \hat{\rho}_d(-\vec{k}, t) | n_0 \rangle \quad (6.24)$$

$$= \frac{m^2 e^4}{N \hbar^4 \epsilon_0^2 4\pi^2} \frac{k_1}{k_0} \frac{1}{k^4} S(\omega, \vec{k}) \quad (6.25)$$

where $S(\omega, \vec{k}) = \frac{1}{2\pi\hbar} \int dt e^{-i\omega t} \sum_{n_0} P_{n_0} \langle n_0 | \hat{\rho}_{dip}(\vec{k}, 0) \hat{\rho}_{dip}(-\vec{k}, t) | n_0 \rangle$, and is the density-density correlation also written as $\frac{1}{2\pi\hbar} \int dt e^{-i\omega t} \langle \hat{\rho}_{dip}(\vec{k}, 0) \hat{\rho}_{dip}(-\vec{k}, t) \rangle$ [122].

Here, $\vec{r}_{l^{(i)}}$ is the position vector of the unit cell l , $\vec{r}_{D^{(i)}}$ the relative position of dipole D to the unit cell centre such that $\vec{r}_d = \vec{r}_l + \vec{r}_D$. Thus, the DDSCS is

6.3 DIPOLE CONTRIBUTIONS TO SPECTRAL INTENSITIES

equivalent to the structure factor expressed using the dipole charge density, in the same way as that of the impact scattering case using the point charge density. In a nutshell, we change from the Schrödinger to Heisenberg picture, followed by identifying that the result resembles that of the dipole charge density correlation function using the discussions from the previous section. Notice that in the last line we pulled out a factor of e^2 from the charge correlation function. This is such because in the next sections when we decompose the dipole moment $\vec{\mu}$ into a charge times a distance, the unit of elementary charge is taken out of this value.

6.3 DIPOLE CONTRIBUTIONS TO SPECTRAL INTENSITIES

We have truncated our analysis of the target's charge distribution at the dipole term, which will now be used to explore the effects on the final energy loss spectrum. The charge distribution is given by [Eq. \(6.17\)](#). We append a time-dependence to both the dipole moment μ in addition to the position of the dipole $\vec{r}_d$, since the molecular dipole moment changes during the vibrational excitation. In order to express the molecular dipole moment's dependency on the atomic coordinates, the most convenient method is to write it as a Taylor expansion in normal mode coordinates, Q_s [\[60\]](#)

$$\vec{\mu}^d(t) = \vec{\mu}^d(0) + \sum_s \left(\frac{\partial \vec{\mu}^d}{\partial Q_s} \right) \Big|_0 Q_s(t) + \text{higher terms} \quad (6.26)$$

where $\vec{\mu}^d(0)$ is the dipole's static permanent electric dipole moment. The rate of change of dipole moment with respect to the normal coordinate can be

expanded via the chain rule to include atomic displacements $\vec{u}_{s,\kappa}$, for mode s and atom κ belonging to dipole d ,

$$\frac{\partial \vec{\mu}^d}{\partial Q_s} = \sum_{\kappa} \frac{\partial \vec{\mu}^d}{\partial \vec{u}_{\kappa,s}} \frac{\partial \vec{u}_{\kappa,s}^d}{\partial Q_s} \quad (6.27)$$

Selection rules based on whether a mode causes a change in the dipole moment will determine if it contributes to the spectral intensities and is reminiscent of IR spectroscopic intensities. This will be investigated in more detail in [Section 11.1](#) when considering specific molecular crystals. The displacement vector $\vec{u}$ can be written in relation to the normal modes of the system related by a fourier transform [[129](#)]

$$\begin{aligned} Q_s(\vec{k}_s, t) &= \frac{1}{\sqrt{N}} \sum_{\kappa} \sqrt{m_{\kappa,d}} \exp(-i\vec{k}_s \cdot \vec{r}_{\kappa}^d) \vec{e}_{\kappa,s}^d(\vec{k}_s) \cdot \vec{u}_{\kappa}^d(t) \\ \vec{u}_{\kappa}^d(\vec{k}_s, t) &= \frac{1}{\sqrt{N m_{\kappa,d}}} \sum_{\vec{k}_s} \vec{e}_{\kappa,s}^d(\vec{k}_s) \exp(i\vec{k}_s \cdot \vec{r}_{\kappa}^d) Q_s(\vec{k}_s, t) \end{aligned} \quad (6.28)$$

where $m_{\kappa,d}$ and $\vec{e}_{\kappa,s}^d$ are the mass and eigenvector of atom κ respectively, and N the number of unit cells in the crystal. Thus we can write $\frac{\partial \vec{u}_{\kappa,s}^d}{\partial Q_s}$ as $\propto \frac{\vec{e}_{\kappa,s}^d}{\sqrt{m_{\kappa}}}$.

In a bulk crystal, $\vec{\mu}^d$ will be the dipole moment of the entire unit cell, and we can thus replace the $\frac{\partial \vec{\mu}^d}{\partial \vec{u}_{\kappa,s}}$ term with the born effective charge (BEC). However, this is not the case in our expansion per molecular dipole, and we now show that this first order change can instead be related to the mode effective charge vector ([MECV](#)),

$$\sum_{\kappa} \frac{Z_{\kappa}^* \vec{u}_{s,\kappa}^d}{(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2}} \quad (6.29)$$

as defined by Gonze *et al.* [[65](#)], where $Z_{\kappa}^* = \frac{d\vec{\mu}}{d\vec{u}_{\kappa}}$ is the BEC for atom κ . We let the total dipole moment be the sum over dipole moments of all molecules such that $\vec{\mu} = \sum_d \vec{\mu}_d$. We also encapsulate time dependence in a function $P(t)$

(containing the oscillatory phase behaviour of the vibrations), in which we multiply with the MECV. Hence, we rewrite Eq. (6.29) as

$$\sum_{\kappa} \frac{d\vec{\mu}}{d\vec{u}_{\kappa}} \cdot \frac{\vec{u}_{\kappa,s}}{(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2}} P(t) \quad (6.30)$$

Expanding via the chain rule to incorporate the normal modes Q_s and using the expressions of Eq. (6.28), Eq. (6.30) becomes

$$\begin{aligned} & \sum_{\kappa} \frac{d\vec{\mu}}{dQ_s} \frac{dQ_s}{d\vec{u}_{\kappa}} \cdot \frac{\vec{u}_{\kappa,s}}{(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2}} P(t) \\ &= \sum_{\kappa} \frac{d\vec{\mu}}{dQ_s} \frac{1}{\sqrt{N}} e^{-i\vec{k}_s \cdot \vec{r}_{\kappa}} \frac{\vec{e}_{\kappa,s} \cdot \vec{u}_{\kappa,s}}{(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2}} P(t) \\ &= \frac{d\vec{\mu}}{dQ_s} \sum_{\kappa} \frac{1}{N} e^{-i\vec{k}_s \cdot \vec{r}_{\kappa}} \frac{\vec{e}_{\kappa,s} \cdot \vec{e}_{\kappa,s} e^{i\vec{k}_s \cdot \vec{r}_{\kappa}} Q_s}{(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2}} P(t) \\ &\propto \sum_d \frac{d\vec{\mu}^d}{dQ_s} Q_s P(t) \end{aligned} \quad (6.31)$$

where the last line possible owing to the orthonormality conditions of the vibrational eigenmodes, $\sum_{\kappa} \vec{e}_{\kappa,s} \cdot \vec{e}_{\kappa,s} = 1$ and $(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2} = \text{constant}$. Thus, we have related the MECV to the first order time dependent change in molecular dipole moment. Therefore, instead of replacing $\sum_s \left(\frac{\partial \vec{\mu}^d}{\partial Q_s} \right) \Big|_0 Q_s(t)$ with simply the BEC multiplied by the atomic displacement vectors, the MECV is used with the additional normalisation constant $(\sum_{\kappa'} \vec{u}_{s,\kappa'} \cdot \vec{u}_{s,\kappa'}^*)^{1/2}$.

The origin of the normalisation can also be understood qualitatively through the following argument. Consider the change in dipole moment $\sum_{s,\kappa} \frac{\partial \mu}{\partial \tau_{s,\kappa}} d\tau_{s,\kappa}$. For a fixed normal mode s , the infinitesimal displacement $d\tau_{s,\kappa}$ should not be replaced simply by the actual eigen-displacement operator, $\vec{u}_{\kappa,s}$ but rather scaled by the normal mode, $\frac{|u_{s,\kappa}|}{\sqrt{\sum_{\kappa} \vec{u}_{\kappa}^* \cdot \vec{u}_{\kappa}}} \hat{u}$. Thus, the contribution of each normal mode s to the total change in polarisation is scaled relative to each other.

We can demonstrate the difference between using this method and that by directly replacing $\frac{\partial \vec{\mu}^d}{\partial \vec{u}_{\kappa,s}^d}$ with the BEC by considering the geometric exposition in Fig. 6.3,

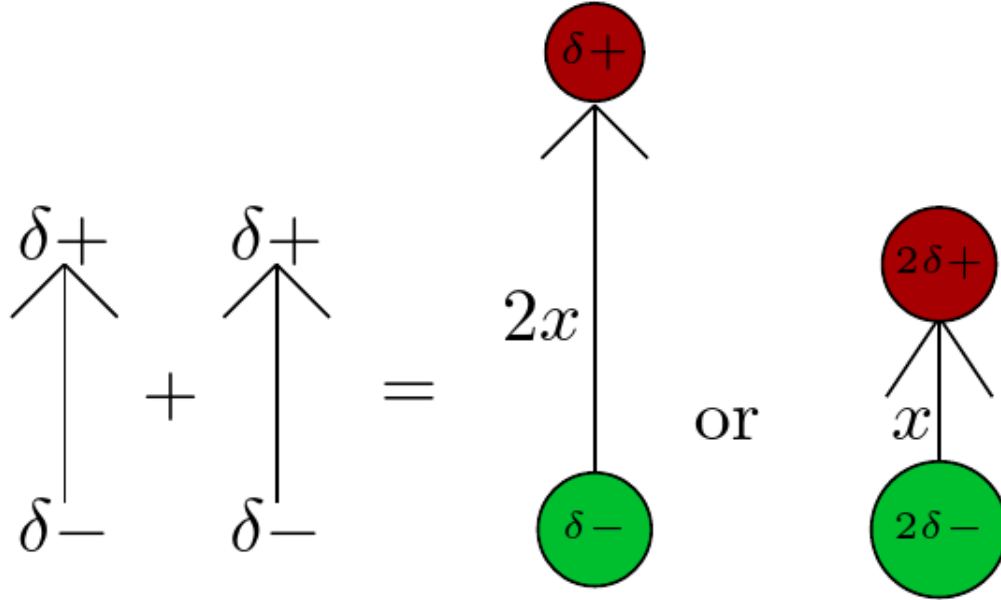


Figure 6.3: Illustration of two methods of getting molecular dipole moment contributions for two dipoles. In summing two dipoles (black arrows) to produce $\vec{\mu} = 2\delta x$, it is equivalent to either charges $|2\delta|$ separated by x or $|\delta|$ separated by $2x$.

Consider two atoms as part of a molecule under the action of a specific phonon mode such that the atomic displacements cause a change in dipole moment, represented as a separation of partial charges $\delta+$ and $\delta-$ charges. Let the charge separation of distance x . The sum of their dipole moments is $\sum_i \delta_i x_i = 2\delta \vec{x}$, two vectors each of $\delta \vec{x}$ represented by the black arrows. This is analogous to adding individual dipole moment contributions for each atom by summing over the BEC multiplied by eigen-displacements. On the other hand, the mode effective charge method gives the vectorised change in charge per normal mode. This is comparable to the case of $\pm 2\delta$ separated by x , which gives the same absolute final change in dipole moment using the formula $(\sum_i \delta_i)$ multiplied by their separation, but generally the two methods do not necessarily need to equal in magnitude.

In general, the sum of the change in charge vector contributed by every atom in the dipole gives the separation of the positive and negative charge centres represented by coloured circles in Fig. 6.3 per phonon mode.

This differs from Dwyer *et al.*'s approach (discussed in Section 6.6) in introducing the dynamic BECs, in which their derivation does not include a mode dependence for the Born tensors. This is because in the treatment of bulk crystals the definition of absolute polarisation is ambiguous so one uses the polarisation per the unit cell.

Furthermore, if we fix mode s to be for example the pure translational modes, the eigendisplacement $\vec{u}_{\kappa,s}$ is the same for all atoms (all atoms displace by the same amount) and thus we have $(\sum_{\kappa} Z_{\kappa}^*)\vec{u}_{\kappa,s} = 0$, i.e. the acoustic sum rule is still satisfied. Numerically, we absorb the time dependence $P(t)$ into the time dependent eigen-displacement $\vec{u}_{\kappa,s}$, which is replaced by the phonon displacement operator previously defined in Eq. (5.12) when computing the correlation function (in the same way as the quantum impact scattering theory). We now have all the tools required to evaluate the dipole charge density correlation (from the structure factor term in Eq. (6.25)) as follows

$$\begin{aligned} \sum_{n_0} P_{n_0} \langle n_0 | \hat{\rho}_{dip}(\vec{k}, t=0) \hat{\rho}_{dip}(-\vec{k}, t) | n_0 \rangle &= \langle \hat{\rho}_{dip}(\vec{k}, t=0) \hat{\rho}_{dip}(-\vec{k}, t) \rangle \\ &= \left\langle \left(\sum_d e^{-i\vec{k} \cdot \vec{l}_d} i(\vec{\mu}_d(t=0) \cdot \vec{k}) e^{i\vec{k} \cdot \vec{r}_d(0)} \right) \left(\sum_{d'} e^{-i\vec{k} \cdot \vec{l}_{d'}} i(\vec{\mu}_{d'}^*(t) \cdot (-\vec{k})) e^{i\vec{k} \cdot \vec{r}_{d'}(t)} \right) \right\rangle \end{aligned} \quad (6.32)$$

$$= \left\langle \sum_{dd'} e^{-i\vec{k} \cdot (\vec{l}_d - \vec{l}_{d'})} \left((\vec{\mu}_d(t=0) \cdot \vec{k}) e^{-i\vec{k} \cdot \vec{r}_d(0)} ((\vec{\mu}_{d'}(t)) \cdot \vec{k}) e^{i\vec{k} \cdot \vec{r}_{d'}(t)} \right) \right\rangle \quad (6.33)$$

$$= \left\langle \sum_{dd'} e^{-i\vec{k} \cdot (\vec{l}_d - \vec{l}_{d'})} \left(\sum_{\kappa} Z_{\kappa,s}^{d*} \left[\sum_s (\vec{e}_{\kappa,s} \cdot \vec{k}) c_{s,\kappa} (a_s e^{i\vec{q}_s \cdot \vec{b}} + a_s^\dagger e^{-i\vec{q}_s \cdot \vec{b}}) \right] e^{-i\vec{k} \cdot \vec{r}_d(0)} \right. \right. \quad (6.34)$$

$$\left. \times \sum_{\kappa'} Z_{\kappa',s'}^{d'*} \left[\sum_{s'} (\vec{e}_{\kappa',s'} \cdot \vec{k}) c_{s',\kappa'} (a_{s'} e^{i\vec{q}_{s'} \cdot \vec{b}'} e^{-i\omega_{s'} t} + a_{s'}^\dagger e^{-i\vec{q}_{s'} \cdot \vec{b}'} e^{i\omega_{s'} t}) \right] e^{-i\vec{k} \cdot \vec{r}_{d'}(t)} \right\rangle \quad (6.35)$$

where $Z_{\kappa,s}^{d*} = \frac{Z_{\kappa}^{d*}}{(\sum_{\kappa} \vec{u}_{s,\kappa} \vec{u}_{s,\kappa}^*)^{1/2}}$. We have also replaced $\mu(t=0)$ and $\mu(t=t)$ only with the first order change in dipole term (i.e. second term in Eq. (6.26)) because the intrinsic, static dipole moment $\mu^d(0)$ (first term of Eq. (6.26)) is a constant for each molecule, with no atomic displacement dependence and hence will not contribute any phonon creation nor annihilation operators in the product. This also means that the material does not need to possess a permanent dipole moment to provide an ultra-low electron energy loss spectrum, as the crux of the energy loss comes from the change in dipole moment.

We now look towards the time dependence of the point dipole's position, $\vec{r}_d(t)$ in $e^{-i\vec{k} \cdot \vec{r}_d(t)}$. The definition of this position is slightly ambiguous as it can be viewed as either the centre of mass or centre of charge. Molecular vibrations do not change the centre of mass, but this is not necessarily true for the centre of charge. Consider two equal and opposite point charges of $m_1 > m_2$ at positions $\vec{r}_1 = 0$ and $\vec{r}_2 = \vec{r}$, such that the centre of charge is at $\vec{r}/2$. Due to the mass inequality in the eigenvectors of the two charges will be opposite and unequal in absolute displacement. Thus at maximum displacement, the centre of charge will be pulled towards the direction of the lighter charge (hence oscillating between this and the equilibrium position $\vec{r}/2$). As the dipole motion is small, we can Taylor expand $e^{-i\vec{k} \cdot \vec{r}_d(t)} \approx 1 - i\vec{k} \cdot \vec{r}_d(t) + \dots$ where $\vec{r}_d(t)$ can be expressed again in terms of the dipole's constituent atoms' phonon displacement operators. However, after a lengthy analysis (Appendix C), one can show that the phonon contributions to the $e^{-i\vec{k} \cdot \vec{r}_d(t)}$ can be approximated as 1, as any higher order terms are negligible compared to the phonon contributions to $\vec{\mu}(t)$.

Finally, we find the expression for the DDCS as

$$\begin{aligned}
 \frac{d^2\sigma}{d\Omega dE_1} = & \left\langle \frac{m^2 e^4}{N\hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar k^4} \int dt e^{-i\omega t} \sum_{bb'} e^{-i\vec{k} \cdot (\vec{b} - \vec{b}')} \sum_{dd'} e^{i\vec{k} \cdot (\vec{l}_d - \vec{l}_{d'})} \right. \\
 & \times \sum_{\kappa} Z_{\kappa}^{d*} c_{s,\kappa} \left[\sum_s (\vec{e}_s \cdot \vec{k}) (a_s e^{i\vec{q}_s \cdot \vec{b}} + a_s^\dagger e^{-i\vec{q}_s \cdot \vec{b}}) \right] e^{-i\vec{k} \cdot \vec{r}_d(0)} \\
 & \times \sum_{\kappa'} Z_{\kappa'}^{d'*} c_{s',\kappa'} \left[\sum_{s'} (\vec{e}_{s'} \cdot \vec{k}) (a_{s'} e^{i\vec{q}_{s'} \cdot \vec{b}'} e^{-i\omega_{s'} t} + a_{s'}^\dagger e^{-i\vec{q}_{s'} \cdot \vec{b}'} e^{i\omega_{s'} t}) \right] e^{-i\vec{k} \cdot \vec{r}_{d'}(t)} \Bigg\rangle
 \end{aligned} \tag{6.36}$$

→ Keep only 1 phonon creation $aa^\dagger$ term

$$\begin{aligned}
 \approx & \left\langle \frac{m^2 e^4}{N\hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar k^4} \int dt e^{-i\omega t} e^{i\omega_{s'} t} \sum_{bb'} e^{-i\vec{k} \cdot (\vec{b} - \vec{b}')} \right. \\
 & \times \sum_{dd'} e^{i\vec{k} \cdot (\vec{l}_d - \vec{l}_{d'})} \sum_{\kappa, \kappa'} \sum_{ss'} c_{s,\kappa} c_{s',\kappa'} (Z_{\kappa,s}^{d*} \vec{e}_{\kappa,s} \cdot \vec{k}) (Z_{\kappa',s'}^{d'*} \vec{e}_{\kappa',s'} \cdot \vec{k}) a_s a_{s'}^\dagger e^{i\vec{q}_s \cdot (\vec{b} - \vec{b}')} \Bigg\rangle
 \end{aligned} \tag{6.37}$$

$$\begin{aligned}
 = & \frac{m^2 e^4}{N\hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi\hbar k^4} \frac{L^6}{(2\pi)^6} \sum_{\vec{G}} \delta(\vec{k} - \vec{q}_s - \vec{G}) \langle n_s + 1 \rangle \\
 & \times \sum_s \delta(\omega - \omega_{\vec{q}_0,j}) \sum_{dd'} e^{i\vec{k} \cdot (\vec{l}_d - \vec{l}_{d'})} \\
 & \times \sum_{\kappa, \kappa'} \left(\frac{\hbar}{2N \sqrt{m_\kappa m_{\kappa'}} \omega_{\vec{q}_0,j}} \right) (Z_{\kappa,s}^{d*} \vec{e}_{\kappa,s}^d \cdot \vec{k}) (Z_{\kappa',s'}^{d'*} \vec{e}_{\kappa',s'}^{d'} \cdot \vec{k})
 \end{aligned} \tag{6.38}$$

where we again only consider the one phonon creation process. We have also used $\sum_{bb'} e^{-i\vec{k} \cdot (\vec{b} - \vec{b}')} e^{i\vec{q}_s \cdot (\vec{b} - \vec{b}')} = (\sum_b e^{-i(\vec{k} - \vec{q}_s) \cdot \vec{b}}) (\sum_{b'} e^{i(\vec{k} - \vec{q}_s) \cdot \vec{b}'} = \frac{L^6}{(2\pi)^6} \sum_{\vec{G}} \delta(\vec{k} - \vec{q}_s - \vec{G})$ for the summation of the unit cells b, b' .

Thus we have derived the dominant term in the ultra-low loss EELS for an aloof beam configuration, via a different method of charge splitting compared to the quantum impact case discussed in [Chapter 5](#). Comparing this result to the impact scattering derivation of [Eq. \(5.17\)](#), we notice that the Debye-Waller factor does not get introduced because we introduce the phonon displacement operators from the change in dipole moment rather than the exponential dipole displacement operator. We also note that the global constants in

both derivations for the impact and aloof beam scattering case are the same, making it easy to directly compare their absolute intensities. This is investigated in section [Part IV](#). This method leads to a natural way of introducing the dynamic Born charges instead of using static, constant charges (e.g. Mulliken charges used by Nicholls *et al.*) that are multiplied by the eigenvectors.

6.4 THEORETICAL RAMAN CONTRIBUTIONS

Ultra-low loss EELS is visually very similar to infrared spectroscopy. This is because the phonon contributions are introduced from changes in the intrinsic dipole moment, which is what is measured in IR spectroscopy. In [Eq. \(6.38\)](#), if a mode has no IR activity, the mode effective charge vector summed over all the atoms per mode vanishes. In the semi-classical case, this is manifested in the low frequency dielectric tensor ([Eq. \(4.44\)](#)), which contains the mode effective charge vectors. However, theoretically Raman active modes can also be excited by EELS by considering the induced dipole moment. In this section, we take a look at the relative contributions of the Raman modes and show that in accordance with the perceived comparability between IR and EELS, Raman active mode intensities are insignificant compared to that of IR active modes.

So far, we have assumed that the dipole moment is given by [Eq. \(6.26\)](#), the changes in the static dipole moment, $\mu_{\text{static}}(t)$. However, the fast electron can also induce a dipole moment a molecule that is proportional to its polarisability. We can therefore write the total time-dependent dipole moment as (omitting the dipole index d)

$$\mu_T = \mu_{\text{intrinsic}}(t) + \mu_{\text{induced}}(t) \quad (6.39)$$

where the induced moment is given by

$$\vec{\mu}_{\text{induced}}(t) = \alpha(t)\vec{E}(t) \quad (6.40)$$

where $\vec{E}$ is the macroscopic electric field and α is the polarisability. We can Taylor expand the polarisability tensor to first order derivatives such that

$$\alpha_{ij}(t) \approx (\alpha_{ij})_0 + \sum_s \left(\frac{\partial \alpha_{ij}}{\partial Q_s} \right)_0 Q_s(t). \quad (6.41)$$

The Raman scattering intensities is related to the square of this first order change in polarisability, given by [130]

$$I \propto |\vec{e}_S \frac{\partial \alpha}{\partial Q_s} \vec{e}_L|^2 \quad (6.42)$$

where $\vec{e}_S$ and $\vec{e}_L$ are the directions of the scattered and incident electric fields respectively. So what is the magnitude of the induced dipole moment relative to that of the intrinsic dipole moment (Eq. (6.26)) contributing to the DDCS? We can perform a back of the envelope calculation for this comparison. The rate of change of the intrinsic dipole moment for the molecular crystals that we will consider are on the order of $\mu_{\text{intrinsic}} \sim |Z^* \vec{u}|e \sim 1 \times 1e\text{\AA}$, where the order of magnitude for the Born charges Z^* and eigen-displacements $\vec{u}$ are average values taken from our CASTEP calculations in the treatment of several molecular crystals. This is discussed further in Part IV.

We must be careful in the treatment of μ_{induced} units. This is because CASTEP outputs of atomic polarizabilities α_{cgs} are in CGS (centimetre-gram-second) units [131] on the order of $\sim 1\text{\AA}^3$, so we will estimate the electric field strength $|\vec{E}|$ for this system as well. In CGS units, Coulomb's constant k_{Coulomb} is dimensionless and set to unity. The force (unit given by 1 dyne

$\equiv g \cdot \text{cm}/\text{s}^2 = 10^{-5}N$) between two electrons separated by a meter (using 100cm) is

$$F = 10^{-4}e_{esu}^2 \text{dyne} = 10^{-9}e_{esu}^2 N = \frac{1}{4\pi\epsilon_0} \frac{e^2}{(1m)^2} = \frac{\mu_0}{4\pi} \frac{c^2 e^2}{(1m)^2} \approx 10^{-7}c_{SI}^2 e_C^2 N \quad (6.43)$$

where e_{esu} and e_C are the electron charge in electrostatic (cgs) units and SI units respectively. $c_{SI} = 2.998 \times 10^8$ is the speed of light in SI units and thus we can relate $e_{esu} = 10c_{SI}e_C \approx 4.8 \times 10^{-10}$. For an electron at impact distance of $30nm = 300\text{\AA}$ away from the sample, the electric field magnitude is

$$|\vec{E}|_{cgs} = \frac{k_E \times e_{esu}}{r^2} = \frac{1 \times 4.8032042 \times 10^{-10}}{300^2}. \quad (6.44)$$

Converting the value of the induced dipole moment back into SI units comparable to that of the intrinsic dipole moment shows that the latter is dominant.

$$\begin{aligned} \vec{\mu}_{\text{induced}} &= e_{SI} \left| \frac{1}{e_{SI}} \times \alpha_{cgs} \right| \left| \frac{4.8032042 \times 10^{-10}}{300^2} \right|_{esu} \times \frac{1}{10c_{SI}} \hat{E} \\ &\approx e_{SI} \left[10^{-5} \alpha_{cgs} \hat{E}_{cgs} \right] \ll \mu_{\text{intrinsic}}^d \sim 1e_{SI} \end{aligned} \quad (6.45)$$

since $\left[10^{-5} \alpha_{cgs} \hat{E} \right] \ll 1$ using [Eq. \(6.44\)](#). Notice that in our simplified approximations above, we only treat the time-dependence of the polarisability and ignored that of the electric field $\vec{E}(t)$. For the purpose of our simplification, it is excessive to consider the electric field time dependence because the time scale at which the induced dipoles oscillate due to (causing changes in polarisability) is much larger than the time scale at which the electron passes. Thus we've treated the electric field as a constant vector.

As the Raman active mode contributions are negligible compared to that of the IR modes, it is not implemented in the numerical section [Part IV](#). However for completeness sake, a numerical assessment is provided below.

The rate of change of polarisability with respect to normal mode coordinate in Eq. (6.42) can be expanded as

$$\frac{\partial \alpha_{ij}}{\partial Q_s} = \sum_{\kappa} \frac{\partial \alpha_{ij}}{\partial u_{\kappa}} \frac{\partial u_{\kappa}}{\partial Q_s} \propto \sum_{\kappa} \frac{\partial \alpha_{ij}}{\partial u_{\kappa}} \frac{\vec{e}_{\kappa,s}}{\sqrt{m_{\kappa}}} \quad (6.46)$$

and since $\frac{\vec{e}_{\kappa,s}}{\sqrt{m_{\kappa}}}$ is proportional to the atomic displacement vector for the mode s , it can be replaced by the phonon displacement operator Eq. (5.12). The polarisability can be related to the total energy ϵ and force F on the atom via [65]

$$\frac{\partial \alpha_{ij}}{\partial u_{\kappa}} = \frac{\partial^3 \epsilon}{\partial E_i \partial E_j \partial u_{\kappa}} = \frac{\partial^2 F_{\kappa}}{\partial E_i \partial E_j} \quad (6.47)$$

where $E_x, x \in \{i, j\}$ is the electric field direction along x . This is helpful in the numerical implementation since for each dipole, Eq. (6.47) is obtained by summing the forces on each atom when exposed to electric fields along the all the cartesian directions.

6.5 TREATMENT OF BULK CRYSTALS

The dipole theory discussed so far cannot be directly applied to bulk crystals because the definition of dipole moment per ‘molecule’ becomes ambiguous. Instead, it is more reasonable to use the polarisation per unit cell instead of dividing it up into ‘dipoles’. We can again use multipole expansion of the specimen charge potential, keep the dipole term (analogous to the treatment of molecular crystals in the previous section) to derive the energy loss. However, instead of expanding the charge around each single molecule treated as a point dipole, we treat each unit cell as a whole instead such that the molecular dipole moment $\vec{\mu}_d$ in 6.7 is replaced by $\vec{\mu}_{\text{cell}}$. The rate of change of the dipole moment of the unit cell with respect to atomic displacements for each unit cell’s absolute polarisation/dipole moment directly relates to the BEC

(instead of the mode effective charge used in [Section 6.3](#)). Hence, numerically we do not need to perform the computation of absolute polarisation. Following through with the rest of the derivation, which is essentially identical to the procedures from [Sections 6.1](#) to [6.3](#), we arrive at the following expression for the DDCS for bulk crystal,

$$\frac{d^2\sigma}{d\Omega dE_1} \approx \frac{m^2 e^4}{N \hbar^4 \epsilon_0^2 (2\pi)^2} \frac{k_1}{k_0} \frac{1}{2\pi \hbar k^4} \frac{L^6}{(2\pi)^6} \sum_{\vec{G}} \delta(\vec{k} - \vec{q}_s - \vec{G}) \langle n_s + 1 \rangle \quad (6.48)$$

$$\times \sum_s \delta(\omega - \omega_{\vec{q}_0, j}) \sum_{\kappa, \kappa'} \left(\frac{\hbar}{2N \sqrt{m_\kappa m_{\kappa'}} \omega_{\vec{q}_0, j}} \right) \times (Z_{\kappa, s}^{\text{cell}*} \vec{e}_{\kappa, s} \cdot \vec{k}) (Z_{\kappa', s}^{\text{cell}*} \vec{e}_{\kappa', s} \cdot \vec{k}) \quad (6.49)$$

This is very similar to [Eq. \(6.38\)](#), except that $Z_{\kappa, s}^{\text{cell}*}$ is simply replaced by the Born effective charge, the change in dipole moment of the entire unit cell. In [Chapter 13](#), we use [Eq. \(6.49\)](#) in conjunction with the semi-classical and quantum impact scattering theories to evaluate the ultra-low loss EELS for bulk crystal Boron Subphosphate.

6.6 OTHER QUANTUM ALOOF BEAM FORMALISMS

Our analysis have focused on the electron energy loss from the material's perspective by treating the electron as a plane wave imparting momentum onto a target characterised by its structure factor. One can also approach the problem from the perspective of the scattered electron, as done by Dwyer [\[37, 132, 133\]](#) where the key quantity of interest is the Møller potential. This is the potential experienced by the fast electron as it excites a vibrational mode s . The Møller potential in two-dimensions has the form [\[132\]](#)

$$V_s(x, y) = \left(\frac{\hbar(n_s + 1)}{2\omega_s} \right)^{1/2} \sum_{\kappa} \frac{\vec{e}_{s, \kappa}}{\sqrt{m_\kappa}} \cdot \nabla_{\kappa} V(x, y) \quad (6.50)$$

where $\nabla_{\kappa} V(x, y)$ is the derivative of the electric potential energy with respect to atom κ 's position. They split the potential into two parts, an 'impact' and a 'dipole' part. The impact part includes the vibrational effects of the charge distribution when not considering bonding, i.e. the potential due to nuclear displacements. The omission of bonding and charge transfer is reminiscent of our quantum impact scattering theory of [Section 5.2](#), because only point charge interactions are considered in the interaction Hamiltonian and charge transfer was not considered in the derivation of [Eq. \(5.17\)](#). The latter 'dipole' part of the Møller potential considers the bonding charges of the electron charge density. The charge density is assigned by unit cell and in taking the derivative of this charge density they introduce the BEC tensors. They applied this work to study hexagonal boron nitride, and argued that as $k \rightarrow 0$, the dipole term dominates over the impact term, which also should be the trend using the quantum and dipole theories in [sections Chapter 5 and Chapter 6](#).

Qualitatively, the Møller potential approach describes inelastic scattering using wavefunctions, such that there is one inelastic wave for each possible excited state of the sample. Our derivation, which follows the Van Hove approach, gives a similar result from a different perspective, but should ultimately be equivalent. We do not need the scattered electron wavefunctions for each excited mode, and group it all together as we do not consider the spatially resolved spectrum as opposed to Dwyer.

A main difference between Dwyers treatment from our work is that we provide an investigation into both molecular and bulk crystals. In the former, we treat the molecules as point dipoles and evaluate their interactions explicitly, through the mode effective charge vector (similar but not equivalent to using the Born effective charge tensors). In the bulk crystal case, we do indeed arrive at the BECs similar to Dwyer. The origin of the dynamic charges are also different. In our case, we obtained these via the Taylor expansion of

the dipole charge density, whereas Dwyer obtained this through the Taylor expansion the vibrating target's long-range macroscopic electric field.

SUMMARY AND DISCUSSION

In this part of the thesis, we've gone through the semi-classical and quantum impact scattering formalisms commonly used in literature the analysis of both impact scattering and aloof beam EELS. We then derived the DDCS for the aloof beam setup by writing the total charge density as a sum of multipole expansions around each molecule in a molecular crystal. We showed that this organically introduced the dynamic BEC tensors that dominate as the momentum transfer $\vec{k} \rightarrow \vec{0}$. This is in contrast to many current methods which discretise the crystal charge density in the Hamiltonian merely as a sum of point charges and then introduce an arbitrary charge transfer term later on such as Milliken charge redistribution or the BECs, to recover long range effects.

The momentum imparted by the fast electron in aloof beam, $\vec{k}$ is often denoted as $\vec{k} \rightarrow \vec{0}$. For example in the semi-classical regime, the dielectric tensor is calculated by approximating $\vec{k} = \vec{0}$. In reality, this is not actually equal to zero, as this corresponds to no momentum exchange and the electron essentially does not interact with the system. Since phonon vibrational frequencies are $\vec{k}$ dependent, this highlights an issue of the semiclassical theory in the context of aloof beam EELS. It will also lead to a divergence in the quantum impact and dipole scattering terms in [Eq. \(5.17\)](#) and [Eq. \(6.38\)](#), since they both have a $\frac{1}{|\vec{k}|^4}$ dependence. Intuitively, the quantum impact scattering term should dominate at higher values of $\vec{k}$, whereas the aloof beam theory should dominate as $\vec{k} \rightarrow \vec{0}$. At the other extreme, $\vec{k} \rightarrow \infty$ does not denote core-loss EELS. This requires introducing electronic transitions instead of phonon transitions in the system's initial and final states $|n_0\rangle$ and $|n_1\rangle$. The impact scattering formalism does not directly include the physics of dipole

scattering and has the issue of non-rigorous analytical charge division (see [Section 5.2](#)), which requires a manual addition of charge transfer. Several authors [[134, 135](#)] have used this manually added term to explain the aloof beam configuration by attributing the ‘dipole’ contribution to the long-range, unscreened Coulomb potential.

There are some complications to the theory that are not formally considered in our work. Firstly, surface polaritons are ignored. These are surface modes present due to the edge of the material, and are nontrivial to include. We have assumed bulk phonon modes throughout our derivation, i.e. neglecting surface contributions from the sample edge. Surface plasmons are collective electronic oscillations at the dielectric/vacuum interface. One can use the free electron energy/Drude model to estimate that of the plasmon energy. In a plasma, the well known plasma frequency is inversely proportional to the electron’s root effective mass, i.e. $E \propto \frac{1}{\sqrt{m_e^*}}$, which result in energy losses of several eVs [[136](#)]. This is well above our region of interest for lattice vibrational modes, and can be effectively ignored together with bulk plasmon excitations. Finally, as electrons become completely delocalised in the limit of purely metallic compounds, the Taylor expansion of the charge distribution breaks down as one cannot constrain the electrons to a specific atom/molecule. This is not an issue with our compounds of interest such as pharmaceuticals and semi-conductor devices in later sections.

Because the target is effectively a thin film, distortions to the phonon dispersion curve arise through various ways [[137, 138](#)]. For example, LO-TO splitting is an important effect introduced in [Section 3.2.4](#). This always exists no matter what the thickness of the sample is because it originates from the nature of the atomic vibrations. In our calculations we assume bulk atomic motion, and hence there will be no thickness dependence in the LO-TO splitting effects to the phonon energies and eigen-vectors as we approach the Γ

point. Other optical effects that can cause distortions are interference, diffraction, etc. which are also neglected. The way that these effects will manifest in our ultra-low loss EELS theories is through the eigenvectors and charge transfers that will occur at the momentum transfer vector. This ignorance can be one of the sources of the discrepancies between our simulated and experimental spectra.

We can make an interesting analogy to an alternative method of calculating energy loss spectra, through *ab initio* molecular dynamics. Here, the statistics and dynamics of nuclei and electron are obtained through their classical equations of motion. This method is less computationally demanding but at the cost of using classical approximations. For example, in the case of IR spectroscopy, the absorption intensity is related to the dipole correlation function $\langle \hat{M}(0)\hat{M}(t) \rangle$ where $\hat{M}$ is the total dipole operator of the sample. In the classical limit, the operators are replaced by their classical counterparts and used in a molecular dynamics simulation. The dipole time correlation function is the canonical ensemble thermal average of the system. The physical intuition of how external perturbations $f(t)$ cause equilibrium fluctuations can be understood via the fluctuation-dissipation theorem [139],

$$\langle \vec{M}(t) \rangle = \langle \vec{M}(0) \rangle + \int_{-\infty}^t f(\tau) \chi(t - \tau) d\tau + O(f^2) \quad (7.1)$$

where χ is a generalised response function of the system. We can make an analogy between this IR and our quantum dipole scattering approach in [Section 6.3](#), where the EELS intensity is also related to the dipole-dipole correlation function and the treatment of equilibrium fluctuations comparable to [Eq. \(7.1\)](#) is the normal coordinate expansion of the dipole moment using [Eq. \(6.26\)](#).

One of the original motivations to use EELS to study energy loss spectroscopy was that they have good spatial resolution. In the aloof beam mode we lose some of the very fine spatial resolution with increasing impact parameter and there is thus a trade-off between good spatial resolution and less sample degradation. This can be somewhat remedied by first detecting the vibrational energy loss profile at a large impact parameter, and subsequently bringing the beam closer to the sample to obtain the spatial profile, inevitably yielding to beam damage. Nonetheless, ultra-low loss EELS still have the advantage over IR and Raman due to its ability of selecting a specific momentum transfer vector. An area of application in which this momentum resolution is useful is in the case of composite materials such as core-shell nanoparticles [140]. Specifically, consider core-shell polymorph pharmaceuticals. These are on the same order of magnitude as the sample size used in TEM and EELS. The microstructure of this consists of a drug enclosed in an envelope shell so we can have a mixing of different drugs and different polymorphs. The increased sensitivity of the dipole theory to the directionality of the k -vector and ability to more accurately predict the vibrational spectrum brings us one step closer to distinguishing for example pure crystals from mixed polymorphs. For example, experimental spectra can be obtained along different momentum transfer directions of a core-shell drug potentially containing a polymorphic mixture (which can potentially be harmful). By simulating the spectra of the possible pure crystal polymorphs, one may be able to identify traces of one or more polymorph to determine the purity of the drug.

Part III

AB INITIO CALCULATIONS USING CASTEP

This part contains the numerical details required for successful DFT simulations. In addition to vibrational properties that are needed for EELS simulations in later sections, in this chapter we are also interested in using DFT for NMR. NMR characterises the absorption/emission spectrum of atomic nuclei with sensitivity to their local chemical environments and orientation. This makes it very attractive in analysing non-ideal crystals consisting of different polymorphs, grain boundaries, etc. Thus, improving NMR simulations combined with ultra-low loss EELS can be used to synergistically study pharmaceutical molecular crystals.

In [Chapter 8-Chapter 9](#), convergence tests, geometry optimisation and calculations of vibrational and NMR parameters on a hand-full of carboxylic and are explored. We work primarily with dispersion corrected PBE and the recently implemented meta-GGA rSCAN functional. Subsequently, [Chapter 10](#) deals with numerical details of the semi-classical and quantum ultra-low loss theories.

CONVERGENCE TESTING : HEXAGONAL BORON NITRIDE

In a periodic crystal, the KS molecular orbitals satisfy Bloch's theorem [83,141] such that (for wave vector $\vec{k}$)

$$\phi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}), \quad (8.1)$$

where $u_{\vec{k}}(\vec{r})$ is periodic upon translations by any real space lattice vectors $\vec{T}$ such that $u_{\vec{k}}(\vec{r} + \vec{T}) = u_{\vec{k}}(\vec{r})$ and can be as a fourier expansion

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k},\vec{G}} e^{i\vec{G}\cdot\vec{r}} \quad (8.2)$$

for coefficients $c_{\vec{k},\vec{G}}$ and reciprocal lattice vectors $\vec{G}$. Therefore, $\phi_{\vec{k}}(\vec{r})$ is a superposition of plane-waves that preserves the periodic boundary condition. Various properties of interest such as charge density, response functions, dielectric constants, etc require an integral over the Brillouin zone (BZ) [142]. For example, the electron charge density expressed in terms of these Bloch waves (indexed by energy band n) is given by [143]

$$n(\vec{r}) \propto \sum_n \int_{BZ} |\psi_{n,\vec{k}}(\vec{r})|^2 \quad (8.3)$$

Numerically, this integral is discretised using a weighted sum over a special grid of k-points, termed the Monkhorst-Pack (MP) mesh grid [142]. Since it is unfeasible to describe the Bloch states using an infinite number of plane waves, one must pick a maximum $\vec{G}_c$, the largest fourier component in the plane wave basis set $e^{i\vec{G}_c\cdot\vec{r}}$ for the sum in Eq. (8.2). This is defined as the

cut-off energy, $E_{\text{cut-off}}$ (since for a free electron this is $\frac{\hbar^2 |\vec{G}|^2}{2m_e}$). $E_{\text{cut-off}}$ and the MP-grid are two main parameters to adjust in testing the convergence of the total ground state energy.

A well converged geometry is essential to determine vibrational properties needed for EELS calculations. The *ab initio* softwares used throughout this work are CASTEP [144] and QUANTUM ESPRESSO [145, 146], both plane-wave codes.

We can demonstrate the importance of convergence tests using calculations performed on hBN. Figure 8.1 (a) and (b) shows that despite the apparent convergence of cut-off energy, a change in k-spacing can greatly shift the calibrated curve. The experimental bond length reported in literature is 1.44Å [147], which from Fig. 8.1 (b) requires a k-spacing of at least $\sim 0.15\text{\AA}^{-1}$. If the geometry optimisation is inadequately well converged and produces excess forces on the atoms, the secular equation will return non-physical, imaginary frequencies. The result of this is demonstrated in the phonon dispersion curve plotted in Fig. 8.1 (c), where a badly converged geometry gives rise to negative phonon modes.

The total electronic wavefunction is represented on a standard FFT grid (reciprocal space). At each grid point, the wavefunction is expanded into a finite sum of plane-waves truncated a cut-off $\vec{g}$ vector. The grid scale determines the maximum $\vec{g}_{\text{max}}$ vector used in this summation. When attempting to account for core charges, one may need to use a finer grid than the standard to better represent the electronic charge density. This is controlled by the fine grid scale parameter. Adjustment to this was not needed for the PBE functional used in boron nitride calculations. However, we revisit this parameter later in Section 9.2 as the default fine grid size was insufficient for the rSCAN functional.

CONVERGENCE TESTING : HEXAGONAL BORON NITRIDE

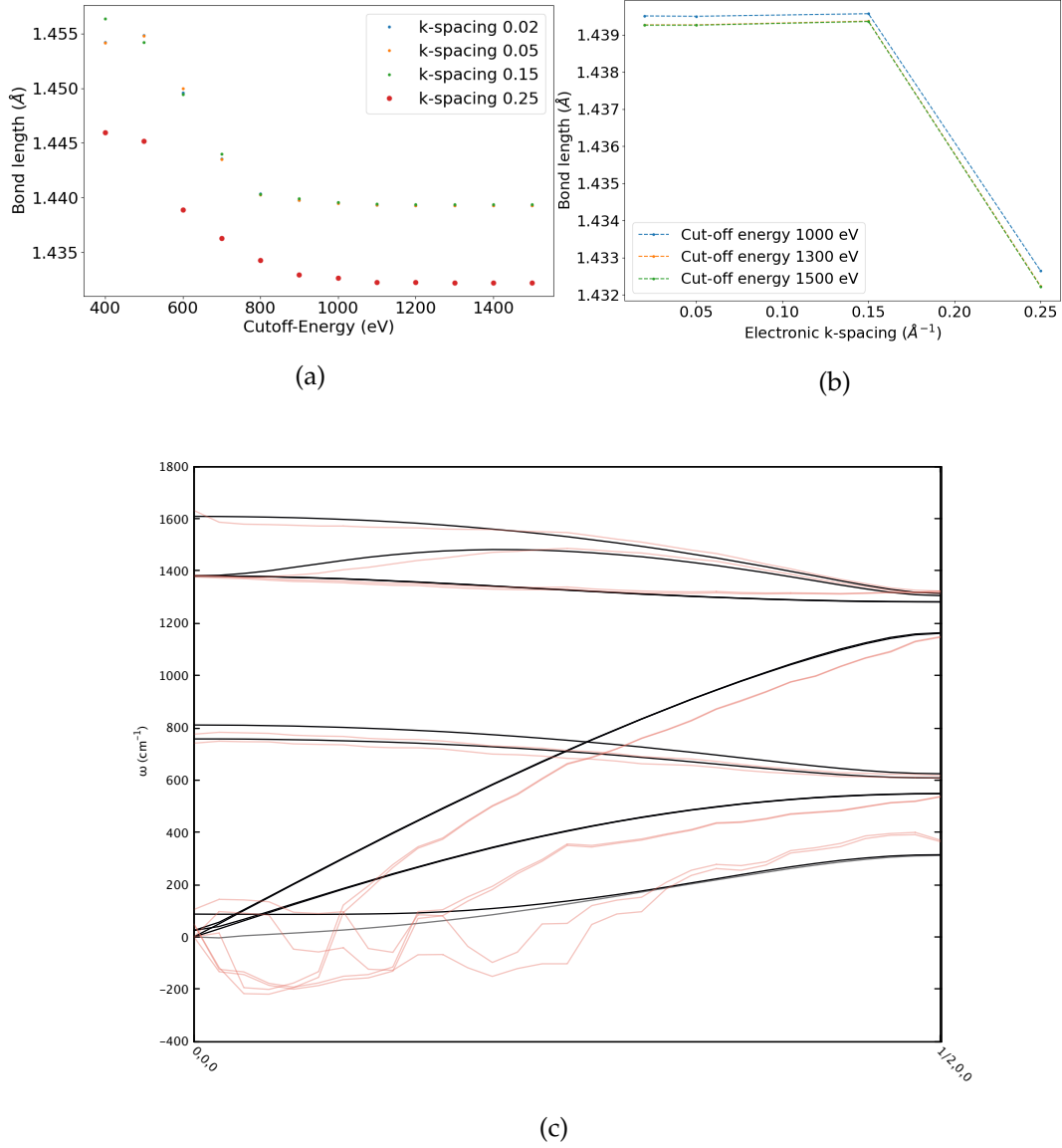


Figure 8.1: Hexagonal boron nitride convergence test. (a) Effect of cut-off energy on equilibrium bond length, stabilising after ~ 900 eV. (b) Effect of k-spacing on equilibrium bond length at different stable cut-off energies. The number of k-points used with k-spacings of 0.02, 0.05, and 0.15 Å⁻¹ are 624, 60 and 2 respectively. (c) Phonon dispersion curve along $\Gamma \rightarrow M$, with good convergence (black) using k-spacing of 0.02 Å⁻¹, $E_{\text{cut-off}} = 1500$ eV and a badly converged (red) plot with k-spacing of 0.45 Å⁻¹ and $E_{\text{cut-off}} = 600$ eV.

BENCHMARKING PROPERTIES OF MOLECULAR CRYSTALS

This chapter uses CASTEP to benchmark and compare the recently implemented meta-GGA functional, Regularised Strongly Constrained and Appropriately Normed (rSCAN), against that of PBE with dispersion corrections through their ability to evaluate material properties. Focus is placed on the vibrational and NMR parameters of a manually selected molecular crystal set.

9.1 RSCAN VS PBE + DISPERSION

The SCAN functional [148] is a meta-GGA which satisfies all the constraints required for a semi-local functional [149]. The E_{XC} energy includes the electron density and its gradient, as well as the orbital kinetic energy densities of the occupied KS orbitals, $\tau(\vec{r}) = \sum_{KS}^{\text{occupied}} \frac{|\nabla \psi_{KS}(\vec{r})|^2}{2}$. This has been demonstrated to improved DFT calculations across a variety of systems by simultaneously being able to capture metallic and covalent bonding effects [150, 151]. Studies have found it especially successful in capturing mid-range vdW effects on variously bonded molecular crystals, as opposed to conventional GGA functionals, which require additional dispersion corrections. However, the errors arising from long-range self interactions are yet to be properly addressed.

Most plane-wave implementations of SCAN are only suited for norm-conserving pseudo-potentials, with associated problems such as numerical instabilities in solving the KS equation. Furthermore, difficulties in the construction of the pseudo-potentials and slow convergence with the plane-wave basis set has set back SCANs popularity. Thus, many users default to more widely accepted

functionals such as PBE. These issues prompted the development of rSCAN by Bartok and Yates [93], which fixes the numerical instabilities encountered in SCAN. Its performance is compared to the PBE functional used in conjunction with either the Tkatchenko-Scheffler (TS) [152] or a many-body dispersion (MBD*) scheme [153]. Further works by Furness *et al.* [154] led to the construction of r²SCAN, which attempts to unify the advantages of SCAN and rSCAN.

9.2 OPTIMISED GEOMETRIES

Tkatchenko and Reilly [155] proposed the X23 dataset of molecular crystals for with the purpose of benchmarking the effects of many body dispersion contributions (MBD and TS) plus thermal corrections to experimental lattice energies. The X23 dataset consists of systems dominated by hydrogen bonding, vdW forces and mixtures of both, making it a comprehensive overview of the prevalent intermolecular environments in molecular crystals. The X23 set (excluding ammonia, which was obtained from Materials Project with ID: mp-779689) are listed in Table F.3 together with their identifier from either the CSD or Crystallography Open Database (COD). We are specifically interested in the structural predictions and their relations to the geometry dependent properties such as the corresponding NMR and phonon spectra.

A geometry optimisation convergence test was first performed on Uracil similar to that of hBN in Chapter 8 to determine satisfactory input parameters for all crystals under consideration in this chapter (See Appendix F.0.1). As a result, the benchmark crystals were subjected to a plane-wave cutoff of 1200 eV, an MP grid spacing of $0.05 \text{ \AA}^{-1}$, and atomic energy and force tolerances of $2.219 \times 10^{-9} \text{ eV}$ and $10^{-3} \text{ eV/\AA}$ respectively. These parameters are also employed for the molecular crystal EELS simulations later in Part IV.

The default value for the fine grid parameter (one) works well for PBE with dispersion corrections, but in rSCAN calculations this results in fluctuating lattice parameters and this lengthening/shortening creates a shearing effect. This aliasing problem is solved when increasing the fine grid parameter to 4, and will be the value used across all functionals for consistency purposes. The combination of functionals and dispersion correction schemes for the DFT simulations include PBE, PBE with TS, PBE with MBD*, rSCAN and rSCAN with MBD*.

Thermal expansion of the unit cell at finite temperature and interactions over length scales larger than the unit cell will result in a momentum vector dependence of phonon eigenfrequencies. It is common to calculate the lattice energies,

$$E_{\text{lattice}} = \frac{E_s}{Z} - E_g, \quad (9.1)$$

to compare against experimental sublimation enthalpies. E_g is molecule's energy in its lowest energetic, gaseous phase. The unit cell has Z molecules and total energy E_s . This is so that vibrational contributions can be added to the sublimation enthalpies, for comparisons against experiments. This will not be of concern to us as we will focus only on the Γ -point. We simplify calculations even further by neglecting thermal effects. This is because the deviations of temperature dependent structures from static DFT structures will be systematic, and we are interested in studying the relative difference in the ability of the functionals to capture long-range dispersion forces. Hence it is more suitable to use reduce the number of factors affecting the result, such as temperature/anharmonic effects. Therefore, without these finite temperature corrections, it is expected that experimental geometries (performed at finite temperature) should give systematically larger lattice parameters.

The percentage volume deviation from literature experiments are shown in [Fig. 9.1](#), comparing the performance of the different functionals and ac-

companying dispersion corrections. As expected, the bare LDA functional systematically notoriously overbinds (especially for molecules) which is commonly reported in literature [156, 157]. Since the XC energy is taken as that of a homogenous electron gas, in highly inhomogeneous environments such as atoms and molecules this becomes an issue. Lattice parameters are usually under-predicted, leading to a large negative volume deviation when compared to literature experiments. The bare PBE functional on the other hand, systematically underbinds, which is also anticipated [158–161], resulting in larger unit cell volumes. The bare rSCAN functional achieves very similar results to PBE+TS (DFPT denote that perturbation theory will be used to calculate subsequent phonon parameters), thus demonstrating its ability to capture long range effects that conventional GGAs cannot do alone. However, MBD* corrected rSCAN systematically overbinds, which is reminiscent of LDA.

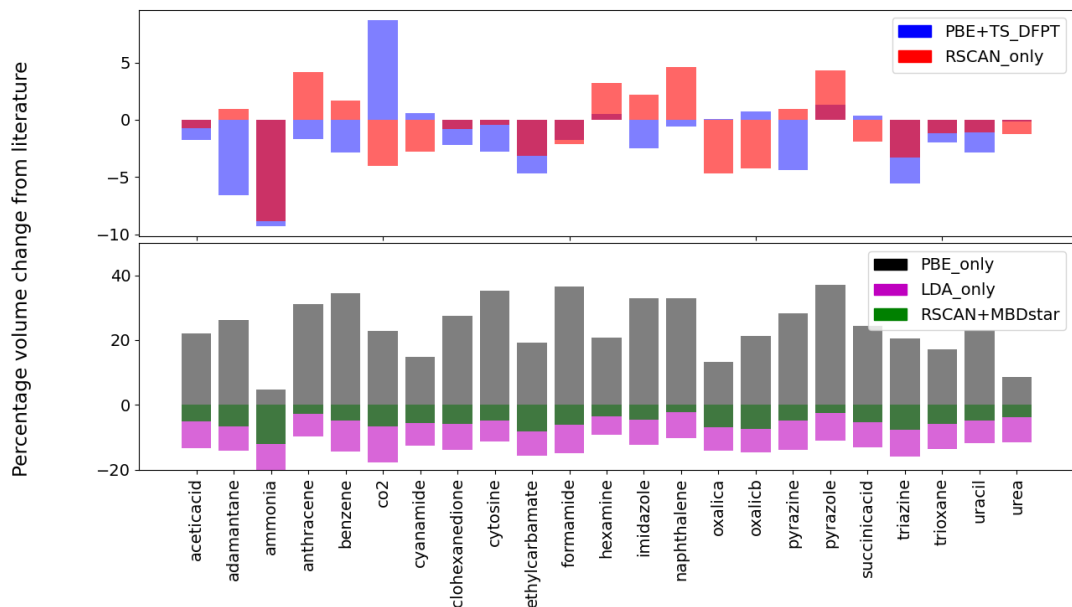


Figure 9.1: Percentage volume deviations from literature of optimised geometries of X23 dataset using various XC functionals and dispersion schemes. A transparency factor applied to the colour bars for ease of comparison may cause the legends to appear dissimilar.

Now that some fundamental behaviours of the functional performances are established with the X23 dataset, we now additionally handpick 10 carboxylic and 10 amino acids with their names and identifiers listed in [Table F.4](#). The carboxylic acids were picked with unit increments to the carbon chain to provide progressively more vdW dominant environments, whilst the amino acids were chosen based on the currently existing literature experiments on their pure crystalline NMR spectra. A relative comparison to literature is presented in [Fig. 9.2](#), showing a similar result as that of [Fig. 9.1](#). rSCAN is also paired with MBD*, which systematically overbinds all the crystals more dramatically than PBE paired with the same dispersion correction. Given that calculations were done without thermal and zero point energy corrections, one would naturally expect a reduction optimised volumes compared to that of experiments. This is generally the case for both rSCAN and PBE+TS. The latter typically underestimates volume more than rSCAN and focusing on the carboxylic acids, this effect becomes increasingly noticeable as the carbon chain gets longer and more intermolecular effects arise. The crystals across both datasets in which rSCAN overshoots in volume prediction are all dominated by London dispersion forces rather than hydrogen bonding. MBD* corrected rSCAN underpredicts volumes across all chosen crystals more severely than MBD* corrected PBE, further supporting the notion that it independently encapsulates dispersion forces.

The exact volumetric percentage deviations from experiments for all of the crystals in question is presented in [Table F.3](#) and [Table F.4](#).

9.3 Γ -POINT PHONONS

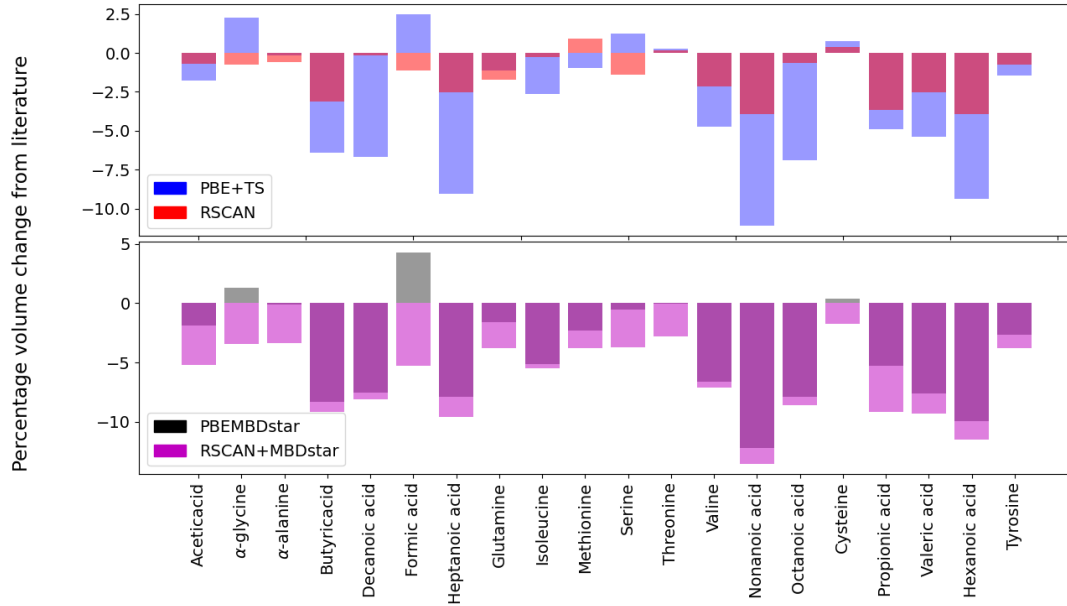


Figure 9.2: Percentage volume deviations from literature of optimised geometries of handpicked molecular crystal dataset using various XC functionals and dispersion schemes.

9.3 Γ -POINT PHONONS

With rSCAN, vibrational modes at the Γ -point are calculated using ultra-soft pseudopotentials and the finite displacement method, since at the time of writing this functional is not yet implemented with the linear perturbation method. This does not require a supercell as there are no $\vec{q} \neq \vec{0}$ vectors that are non-commensurate with the unit cell.

For the same crystal, it is not guaranteed that different functionals will retain the ordering of the modes, especially for eigenvalues that are closely spaced. Thus, the orthonormality of the modes' eigenvectors are checked for each crystal to ensure that no mode re-orderings occur. Focusing on the handpicked dataset in Fig. 9.2, PBE+TS tends to overbind systems more than rSCAN, which suggests that we would expect rSCAN to give larger lattice parameters, more relaxed structures and thus lower phonon frequencies due

to lower restoring forces. However, comparisons of the vibrational frequencies for the handpicked dataset using PBE+TS and rSCAN indicates the exact opposite trend, shown in Fig. 9.3. rSCAN consistently shifts these modes to higher values and this trend becomes increasingly apparent with increasing frequency. The deviations are outside the limits of errors possibly arising from fluctuations of input parameters (such as cut off energy, k-point spacing and energy/force tolerances). These deviations are also visibly outside the region spanned by variations due to the choice of dispersion scheme, as shown by the red dots which compares the MBD* and TS corrections using PBE. Hence, the variations are functional based.

9.3 Γ -POINT PHONONS

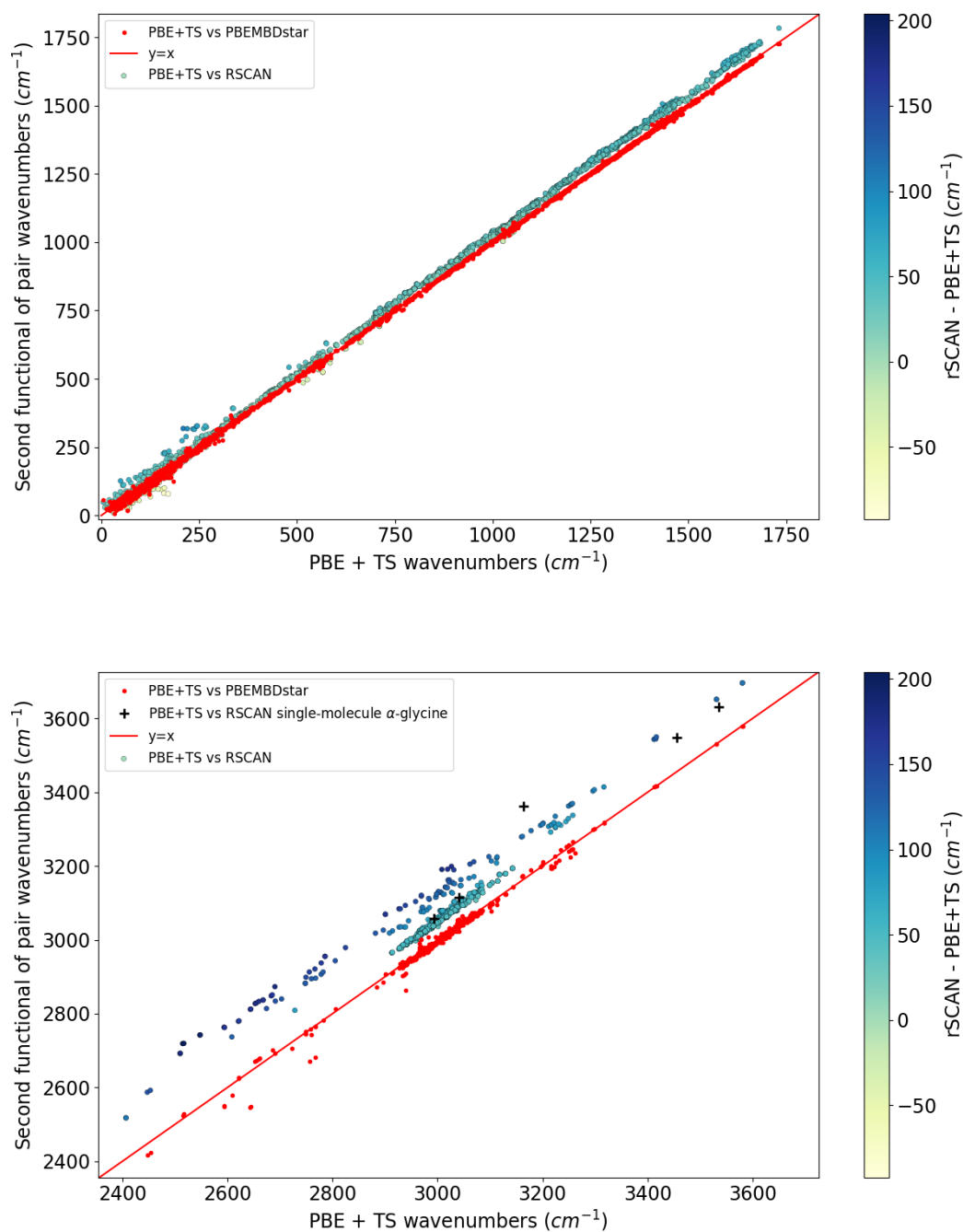


Figure 9.3: Comparisons between PBE+TS vs PBE+MBD*, as well as PBE+TS vs rSCAN of Γ -point vibrational modes of the handpicked crystal dataset. The colour bars on the RHS are included to help visualise the range of the relative frequency differences between rSCAN and PBE+TS. (Top) The lower frequency vibrations, i.e. heavier atomic motion. (Bottom) Modes corresponding to intramolecular hydrogen bonds (such as C-H, N-H and O-H at frequencies above $2000cm^{-1}$).

Figure 9.3(b) also includes the vibrational mode calculations of a single molecule of α -glycine (shown in black crosses), isolated in a supercell to avoid interactions between its periodic images. The performance differences between rSCAN and PBE+TS for the single molecule are on the same order of magnitude as that of its crystalline form, which suggests that intra-molecular bonds are the main source of these frequency shifts, rather than intermolecular separation and lattice relaxation. Visually, there is a cluster of modes that rSCAN consistently shifts upwards by $\sim 50\text{cm}^{-1}$, as well as an umbrella of frequencies shifted by $\sim 100\text{cm}^{-1}$. A closer inspection of the atoms participating in these modes show that the former is attributed to C-H stretches. This is clustered around 3000cm^{-1} and agrees with Hooke's mechanical spring and mass approximation of the vibrational frequency range,

$$f = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (9.2)$$

where k and μ are the force constant and reduced mass respectively [162, 163]. The highest frequency deviations (100cm^{-1}) correspond to O-H and N-H stretching modes and the bonds participating in each mode is colour coded in Fig. 9.4. The shifts in phonon frequencies are quantified as the percentage decrease of intra-molecular bond lengths from PBE+TS to rSCAN, summarised in Fig. 9.5 and Table 9.1.

9.3 Γ -POINT PHONONS

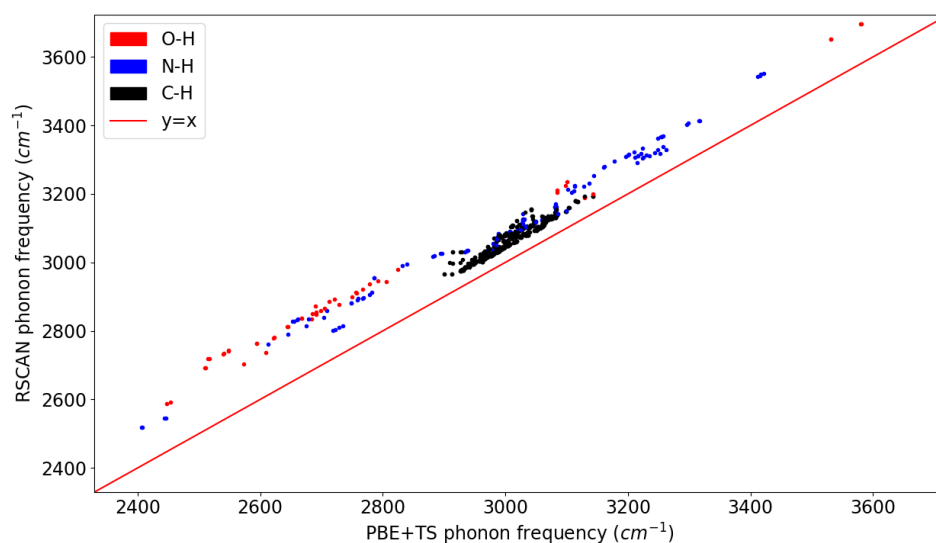


Figure 9.4: Comparing PBE+TS vs rSCAN performance on the handpicked molecular crystal dataset phonon modes, colour coded according to which atoms participate the most in the eigenvector.

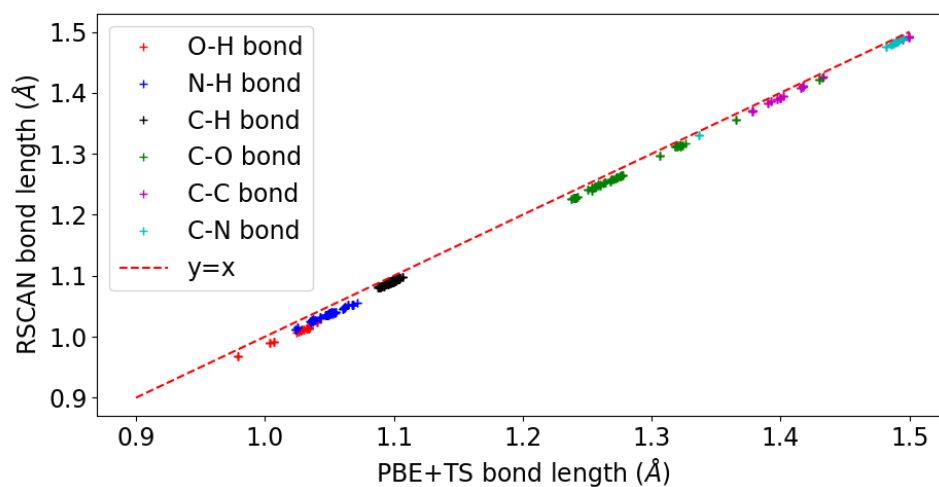


Figure 9.5: Intra-molecular bond lengths from rSCAN and PBE+TS optimised geometries of handpicked molecular crystals, grouped by the corresponding atoms attached.

Bond type	O-H	N-H	C-O	C-H	C-C	C-N
MRD	-1.68	-1.19	-0.83	-0.72	-0.53	-0.40

Table 9.1: The mean relative deviation (MRD) of the averaged percentage change of bond lengths from PBE+TS to rSCAN for the handpicked molecular crystal data set.

Comparing rSCAN against PBE+TS, the consistent and gradual increase of phonon frequency deviations with increasing wavenumbers due the shortening of intra-molecular bonds may be a positive affirmation. It has been shown in literature that dispersion corrected PBE can under-predict high frequency hydrogen based phonon modes [164,165], thus substantiating the overall trend.

9.3.1 NMR spectroscopy - a brief introduction

Before delving into simulating NMR parameters, we begin with a bit of theoretical background. The theory of NMR is hinged on the interactions between an applied magnetic field and nuclear spin. When a magnetic field B_0 is applied, the eigenstate energies of the the angular momentum operator for a particle with spin M is given by [166]

$$E_m = -m\hbar\frac{1}{2m}B_0 \quad (9.3)$$

where m can take on integer values between $\pm|M|$. For example, for a spin half nucleus the splitting of the spin up and down states under the magnetic field gives rise to the Zeeman effect.

An externally applied magnetic field $\vec{B}_0$ induces an electric current, which in turn produces an induced magnetic field $\vec{B}_{\text{in}}$. This is related to the applied field via

$$B_{\text{in}} = -\hat{\sigma}(\vec{r})\vec{B}_0. \quad (9.4)$$

For insulating and non-magnetic material only orbital angular momentum contributes to the electronic current. In general, the chemical shift can be anisotropic, i.e. they are field orientation dependent, which causes broadening in the NMR spectrum and produces a non-diagonal chemical shift tensor $\hat{\sigma}(\vec{r})$.

Practically, an NMR spectrum displays the shift in frequencies from a reference compound using the chemical shift measured in parts per million (ppm) as illustrated in Fig. 9.6. This is defined by

$$\delta(ppm) = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6 \quad (9.5)$$

where ν is the measured NMR frequency, and ν_{ref} is that from a reference compound, defined at $0ppm$.

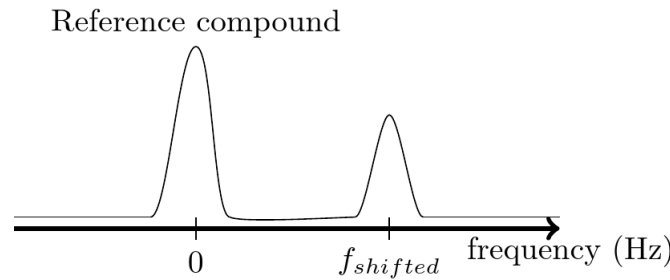


Figure 9.6: NMR spectrum of reference compound defined at $0ppm$ and a shifted frequency which is dependent on the strength of the applied magnetic field.

A larger field strength results in higher frequency shifts, and hence it is important to correctly calibrate the results using this reference. The environment of an atom greatly affects its chemical shift. For example if a carbon bonded to an atom X that is more electronegative, it hoards the electron cloud, effec-

tively de-shielding the carbon and increasing the chemical shift. The chemical shift is also practically defined as [167]

$$\delta(ppm) = \sigma^{ref} - \sigma \quad (9.6)$$

where σ is the isotropic average ($\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$) of the magnetic shielding tensor that can be obtained from a DFT calculation.

Numerically, NMR parameters are implemented in CASTEP using the GIPAW method [168, 169, 169]. The induced magnetic field can be obtained through perturbation theory so that $\sigma(\vec{r})$ can be computed using Eq. (9.4).

Another physical quantity of interest is the electric field gradient (EFG). This is a measurement of change in electric field due to atomic displacements in a nucleus arising from the surrounding electronic and nuclear charge densities. The EFG, $V_{\alpha\beta}(\vec{r}) = \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta}$ [170], the second derivative of the electrostatic potential (excluding nuclear contributions), is a ground state property and can be written as [171]

$$V_{\alpha\beta}(\vec{r}) = \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|^3} \left[\delta_{\alpha\beta} - 3 \frac{(r_\alpha - r'_\alpha)(r_\beta - r'_\beta)}{|\vec{r} - \vec{r}'|^2} \right], \quad (9.7)$$

which depends on the static charge density, $n(\vec{r})$.

9.4 AB INITIO NMR CHEMICAL SHIFTS

The isotropic chemical shifts (CS) and electric field gradients EFG are common NMR parameters pertinent to experimentalists. These are computed using the GIPAW method introduced in Section 3.5, and the values for ^{13}C and ^{17}O compared to experiments [172–177] are presented in Fig. 9.7. The slope of the isotropic chemical shift $\sigma_{\text{CalculatedCS}}$ was limited to -1 and the intercept is determined by minimising the root mean square error (RMSE).

Normally, crystalline NMR experiments produce broad and featureless spectra, which is a result due to anisotropic interactions that the nuclei experience in the solid state. This issue is resolved using the Magic Angle Spinning (MAS) technique [178], which improves spectral resolution to reveal peaks at the isotropic shift values. Hence, these are obtainable experimental NMR parameters which we can compare simulations against.

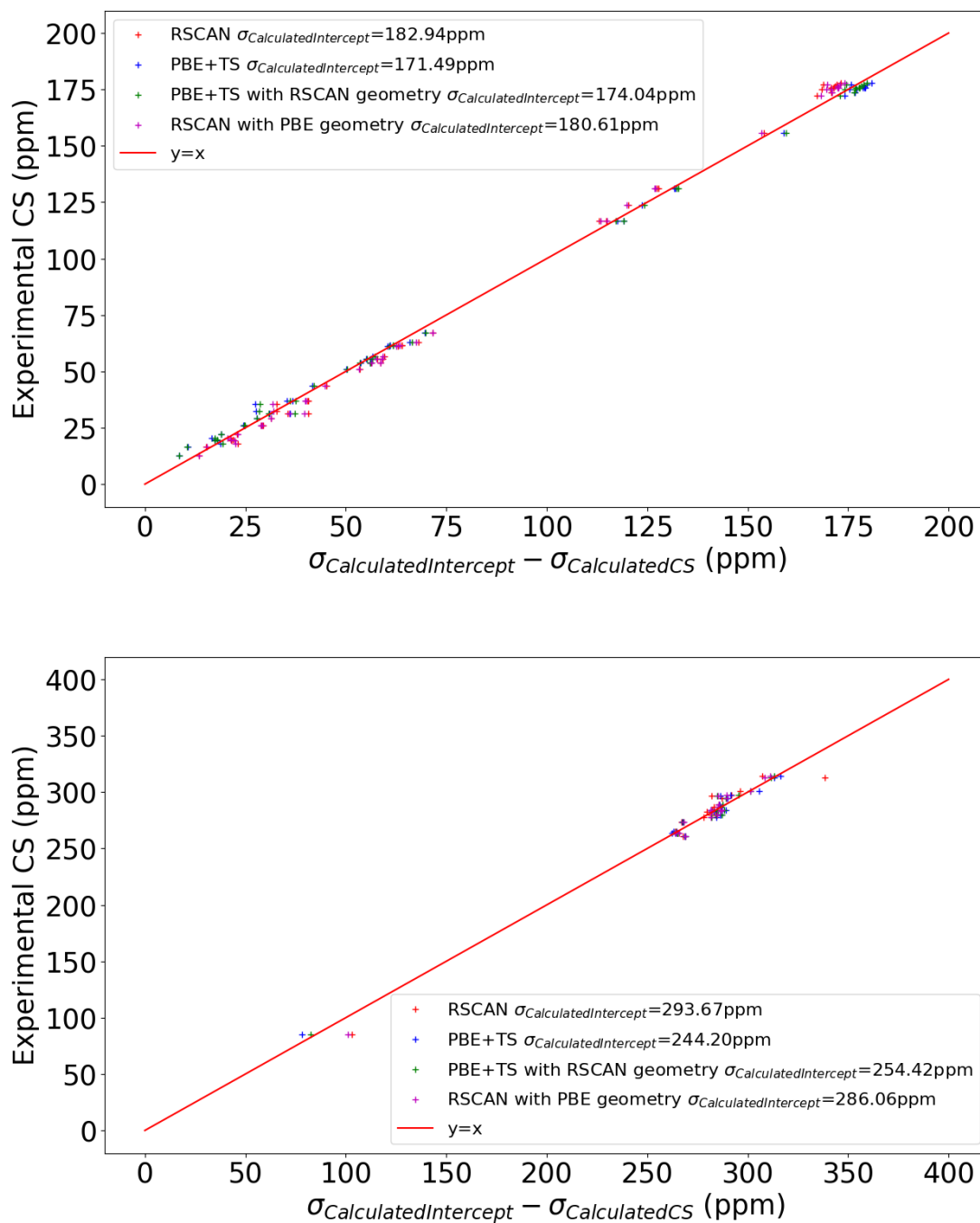


Figure 9.7: Plot of isotropic chemical shifts for (top) ^{13}C and (bottom) ^{17}O compared to that of literature. All experimental values chosen have the same reference compound from the referenced literature.

Calculations of NMR parameters include both functional and geometry effects. In order to separate these, chemical shifts calculated using rSCAN were

re-calculated using the optimised geometry from PBE+TS and vice versa, summarised in Table 9.2. This can be done because NMR calculations do not need to include dispersion corrections, as they amend energies, forces and stresses after each self consistent cycle without altering the wavefunction (and hence charge density), from which the NMR parameters are determined.

It is pleasing that the additional physics in rSCAN result in a more accurate magnetic shielding, as demonstrated in Fig. 9.7 (calculated intercepts) for ^{13}C and ^{17}O (where the absolute shielding scale was established as 307.9ppm for ^{17}O and 188.1ppm for ^{13}C) [172, 179–181]. However, this has little experimental consequences as the differences cancel when converting to the experimental observed chemical shift. In DFT simulations, magnetic shielding can be decomposed into several components when related to the atomic structure via [182]

$$\sigma = \sigma_{core} + \sigma_{dia}^{loc} + \sigma_{para}^{loc} + \sigma^{lr} \quad (9.8)$$

where σ_{core} comes from the core electrons, uncoupled to the chemical environment. Using PBE with TS corrections, core contributions are 200.51ppm and 271.08ppm for carbon and oxygen respectively. Similar for rSCAN, core contributions are 200.83ppm and 271.29ppm respectively. The fact that these shielding values from PBE vs rSCAN are very comparable means that the core charge densities between the two functionals are similar and hence do not contribute to the discernible improvement in predicting the absolute magnetic shielding. σ^{lr} denotes the long range electric current contribution to the induced magnetic field and $\sigma_{dia}^{loc} + \sigma_{para}^{loc}$ denotes the short range diamagnetic and paramagnetic induced current responses. The diamagnetic current increases the magnetic shielding and is only dependent on the applied field strength and charge. On the other hand, the paramagnetic current decreases shielding and depends on $\frac{1}{\Delta E}$ where ΔE denotes orbital energy difference and effectively corresponds to the band gap energy [183]. It has been shown that

meta-GGAs' such as rSCAN improves band gap energy predictions [184] and therefore this could be the rationale behind rSCAN's observed superior absolute magnetic shielding predictions.

Parameter (ppm)	rSCAN	rSCAN w/ PBE geometry
^{13}C RMSE	3.92	3.56
^{17}O RMSE	8.49	5.89
Parameter (ppm)	PBE+TS	PBE+TS w/ rSCAN geometry
^{13}C RMSE	2.66	2.48
^{17}O RMSE	5.05	4.45

Table 9.2: RMSE of isotropic chemical shift for handpicked dataset vs. literature. The calculated chemical shifts are those shown in figure 9.7, with slopes constrained to -1 and optimised intercepts. rSCAN w/ PBE geometry denotes using rSCAN to calculate the CS with a unit cell optimised with dispersion corrected PBE, and vice versa for PBE w/ RSCAN geometry.

9.4.0.1 Summary

The theme of this chapter was to exhibit and quantify the ability of the semi-local meta-GGA, rSCAN to capture long-range dispersion effects in molecular crystals. Benchmark tests were performed both on the X23 and a manually selected set of carboxylic and amino acids. The results show that when comparing against literature experiments, the bare rSCAN functional performs exceptionally well compared to PBE+TS and PBE+MBD*, in terms of its ability to reproduce equilibrium lattice parameters and NMR isotropic chemical shifts. This remarkable performance is further corroborated by fact that rSCAN has been shown to produce a much more accurate absolute magnetic shielding for ^{17}O and ^{13}C . We have also shown that it is unfavourable to include MBD* corrections to rSCAN, as results are evocative of LDAs overbinding behaviour.

Computing the Γ -point vibrational modes of the handpicked molecular crystals revealed that rSCAN shifted all the modes in question upwards,

which was elucidated by a systematic reduction of intra-molecular bond lengths (and yet does not result in dramatic over-binding like LDA). This shift increases for higher frequency vibrations, especially for those dominated by N-H, O-H and C-H stretches. Lower frequency vibrational modes such as C-C stretching, C-H wagging, etc were also shifted to the right, which further supports the source of this phenomenon being intra-molecular.

Since rSCAN is very similar to PBE+TS in geometry and phonon calculations, we use the latter for EELS simulations in the following chapters due to convenience.

10.1 NUMERICAL IMPLEMENTATION OF ULTRA-LOW LOSS THEORIES

In this section we dissect the numerical treatment details of the semi-classical, quantum impact and dipole scattering DDCS (Eq. (4.39), Eq. (5.17) and Eq. (6.38) respectively), such that they can be applied to a series of molecular and bulk crystals.

10.1.1 *Semi-classical theory*

In the semi-classical case, the main material response is encapsulated in the polarisability tensor α , which requires the BECs and eigenvectors outputs from CASTEP as detailed in Eq. (4.34) and Eq. (4.44). The eigenvectors from the *ab initio* calculations already satisfy the mass normalisation constraint of Eq. (4.45), which means they are indeed the eigenvectors, instead of eigendisplacements (related by mass normalisation), and Eq. (4.39) can be straightforwardly computed.

10.1.2 Born effective charges

The BEC ¹ for an atom κ can be expressed as the second derivative of total energy E [65] via

$$Z_{\kappa,\alpha,\beta}^* = \frac{\partial^2 E}{\partial \tau_{\kappa,\alpha}(\vec{k} = \vec{0}) \partial \mathcal{E}_\beta} \quad (10.1)$$

where α and β are directional indices and $\mathcal{E}$ is the perturbing electric field. There are two possible methods to calculate this derivative, through perturbation theory or finite difference as outlined in Section 3.5.2. The former is more efficient and commonly used. However, if we want to treat the electron correlation with a meta-GGA such as rSCAN, for which DFPT is not yet available, quantities such as the BEC can only be computed using finite difference and this requires the absolute polarisation of the unit cell.

It is famously difficult to uniquely define the absolute electric polarisation of a crystalline insulator. Consider the 2D lattice arrangement of positive and negative charges in Fig. 10.1.

¹ Note that that CASTEP outputs the atomic born effective charge tensors $Z_{\kappa,\alpha,\beta}^*$, whereas its appearance in both the semi-classical (Eq. (4.44)) and quantum dipole Eq. (6.38)) theories are in the context of the mode effective charge vector (Eq. (6.29)), which is the BECs along the direction of the atoms eigen-displacement.

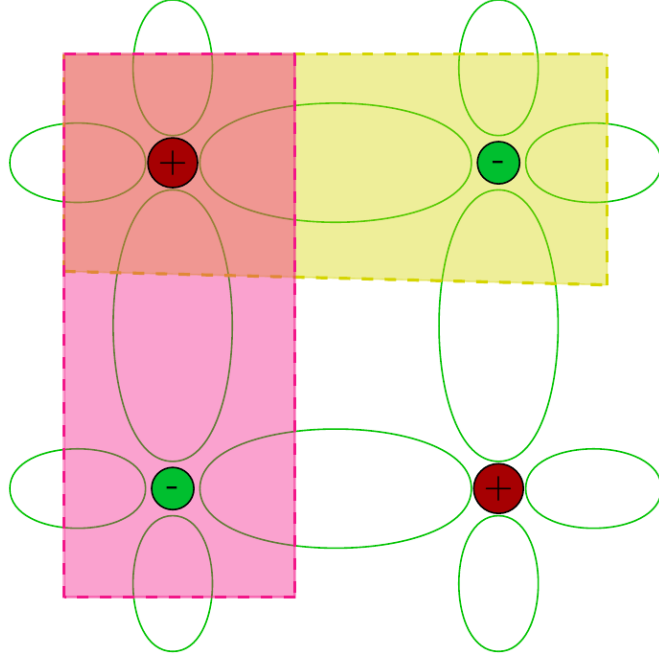


Figure 10.1: Conceptual sketch of the ambiguity in defining the polarisation per unit volume, as it is completely determined by the placement of the boundaries of the unit cell. The green ovals represent electronic charge clouds surrounding a 2D ionic square lattice.

Naively, one can define the polarisation per unit cell as its dipole moment per volume,

$$\vec{P} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} e \vec{r} n(\vec{r}) dV \quad (10.2)$$

for number density $n(\vec{r})$. However, the different placements of the unit cell box with constant volume, V_{cell} (denoted by the coloured squares) give different values of $\vec{P}$. An attempt to get around this can be to pick a ‘natural’ choice of the unit cell based on symmetry or perform an average over all unit cell positions, but these usually result in vanishing polarisations. Therefore it is imperative to be able to define it with an invariant system property, as done using the modern theory of polarisation [185]. Consider a Bloch-like state that is periodic in nature, describing an energy band n , and parametrised by

$\vec{k}$ (often the wavevector), $u_{n\vec{k}}$. From this we can introduce Berry phase [186], ϕ_n , a gauge-invariant quantity

$$\phi_n = \int \langle u_{n\vec{k}} | i \partial_{\vec{k}} u_{n\vec{k}} \rangle d\vec{k}, \quad (10.3)$$

from which we can define the polarisation,

$$\vec{P} = -\frac{e}{2\pi} \sum_n^{\text{occ}} \phi_n \quad (10.4)$$

This unambiguous way of defining the absolute polarisation means that for a unit cell, the BEC can be calculated using the finite difference

$$Z_{\kappa,\alpha,\beta}^* = \frac{\Delta P_\beta}{\Delta \tau_{\kappa,\alpha}}. \quad (10.5)$$

10.1.3 Quantum impact scattering theory: Charge partitioning, X-ray and electron form factors

In the quantum impact energy loss DDCS derivation, nuclear charge is treated as the ionic charge Z_i for atom i . However, in reality the nuclear charge is screened and there are various methods of numerically treating this charge transfer. Nicholls et al. [48] rewrote the $Z_i - f_i(\vec{k})$ part of Eq. (5.17) as a ‘total form factor’

$$F(\vec{k}, Z_i) = f_i(\vec{k}) \frac{(Z_i - Z_i^*)}{Z_i} + Z_i e \quad (10.6)$$

where Z_i^* is the atomic charge calculated using Mulliken charges. In this static charge transfer analysis, the charge associated to an atom is obtained from the density matrix of a localised set of basis functions [187]. There is a downside of simply using the original plane wave basis set as their electronic information is delocalised in space. Thus the technique that is commonly adopted

is to project the plane wave states onto a localised basis [188]. The common choice for this is the atomic pseudo-potentials. Mulliken’s population analysis is one of the most commonly used method because it provides realistic chemical trends, but it is not physically well defined. This is because the orbital charge assigned to an atom solely because the orbital is centred around said atom, and is thus very sensitive to the localised atomic basis set that is picked. It also does not preserve the dipole and higher multipole moments, which are important in the computation of the material’s electric potential. Thole et al. [189] has shown that by taking into account conservation of the dipole moments, this analysis can be generalised produce more accurate potentials and hence better capture Coulomb interactions, but the original method is implemented in CASTEP.

There are also numerous alternative charge analyses methods that can be used to compute the partial charge Z_i^* . We will discuss the types accessible from a CASTEP calculation, i.e. the Bader, Hirshfield and Born effective charge analyses as their effectiveness will be compared in Chapter 13.

In Bader’s charge analysis [190, 191], the atoms of the crystal/molecule are defined only on their electronic charge densities, separated from each other by zero flux surfaces, which are bounded by points $\vec{r}$ such that $\nabla\rho(\vec{r}) \cdot \hat{n}(\vec{r}) = 0$ for normal vector $\hat{n}(\vec{r})$ to the surface. This is an intuitive way of charge partitioning. CASTEP does not calculate this directly, but the charge density profile from an electronic structure calculation can be analysed using post-processing Bader analysis program by the Henkelman group [192].

The Hirschfeld charges [193] on atom i is defined as

$$Z_{\text{hirschfeld}} = Z_i - \int d\vec{r}^3 \frac{\rho_i(\vec{r})}{\sum_i \rho_i(\vec{r})} \rho_{\text{molecule}}(\vec{r}) \quad (10.7)$$

where Z_i is the unscreened nuclear charge (i.e. number of electrons), ρ_i is the atomic ground state charge density (assuming a free atom) and ρ_{molecule} is the molecular charge density. The charge at each point is distributed between all atoms in proportion to their free charge. Similar to the Mulliken charge analysis, this method preserves charge but not higher multipole moments, and Lu *et al.* [194] have shown that the additional constraint of preserving atomic dipole moments in the Hirschfeld analysis result in improved performance but our calculations using CASTEP will not include these multipole additions.

The discussion so far has been to statically partition charge. However, it may make more sense to replace Z_i^* with a dynamic charge transfer such as BECs due to the movement of atoms during phonon excitations. However, it is not as trivial to incorporate the Born effective charge as it is a tensor. One can attempt to summarise the contribution in a single value as one third of the trace of the 3×3 matrix. Alternatively, it may be more intuitive to multiply the atomic Born matrix with the eigenvector, creating a mode effective charge like term. This vector describes the direction of change in charge caused by the atomic displacement, its magnitude can be used to approximate the charge transfer. This use of BECs was done by Senga *et al.* [135] using the same quantum impact scattering formalism for the bulk crystal of hexagonal boron nitride and graphene monolayers.

The X-ray atomic form factor, $f_d(\vec{k})$ in Eq. (10.6) describes the X-ray scattering amplitude off the electron cloud of the isolated atom in question. This interaction increases with atomic number simply due to the increasing number of electrons involved. Numerically, it is well approximated by a Gaussian sum of the form

$$f(\vec{k}) = \sum_i^4 a_{i=1} \exp\left(-b_i \left(\frac{k}{4\pi}\right)^2\right) + c \quad (10.8)$$

where the coefficients a, b and c for all neutral atoms are tabulated in the International Tables for Crystallography (ITC) [195].

However, the $\frac{Z_i - f_i(\vec{k})}{k^2}$ term in the impact scattering formalism is very similar to the Mott-Bethe formula for the electron form factor (up to a constant) [196], which is intuitively the more appropriate choice of form factor to use in simulations. This is given by

$$f_e^{\text{Mott-Bethe}}(\vec{k}) \propto \frac{Z_{\text{atom}} - f^X(\vec{k})}{k^2} \quad (10.9)$$

where Z_{atom} is the atomic number and $f^X(\vec{k})$ is the X-ray scattering form factor for the corresponding atom. Recall that we need to account for nuclear screening and charge transfer (similar argument as the attempt by Nicholls et al. discussed in Eq. (10.6)). Thus, instead of Eq. (10.6), we re-write $\frac{Z_i - f_i(\vec{k})}{k^2}$ to resemble the Mott-Bethe form factor

$$\frac{Z_{\text{atom}} - f^X(\vec{k})}{k^2} + \frac{\delta Z}{k^2} \quad (10.10)$$

where we have introduced a charge transfer term $\delta Z = Z_{\text{actual}} - Z_{\text{atom}}$ due to bonding. The first term describes the scattering of electrons off of the isolated neutral atom, whilst the second can be seen as the long-range Coulomb interactions that dominate at low momentum transfers. This term is deemed the dipole contributions which is how Allen *et al.* [134] justifies using Eq. (10.10) to describe the aloof beam mode. As $k \rightarrow 0$, the X-ray form factor approaches $f_X(\vec{k} = \vec{0}) = \int [\rho(\vec{r})e^{i\vec{k} \cdot \vec{r}}]d^3r = Z_i$ such that the first term in Eq. (10.10) becomes undefined. Ibers showed in 1958 [197] that through a power series expansion and taking the limit $k \rightarrow 0$, this we get

$$f_e(k \rightarrow 0) = \frac{4\pi^2 m e^2}{3h^2} Z \langle r^2 \rangle \quad (10.11)$$

where $\langle r^2 \rangle$ is the mean-square radius of the atom. Similar to the X-ray form factors, this can also be approximated by a Gaussian sum of the form

$$f_e(k) = \frac{4\pi^2 m e^2}{3h^2} Z \langle r^2 \rangle = \sum_{n=1}^5 a_n \exp(-b_n k^2) \quad (10.12)$$

where the coefficients are tabulated in the ITC (Volume C, Section 4.3).

Normally, the global constant χ in Eq. (10.10) can be ignored as they can be lumped into the scaling factor between experiment and theory. However, we would like to compare the absolute intensity spectra between the quantum impact scattering theory and our dipole theory, which makes it important to determine χ . There are several slight variations for this coefficient used in literature. The ITC presents this as $\frac{2\pi m e^2}{h^2 \epsilon_0}$. Ibers [197] uses $\frac{8\pi^2 m e^2}{h^2}$. Rez *et al.* [198] uses $\frac{m e^2}{2h^2}$. Van Dyck *et al.* [199] uses $\frac{m e^2}{2\pi h^2 \epsilon_0}$. The loose usage of dimensionless factors make it difficult to determine which expression to use. This is cleared up by Spence and Zuo [200], which explicates that the terms electron scattering factor and atomic scattering factor (for electrons) are used interchangeably, but only differ by a constant under the first-order Born approximation. In SI units, the atomic scattering factor is what we want to use the Gaussians of Eq. (10.12) to approximate with, and has the proper definition as

$$f_e(k) = \frac{m_e e^2}{8\pi \epsilon_0 h^2} \frac{Z_{\text{atom}} - f^X(\vec{k})}{k^2}. \quad (10.13)$$

such that the SI units for $f_e(k)$ work out correctly as (Å). This is the quantity that is relatable to the intensity of the scattered wave. This is further discussed and endorsed in the comprehensive review by Peng [201]. Hence in our numerical calculations, the first term in Eq. (10.10) is obtained through diving Eq. (10.12) by $\chi = \frac{m_e e^2}{8\pi \epsilon_0 h^2}$.

Recall from Section 6.6 that this impact scattering formalism have been used to describe the dipole scattering behaviour in the aloof beam mode. For ex-

ample, similar to Dwyer, LJ Allen *et al.* [134] also treats the inelastic scattering of electrons in terms of a potential that is related to the single phonon excitation due to vibrational effects. However they do not explicitly treat a 'dipole' potential, and the result contains the electron scattering factor Eq. (10.10). As $k \rightarrow 0$, they attribute the diverging $\frac{\delta Z}{k^2}$ term to be the dipole scattering term that dominates.

10.1.3.1 Choice of static charge transfer δZ - Boron nitride

In this section, we explore the choice of δZ in Eq. (10.10) for the quantum impact scattering theory by comparing using Mulliken charges against the magnitude of mode effective charge vectors for boron nitride.

Cubic and hexagonal boron nitride are two widely studied polymorphs. The convergence for hBN was discussed in Fig. 8.1 and similar numerical specifications were used for cBN. Several authors have published experimental low loss EELS for BN in extensive studies in both impact and aloof configurations [56, 202–204]. Nicholls *et al.* [48] published momentum-resolved EELS for both hBN and cBN using the quantum impact scattering theory for $0 < |\vec{k}| \leq 1.7 \text{ \AA}^{-1}$ along the $\Gamma - X$ (cBN) and $\Gamma - K$ (hBN) phonon dispersion path. As the momentum transfer is much larger than that sustained in the aloof beam configuration, we focus on the quantum impact scattering theory. In the numerical treatment of Eq. (5.17), recall that Nicholls *et al.* used the X-ray atomic form factors (Eq. (10.6)) whilst we employed the electron form factor. As the imparted momentum decreases, the dominant contribution in the quantum impact theory comes from the charge transfer term in Eq. (10.10), for which there are multiple ways to summarise the absolute charge on each atom (via Mulliken, Hirshfeld charges etc.). Figure 10.2 displays the performance of multiple static (phonon mode independent) charge transfers using the quantum impact scattering theory for both hBN and cBN. Gaussian ap-

proximations of the atomic form factor (AFF) with Mulliken charges (similar to that employed by Nicholls *et al.*) show some discrepancies to the publication, which requires corrections. This is compared to utilising Gaussian approximations for the electron form factor (EFF), where we compare Mulliken charges against mode effective charge vector magnitudes.

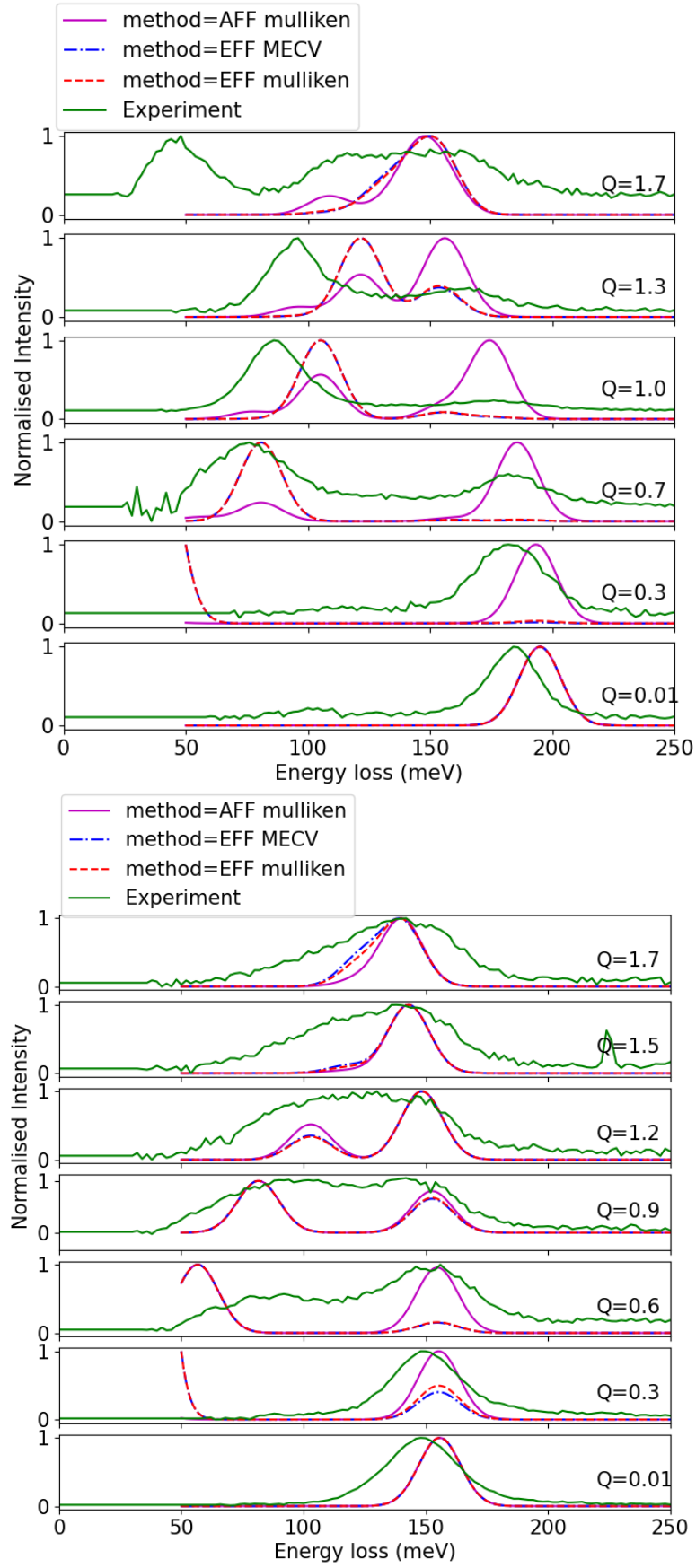


Figure 10.2: Momentum resolved ultra-low loss EELS simulation of (top) hBN along $\Gamma - K$ and (bottom) cBN along $\Gamma - X$ momentum resolved ultra-low loss EELS spectra. The quantum impact scattering theory is used for all simulations. Q denotes the magnitude of the imparted momentum. *The experimental data obtained by Nicholls et al. are presented with permission from the authors and publisher.* The experimental spectra are shown in green and all plots are normalised.

As we approach the Γ point, the decrease in momentum compensation magnitude in both hBN and cBN causes the separation of two distinct peaks in the ultra-low loss energy spectrum. The EFF methods show an improvement in raising the peak intensity at the lower energy compared to that using AFF for values of momentum transfer above $\sim 0.6\text{\AA}^{-1}$. For completeness' sake, we also plot the effect of describing the static charge separation using Hirshfeld and the average of the BEC trace in [Appendix H.1](#). Since these are mode independent, they alter the relative contributions each atom has on each mode by the same amount, so the general shape of the energy loss curves are similar (shown in [Fig. H.o](#)).

Peaks at energies below 50meV are cut-off in theoretical simulations, as they can potentially be masked by the ZLP tail and thus indiscernible after background subtraction. Intuitively, long range dipole contributions should dominate at Γ and the quantum impact theory becomes less physically sound. It becomes invalid at exactly $Q = 0\text{\AA}^{-1}$ due to divergence and thus a simulated spectrum using $Q = 0.01\text{\AA}^{-1}$ is manually picked to be practically comparable with literature. The method used for charge transfer treatment result in significant differences in the relative intensities, which is problematic as this choice can be quite arbitrary.

For momentum resolved impact scattered EELS in bulk polar dielectrics, phonon-polariton excitations are important in explaining unmatched peaks. These quasiparticles arising from the coupling between optical phonon modes occur in the dispersion diagram where the photon dispersion meets that of the optical phonon branch. Polaritons are formed in order to avoid the crossing between the two dispersion curves due to the non-crossing rule [205, 206]. As a result, in a narrow energy range (the phonon reststrahlen band) the EM wave cannot propagate and is hence confined. Polariton peaks can conglomerate with the pure vibrational peaks and hence appear to shift the peak positions. Li *et al.* recently performed aloof and bulk STEM EELS on both 10nm thick and monolayer flakes of hBN and showed that when the beam is on sample, hyperbolic phonon-polaritons can be excited with a momentum compensation in the order of magnitudes circa $10^{-2} \text{\AA}^{-1} - 10^{-1} \text{\AA}^{-1}$. Boron nitride is a hyperbolic material because the parallel and perpendicular components of the dielectric permittivity tensor with respect to the optic axis have different signs. Since all $|\vec{k}|$ values are well within the excitable impact scattering range, hyperbolic phonon-polaritons across the entire reststrahlen band can be excited. On the other hand, the small momentum transfer available in aloof mode disallows the probing of the entire band and hence phonon-polariton excitations are less significant. Boron nitride also has very few distinct peaks for a dependable, quantitative comparison between the impact and dipole quantum theories and consequently, we attempt to do so by moving onto a larger bulk crystal structure in [Chapter 13](#).

10.1.4 Debye-Waller factor

Debye-Waller factor first was introduced in Eq. (5.15). The space-time average in the exponential numerator can be equivalently represented as [207]

$$T(\vec{k}) = \exp \left(-2\pi^2 \sum_{j=n}^3 \sum_{l=m}^3 k_n U^{nm} k_m \right) \quad (10.14)$$

where U^{nm} are the mean-squared atomic displacement factors, which can be calculated using CASTEP. Often in crystals, this is not isotropic so the DWF is directionally k dependent. Since the eigenvectors and hence mean atomic displacement depend on both temperature and wavevector, both must be taken into account in calculations.

10.1.5 Molecular dipole positional vector

In the quantum dipole treatment of the DDCS, Equation (6.38) requires the position vectors of each molecular dipole in the unit cell. The modern theory of polarisation allows us to define the centre of charge

$$\vec{r} = \langle w_n | \vec{r} | w_n \rangle \quad (10.15)$$

where $|w_n\rangle$ is the wannier function representation of band n . The wannier function centred around $\vec{R}$ is the Fourier transform of a Bloch function, $|\psi_{n\vec{k}}\rangle$ [186],

$$|w_{n\vec{R}}\rangle = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} e^{i\vec{k}\cdot\vec{R}} |\psi_{n\vec{k}}\rangle d^3k, \quad (10.16)$$

such that if the Bloch state is a smooth function in reciprocal space, the wannier function would be a localised, quickly decaying function in real space. Therefore, by employing softwares such as Wannier90 [208] to obtain the wan-

nier basis for our molecules, we can find their centre of charge positional vectors using [Eq. \(10.15\)](#). However, for the purposes of our calculations, we manually divide up the molecules into their own boxes and perform a single point calculation. This allows us to obtain the positional vectors of the centre of positive and negative charges using CASTEP. Their average vector is then used as the approximate for the point dipole position. This vector is mode-independent and hence will not affect the relative mode contributions, which is our main point of concern but the method of calculating the centre of charge using the wannier basis can be used in the future for further refinement of the code.

Part IV

ULTRA-LOW LOSS EELS SIMULATIONS

We now focus on specific crystals to consolidate the theoretical work in [Part II](#) and numerical methods in [Part III](#) by evaluating the DDCS for numerous molecular and bulk crystals using both the semi-classical and quantum treatments.

11.1 β -GUANINE

We return our attention to the guanine crystals first introduced in [Chapter 2](#), for which there is ultra-low loss EELS data. β -guanine crystallises in the monoclinic $P112_1/b$ space group. Rez *et al.* [54] extracted, purified anhydrous guanine from Japanese Koi fish and performed aloof beam EELS at several impact parameters in the range of 10 – 250nm. The e-beam (in vacuum) travelled parallel to the (100) crystal axis, such that most of the momentum transfer occurred in the plane of the crystal perpendicular to the beam direction. They have also performed IR absorption spectroscopy on the same sample showing close agreement, thus successfully demonstrating the similarities between IR and EELS. In beam sensitive specimens such as this, damage avoidance means restricting the electron beam's impact parameter and hence limiting spatial resolution. Guanine is a good candidate to compare the semi-classical and quantum theories due to the wide range of bond types, both intra and inter-molecular.

The structure of anhydrous biogenic guanine was believed to be the α polymorph until 2015, when Hirsch *et al.* [209] demonstrated, via X-ray and electron diffraction data that their proposed and synthesised β -polymorph matched that of naturally occurring biogenic samples. The structure, visu-

alised in Fig. 11.1, shows the stacking behaviour along the a lattice vector. This is also the direction parallel to the experimental e-beam.

Geometry optimisation and convergence tests were performed with PBE+TS (Appendix G for details) such that for subsequent phonon calculations, a plane wave cut-off of 1200eV and a k-spacing of $0.1\text{\AA}^{-1}$ were used, with force and energy tolerances of $2 \times 10^{-3} eV\text{\AA}^{-1}$ and $0.22 \times 10^{-9} eV$ respectively. This gave the following lattice parameters: $a = 3.50\text{\AA}$, $b = 9.70\text{\AA}$, $c = 18.47\text{\AA}$ and $\gamma = 118.52^\circ$. These lattice parameters are within 3% of those reported by their original proposers [209].

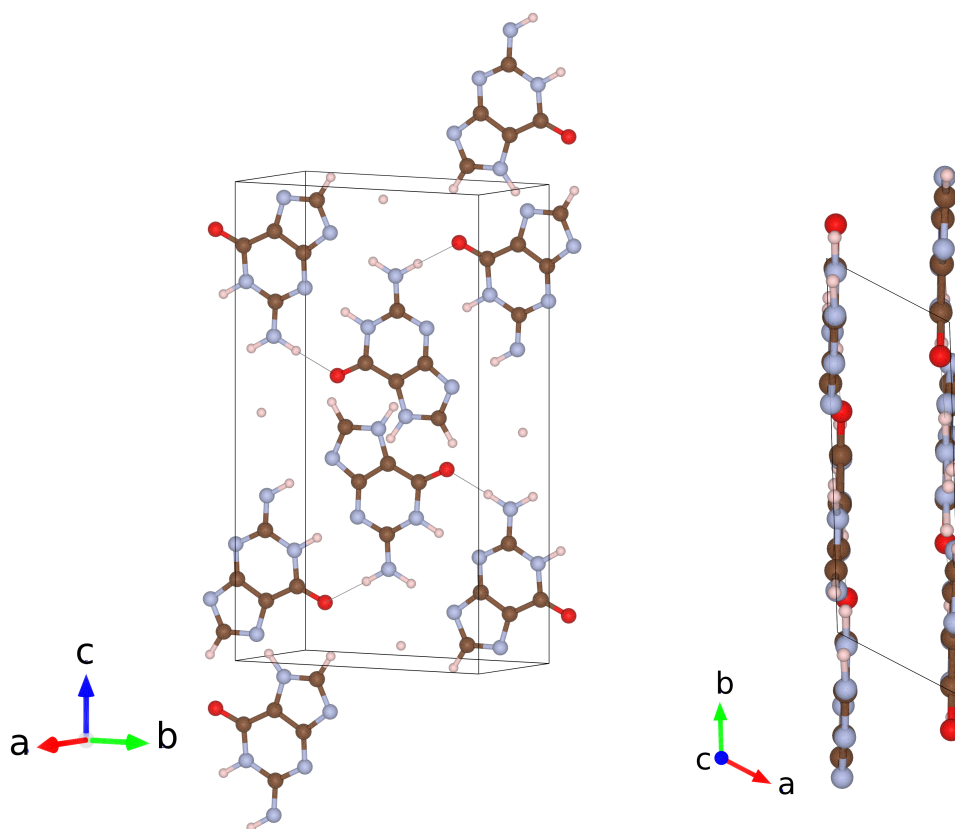


Figure 11.1: β -guanine unit cell structure visualised in VESTA. Hydrogens, are shown in white, nitrogen in blue, oxygen in red and carbon in brown. The electron beam orientation in Rez *et al.*'s aloof beam experiment [54] is along the lattice a -vector.

11.1.1 *Semi-classical result*

We first aim to reproduce the semi-classical ultra-low loss EELS for β -guanine that have been performed by Radtke *et al.* [55], thus Go6 or the Grimme dispersion correction [210] is chosen to accompany the PBE functional. First, we plot the real and imaginary components of the low-frequency dielectric tensor (Eq. (4.44)) in Fig. 11.2. Recall that the eigenvectors $\vec{e}$ output by CASTEP satisfy the orthonormality condition but the mode oscillator strengths (Eq. (4.44)) require the displacement vectors, $\vec{u}$, thus care must be taken to make sure to use $\frac{\vec{e}}{\sqrt{m}}$. We also employ a similar line broadening parameter $\Gamma_m = 4cm^{-1}$ as that of Radtke *et al.*, such that the dielectric tensor is actually

$$\epsilon_{\alpha,\beta}(\omega) = \epsilon_{\alpha,\beta} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha,\beta}}{\omega_m^2 - (\omega + i\Gamma_m)^2}. \quad (11.1)$$

Natural line broadening comes from intrinsic effects in the absorption or emission process. A vibrational mode with some finite lifetime Δt has an uncertainty in energy due to the uncertainty principle, which manifests in a spread of the peak energy. Thermal motions of the atoms can also contribute to broadening [211, 212].

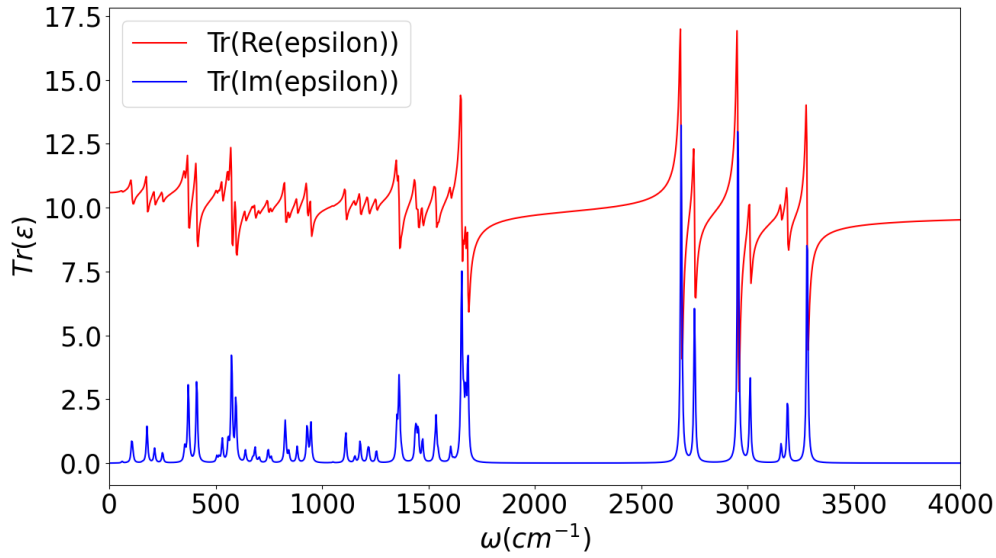


Figure 11.2: Trace of the real and imaginary components of the dielectric tensor for β -guanine with respect to vibrational frequency.

β -guanine belongs to a centrosymmetric point group. This means that it contains an inversion centre and that inversion is a symmetry element of its space group. A powerful consequence of group theory dictates that the Raman and IR active modes are mutually exclusive [213]. Since only phonon modes that can generate a macroscopic polarisation can provide non-zero contributions to the mode oscillator strength (and hence in the dielectric tensor) in Eq. (11.1), only IR modes will contribute to the final frequency dependent energy loss. This also explains why the experimental IR and EELS spectra by Rez *et al.* look very similar. A qualitative way of explaining this complementarity arises from the electronic characterisation of the vibration. For example if a bond is already strongly polarised, a small change in its length during vibration will only have a very small (negligible) effect on the polarisation. Thus vibrations involving polar bonds in crystals of high symmetry are weak Raman scatterers. However, polarised bonds will carry their electron clouds during vibrations, hence resulting in large dipole moments and strong IR absorption. Conversely, neutral bonds (such as the C-C bond) have large

changes in polarisability during vibrations, but the dipole moment is not as affected, making the mode a strong Raman scatterer.

11.1.1.1 *Calculation of β -guanine ultra-low loss EELS spectrum*

Now that the dielectric tensor is procured, we insert [Eq. \(11.1\)](#) into [Eq. \(4.34\)](#) to obtain the polarisability tensor, where only the imaginary component of the contributes to the energy lost by the electron through vibrational excitation. Finally then we can plot the energy loss probability ([Eq. \(4.39\)](#)) to produce the ultra-low loss EELS spectrum comparable to experiment, shown in [Fig. 11.3](#). This figure contains two simulated spectra corresponding to two different relative orientations between the beam and crystal.

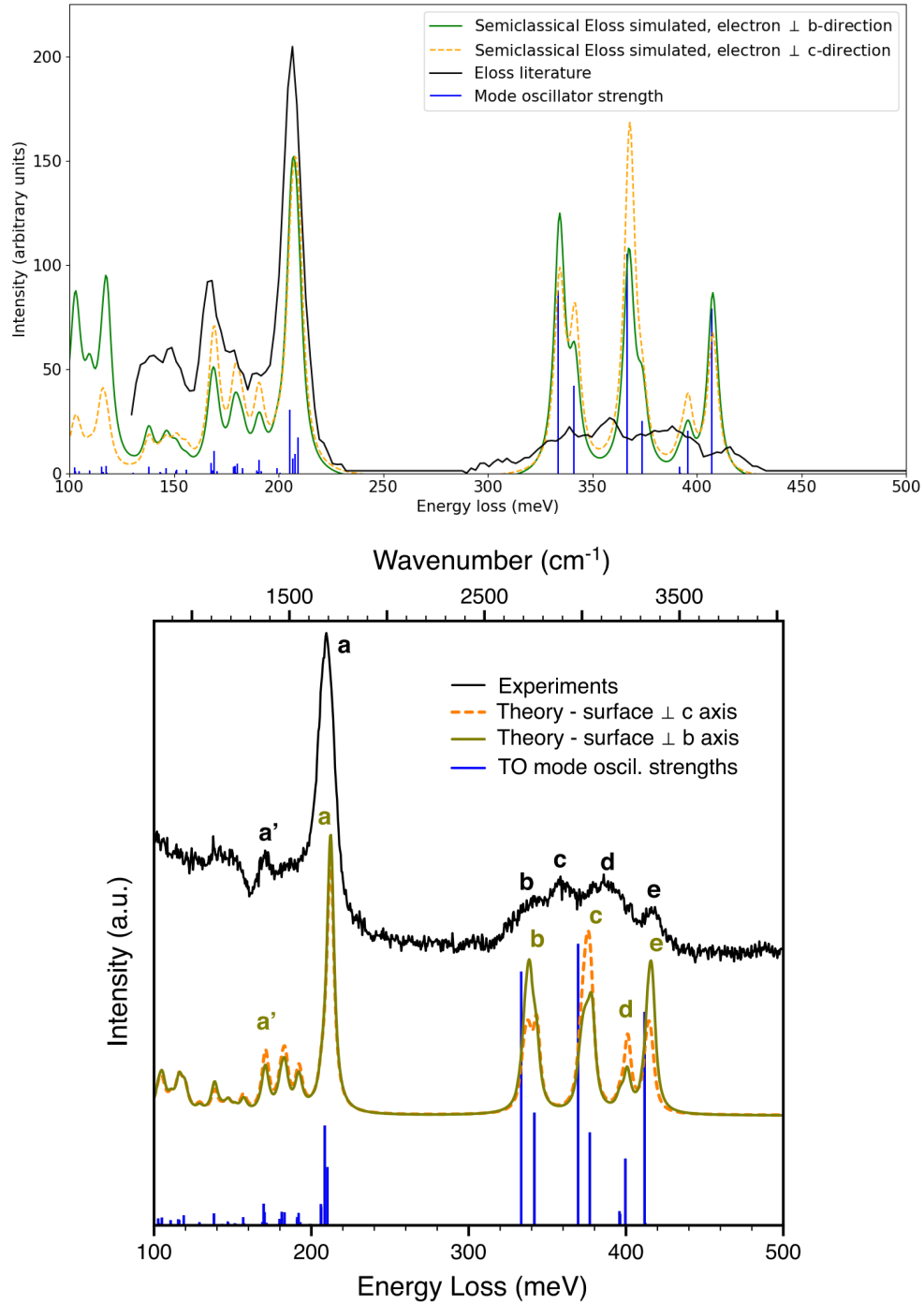


Figure 11.3: (Top) Semi-classical β -guanine simulated energy loss spectra *vs* experiment (labelled Eloss literature). This is done for two different relative orientations between the beam and sample geometry. Lorentzian smearing with a FWHM of 5meV has been applied and the mode oscillator strength intensities are shown in blue. *Experimental spectrum is credited to Professor Peter Rez and Katia March, for an aloof beam at impact parameter $b \sim 30\text{nm}$.* (Bottom) Figure 3 of publication by Radtke *et al.*, with permission granted for usage [55]

In a real experiment, instrumental broadening must also be accounted for, which is usually taken as the convolution of the spectrum profile and the instrumental profile. We employ the same Lorentzian smearing as Radtke *et al.*, with a full width at half maximum of $\Gamma = 5\text{meV}$. This is a function of the form

$$\frac{1}{\pi} \frac{\frac{\Gamma}{2}}{(x - x_0)^2 + (\frac{\Gamma}{2})^2} \quad (11.2)$$

centred at peak x_0 . Since the e-beam is perpendicular to the crystal bc -plane, the difference between the spectrum labelled $\perp b$ and c directions denote whether the beam is at an impact parameter distance away from the ac -plane or ab plane respectively (see Fig. 11.1) for reference.

The results published by Radtke *et al.* is also presented in Fig. 11.3 and shows a similar overall trend to our simulations. However, there is a significant difference between the relative intensities of the NH_2 stretches at the largest experimental peak around 200meV , and the high frequency hydrogen dominated stretches above 300meV . In attempt to determine if the discrepancies arise from the DFT calculations, the calculations are redone in QUANTUM ESPRESSO with the exact same inputs as those used by Radtke *et al.*. The results are presented in Appendix G.0.1, and do not show any discernable differences to that of Fig. 11.3. It is likely the differences come from post processing procedures such as the Lorentzian smearing process, but the mode oscillator strengths in Fig. 11.3 clearly show that the largest contributions should come from the hydrogen vibrations at high frequencies (and match that of Radtke's results), which should be reflected in the energy loss spectrum. This gives credibility to the appearance of our simulated spectrum in Fig. 11.3.

The experimental spectrum in Fig. 11.3 appears to resemble a mixture of the signals from the beam b and c directions. This is reasonable because in a real experiment, the e-beam passing perpendicular to the bc -plane should probe

an amalgamation of signals from momentum vector transfers along directions not only parallel to the b or c lattice vectors, but a linear combination $\vec{k}_{\text{impart}} = \eta \hat{b} + \lambda \hat{c}$ for constants η and λ . This is because contributions from molecules at different parts of the crystal have different relative orientations to the electron beam, so that the alignment is not exactly perpendicular to a single lattice vector. For example, if the beam is $\perp$ the b lattice vector, as we travel along the edge the crystal towards 'infinity', contributions from the far edges will approach the setup where the beam is $\perp$ the lattice c -direction. This effect will of course decay with distance so the majority of the contributions still come from the direction $\perp \vec{b}$. In addition, it is possible for the crystal to be non ideal, composed of crystallites and thus regions twisted relative to each other.

As shown in Fig. 11.3, the NH_2 stretch modes give the highest peak experimentally around 200meV . For comparison with theory, this peak is not scaled *exactly* to that of the simulated spectra due to the background tail from the elastically scattered electrons near the ZLP. We make a crude approximation to estimate the reduction of this maximum peak by taking the difference between a windowed average of the regions just before and after this largest experimental peak. This difference is the amount by which simulations are shifted downward by, and the same method is used for comparisons against quantum theories later.

In reality, the electron does indeed impart momentum onto the system such that we can improve on the approximation $\epsilon(\vec{k} = 0)$ by evaluating the dielectric tensor along the corresponding direction $\hat{k}$ using [65]

$$\epsilon_{\hat{q}}(\omega) = \begin{pmatrix} \hat{k}_1 \\ \hat{k}_2 \\ \hat{k}_3 \end{pmatrix} \left(\epsilon(\omega) \begin{pmatrix} \hat{k}_1 \\ \hat{k}_2 \\ \hat{k}_3 \end{pmatrix} \right)^T \quad (11.3)$$

where $\epsilon(\omega)$ is the low frequency dielectric tensor presented in Eq. (4.44). The momentum transfer occurs along the directions parallel (along lattice a -vector) and perpendicular to the electron's travel. Thus in the case for an electron beam perpendicular to the lattice b -vector, $\hat{k}$ is expressed as the unit vector $\widehat{\vec{a} + \vec{b}}$ (and similarly $\hat{k} = \widehat{\vec{a} + \vec{c}}$ when the beam is perpendicular to the c -vector). With this amendment, the energy-loss spectra in Fig. 11.3 are re-evaluated in Fig. 11.4, a visibly alters the relative intensities especially in the high frequency region above 300meV . Relative intensity differences between the cases for the electron perpendicular to the b and c directions are now much more pronounced, highlighting the importance of the imparted momentum directionality. In the referenced experiment performed by Rez *et al.* [54], the fast electron travels along the stacking lattice a -direction, perpendicular to the bc -plane. However, realistically the beam should be perpendicular to a linear combination of the b and c directions, because there are always aloof contributions from parts of the crystal far away from the beam. Thus, as a crude approximation, a sum both directions is plotted in red, also normalised to the experimental spectrum.

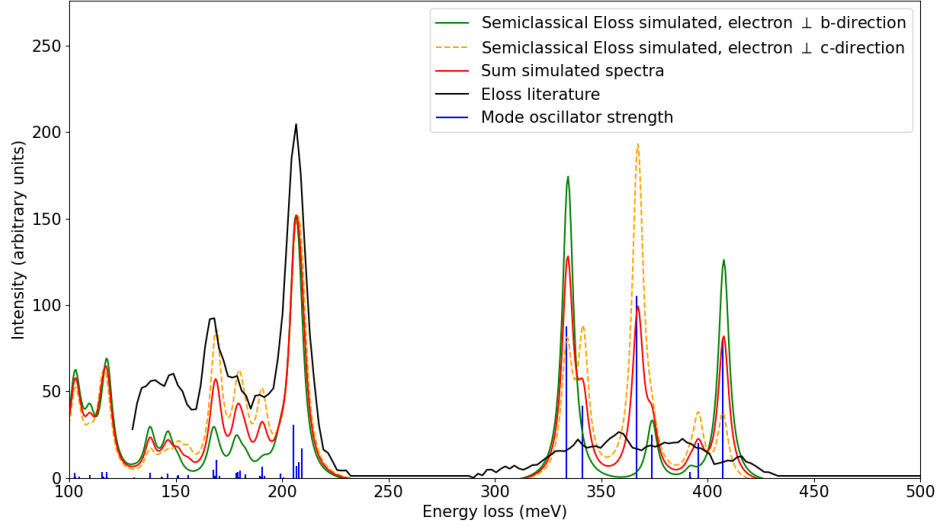


Figure 11.4: The same treatment as Fig. 11.3 including a momentum transfer dependence to the dielectric tensor, $\epsilon(\hat{k}, \omega)$. The sum of simulated spectra for cases where the beam is $\perp$ to the b and c directions is plotted in red.

This sum shows improved relative intensity predictions compared to the individual directional-dependent plots, because the momentum contributions are complementary to each other. This practice of summing over the energy loss spectra over several directions is due to the reduced resolution from the aloof beam experiment, whereby long-range dipole interactions from parts of the sample with various orientation to the beam cannot be ignored, and this fact is re-emphasised in the subsequent quantum simulations.

11.1.2 Quantum impact scattering vs quantum dipole theory result

Although the momentum transfer wavevector is small, it is not negligible and cannot be set to $\vec{k} = \vec{0}$ in the quantum theories of DDCS due to the divergence in Eq. (5.17) and Eq. (6.38). For a 60keV electron beam at an energy loss of $\sim 200\text{meV}$ (order of magnitude of vibrational modes), the magnitude of the longitudinal momentum transfer along the electron's direction of travel is $k_l =$

$\frac{\omega}{v_e} \sim 10^{-4} \text{\AA}^{-1}$, where v_e is the electron velocity. The perpendicular component of momentum transfer is typically much larger and for the purposes of our simulations, we treat this on the order of $10^{-3} \text{\AA}^{-1}$, an order of magnitude larger [214]. For both impact and dipole methods, if the momentum transfer $\vec{k}$ is directed along the lattice c -axis, we will label this in the future plots as $\perp c$ -axis, denoting that the e-beam is perpendicular to the direction of $\vec{k}$. In the phonon calculation, the phonon k -point in CASTEP is specified by the coefficients of the reciprocal lattice vectors. For example for β -guanine, the lattice c -vector is given by $[0, 0, 18.47] \text{\AA}$ and the corresponding reciprocal $\vec{c}^* = [0, 0, 0.34]$. Thus it is sufficient to pick the k -point $(0, 0, 2.9 \times 10^{-3})$ in order to obtain a $\vec{k} = [0, 0, 10^{-3}]$, parallel to the lattice c -axis. More generally, for lattice vectors a_i, b_i and c_i with the reciprocal vectors a_i^*, b_i^* and c_i^* respectively, the linear combination $\alpha a_i^* + \beta b_i^* + \gamma c_i^*$ can be made parallel to any of the unit cell lattice vectors (e.g. take a_i) and the coefficients can be ascertained via

$$\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} a_1^* & b_1^* & c_1^* \\ a_2^* & b_2^* & c_2^* \\ a_3^* & b_3^* & c_3^* \end{pmatrix}^{-1} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}. \quad (11.4)$$

In the case of the quantum impact scattering method (which from now on we refer simply as the monopole method) there are several candidates for the charge transfer δZ in Eq. (10.10), and the method chosen here is the mode-independent Mulliken charges.

Simulations of both monopole and dipole theories are presented in Fig. 11.5, where the former is scaled to the latter, and the dipole spectrum is scaled to experiment on the top figure. This confirms the intuition that the dipole scattering dominates over the monopole in the case of the aloof beam EELS, with very low momenta transfer. This is evident from the $\propto \frac{1}{k^4}$ relationship in the quantum DDCS equations (Eq. (5.17) and Eq. (6.38)). Increasing $|\vec{k}|$ corre-

11.1 β -GUANINE

sponds to transitioning into the impact scattering regime, where the gaussian sum term in the electron form factor (Eq. (10.10)) dominates over the long range Coulomb contribution.

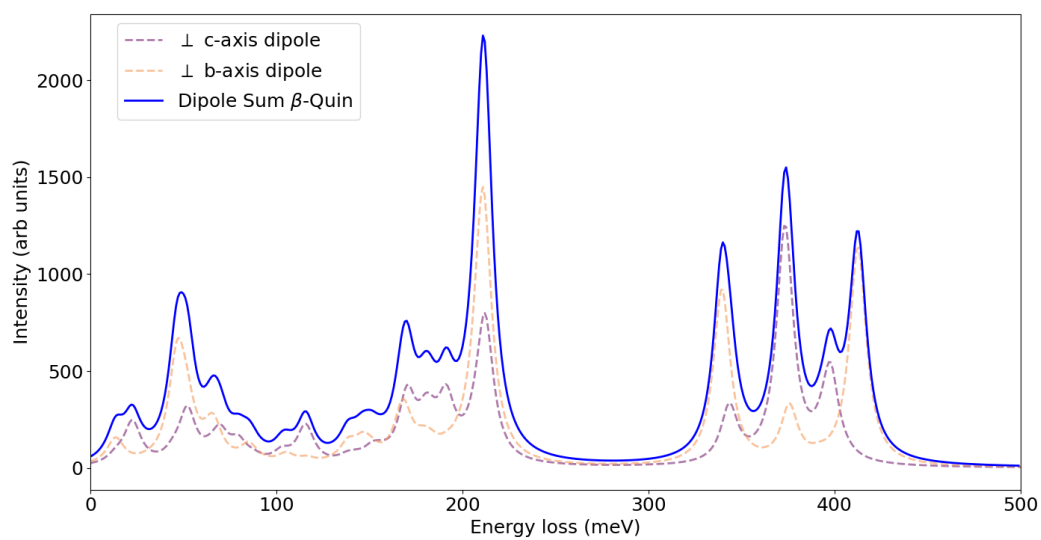
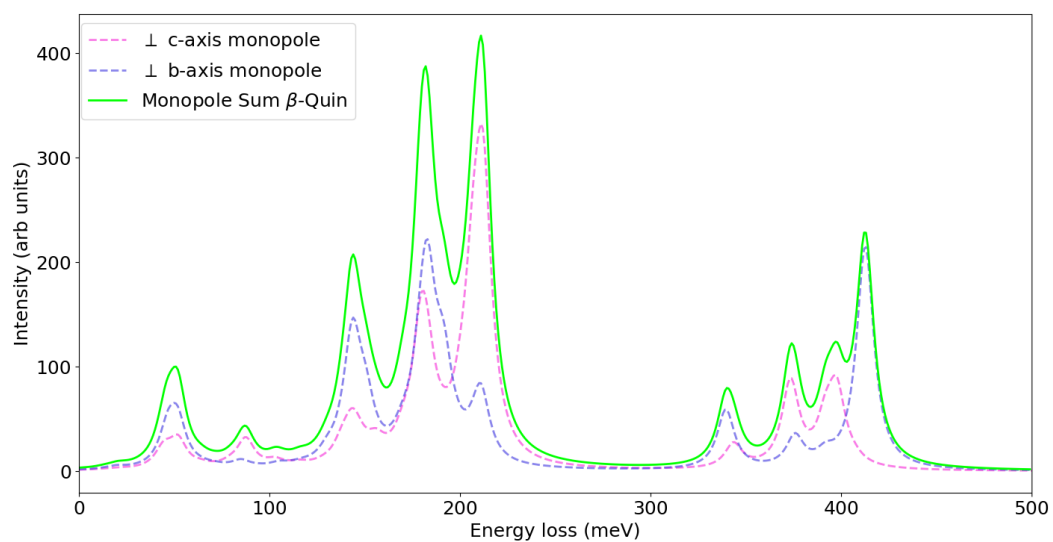
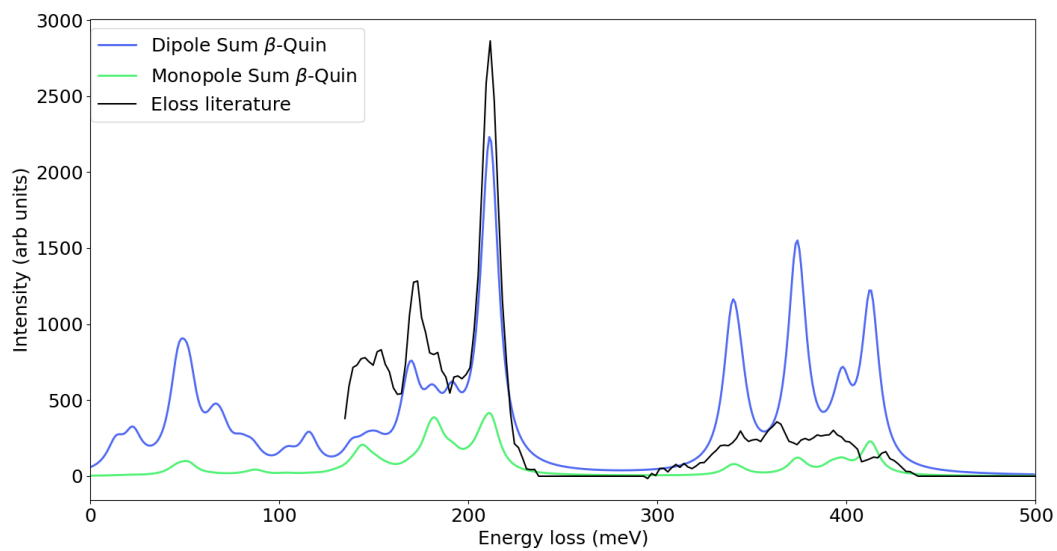


Figure 11.5: (Top) Quantum impact and dipole scattering simulations compared to experiment for β -guanine ultra-low loss EELS. *Experimental spectrum is credited the same as that of Fig. 11.3.* (Middle) Decomposing simulated total monopole spectrum into momentum imparted components along different lattice vector directions. (Bottom) Similar to middle figure, but decomposition of simulated total dipole spectrum.

The total energy loss (solid lines) are the sums of spectra calculated for momenta transfers along the b and c lattice vectors, which corresponds to the electron beam being perpendicular to the b and c axis respectively to match the semi-classical orientation nomenclature. The decomposition of the total energy loss for the monopole and dipole spectra are displayed in the middle and bottom figures of Fig. 11.5 respectively. As an example, if the b lattice unit vector was $\hat{b} = [0, 1, 0]$, then the k -point for this phonon calculation will be performed at $10^{-3}\hat{b}$. More sophisticated methods of averaging over different k -vectors such as including momentum transfers in between the $\vec{b}$ and $\vec{c}$ can be done, but the proof of concept in Fig. 11.5 shows that with the given experimental reference, quantum theories do indeed demonstrate better relative intensities than the semi-classical method.

11.1.3 Role of dispersion correction

Dispersion corrections play a major role in the theoretical simulations of phonon eigenvalues, relative intensities of the dielectric tensor, and hence contribute to the mismatch between experimental and simulated EELS spectra. This was demonstrated earlier in the benchmark tests of Part III. Figure 11.6 displays the range over which different dispersions can shift the peaks in the dielectric tensor (and hence phonon modes). The shift in frequencies is not

linear, becoming more apparent at higher frequencies. This shift is on the order of magnitude of matched peak differences between simulation and experiments. A poor DFT calculation can even lead to the merging/masking of important peaks.

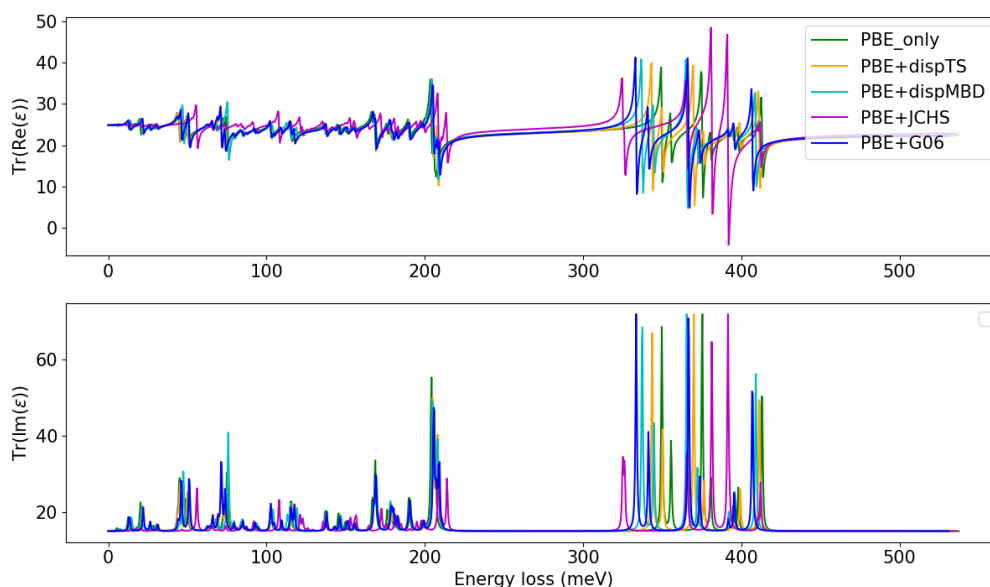


Figure 11.6: Trace of (top) real and (bottom) imaginary dielectric tensors for five dispersion corrected PBE calculations for β -guanine.

11.1.4 A note on thermal corrections

Alongside dispersion corrections, another factor contributing towards disagreements with observed vibrational frequencies not considered in our models is the lack of vibrational anharmonicity corrections. This problem is caused by deviations from the harmonic oscillator model when solving the dynamical matrix. The deviations can be minor in the case where the potential around equilibrium is deep and thus follow a well behaved harmonic behaviour, such as high frequency stretches [215]. It is more common for anharmonic effects to manifest low-frequency vibrations where the poten-

tial is more Morse like. However, the low frequency stretches of β -guanine are not well resolved experimentally, so we persevere with the harmonic approximation.

As a sanity check, we now perform some calculations to investigate anharmonic effects to confirm their negligible consequences. The harmonic potential is symmetric, such that all average atomic positions are at their equilibrium positions. This leads to vanishing thermal expansion coefficients at all temperatures, therefore anharmonic corrections are crucial to describe thermal effects. To do this, the quasi-harmonic approximation is often employed where phonon-phonon coupling is ignored. Since experiments are not near the melting point and the structure is stable at 0K, the quasi-harmonic approximation should work well. Molecular dynamics simulations can be used to go beyond this approximation but is outside the scope of this work. Phonon frequencies can change with unit cell expansions/contractions at different temperatures. This is manifested in third order derivatives of the potential and related to the Grüneisen parameters [216–218]. One popular way to define this is [219]

$$\gamma_{ks} = -\frac{\partial \ln(\omega_s(\vec{k}))}{\partial \ln(V)}, \quad (11.5)$$

which describe the anharmonicity of each phonon branch s through the volume dependence of the vibrational frequencies. To compute this parameter, the unit cell is manually contracted and expanded by 1% from equilibrium. A geometry optimisation is re-performed with fixed cell lattice parameters so that the atoms are fully relaxed before performing the phonon calculations. The finite difference method can then be used to approximate Eq. (11.5) for each vibrational mode.

Figure 11.7 show the microscopic/phonon-mode Grüneisen parameters calculated for the spectrum $\perp b$ -axis from Fig. 11.5 with respect to angular

frequency. As expected from previous arguments, the parameters with larger magnitudes occur at the lower frequency range. Post-processing analyses showed that some modes were reordered between the different runs with volume expansion/contraction, and these were corrected for.

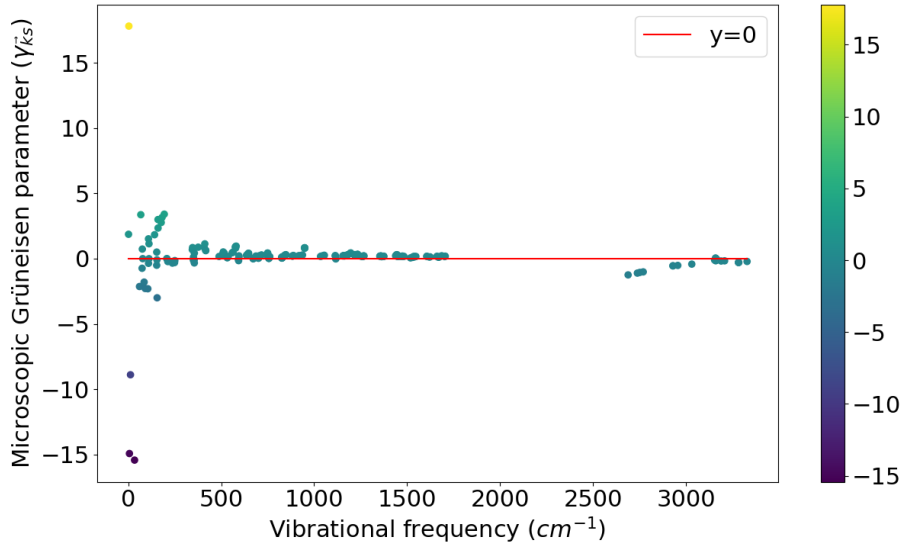


Figure 11.7: Color coded scatter plot of β -guanine Grüneisen parameters at $\vec{k} = [0, 10^{-3}, 0]$.

Intuitively, Grüneisen parameters are generally expected to be positive because an increase in cell volume should lead to a relaxation, and a reduction of bond force constants, hence a decrease of phonon frequencies. This is generally the case but out of the 192 phonon branches, 42 were negative. Studies involving negative Grüneisen parameters are often in the context of materials exhibiting negative thermal expansions [220]. Atoms populating an anharmonic potential will typically attain higher equilibrium separation distances with increasing temperature, leading to volume expansion. However, materials (such as perovskites) can sustain phonon modes that majorly contributes to the thermal expansion which cause a reduction in volume. The negative Grüneisen parameters in the case of β -guanine have simpler origins, whereby despite relaxing the unit cell at a larger volumes, there are contractions of

bond lengths. As the volume expands and the molecules become further apart, the long-range attractive forces are weakened and thus can result in the shortening of single molecule intramolecular bond lengths. A further analysis revealed that for all the modes with negative Grüneisen parameters, the major contributing bond vibrations are intra-molecular. The negative modes $\omega_s < 1000$ corresponding to the bending and stretching of intramolecular $C - N$, $C - O$ and $C = N$ bonds contain a mix of stretched and contracted bond lengths, whilst all modes $\omega_s > 2500$ with negative $\gamma_{\vec{k}s}$ are dominated by intramolecular hydrogen stretching modes with contracted bond lengths. Anharmonic effects can be more tangibly and quantitatively determined by computing the related macroscopic quantity; the volumetric thermal expansion coefficient [221],

$$\alpha_{V,\vec{k}}(T) = \frac{\sum_s \gamma_{\vec{k}s}(T) C_V(\omega_s, T)}{B_T V}, \quad (11.6)$$

where C_V is the mode specific heat

$$C_V(\omega_s, T) = k_B \left(\frac{\hbar \omega_s}{k_B T} \right)^2 \frac{\exp\left(\frac{\hbar \omega_s}{k_B T}\right)}{[\exp\left(\frac{\hbar \omega_s}{k_B T}\right) - 1]^2}, \quad (11.7)$$

B_T the bulk modulus, a property related to the second derivative of the total internal energy E at equilibrium ground state,

$$B_T = -V \left(\frac{\partial P}{\partial V} \right) \Big|_T = V \left(\frac{\partial^2 E}{\partial V^2} \right) \Big|_T. \quad (11.8)$$

C_v must be converted to eV/K so that dimensional analysis ensures the congruity in the units for volumetric thermal expansion coefficients, $[\alpha_{V,\vec{k}}(T)] \rightarrow \frac{eVK^{-1}}{[eV\text{\AA}^{-3}][\text{\AA}^3]} = \frac{1}{K}$. Typically at a specific temperature, the total energy is fitted to the lattice constant using the Birch–Murnaghan equation of state [222, 223] so that B_T can be related to the stiffness coefficients relating to each lattice pa-

parameter. However for our purposes B_T can be approximated using the same numerical procedure as that of the Grüneisen parameters in Eq. (11.5). The cell is manually expanded (and contracted) by 1,3 and 5 % of the original volume. One can use the Birch-Murnaghan equation of state [224] to fit the total energy as a function of volume, but we simplify this by using a second order polynomial, such that the curvature is used to estimate $\frac{\partial^2 E}{\partial V^2}$. This estimate will also not investigate the temperature dependence of B_T as this is beyond the quasiharmonic limit. Figure 11.8 presents the estimate for B_T as well as $\alpha_v(T)$. The volumetric thermal expansion coefficients are very small, such that volumes are effected on the order of $\sim 10^{-5}$. At low temperatures, α dips below zero and these *small* negative values are attributed to be due to numerical noise from the low frequency modes previously seen in Fig. 11.7. As expected, contributions of the negative Grüneisen parameters in Fig. 11.7 do not result in negative thermal expansion at low temperatures, suggesting that the molecular crystal will exhibit normal expansion behaviours with increasing temperature.

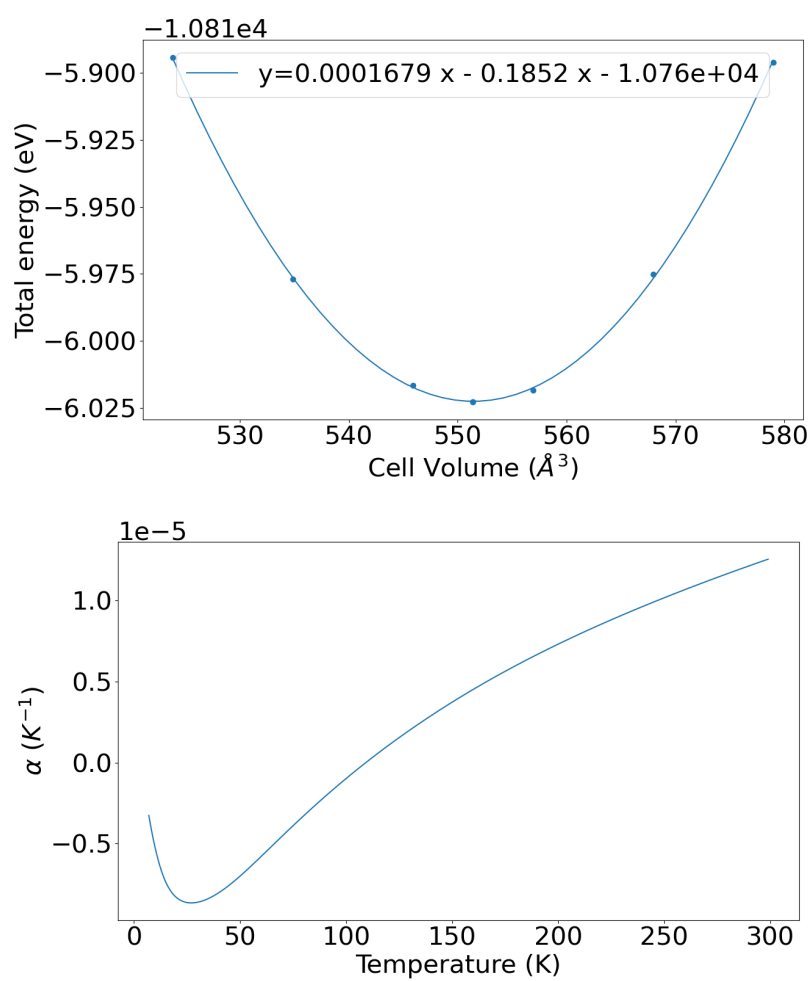


Figure 11.8: (Top) Quadratic fit of total energy with respect to unit cell volume such that bulk modulus is related to the curvature and (Bottom) temperature dependence of volumetric thermal expansion coefficient.

DIFFERENTIATING MOLECULAR CRYSTAL POLYMORPHS WITH QUANTUM DIPOLE THEORY

So far, we have built and discussed the framework of the quantum approach to ultra-low loss EELS, performed case studies of acquiring material specific properties using DFT and showed the improvement of the quantum theories over the semi-classical for β -guanine. In this chapter we bring these together to test the quantum theories' performance against experiment on Quinacridone, as well as make predictions on other molecular crystals for potential future work. To make the process more straightforward, we pick materials that are easy to work and have easily distinguishable polymorphs to test such that the results can provide the bedrock for further improvements to the theory.

12.1 QUINACRIDONE

Quinacridone is a pigment with several polymorphs that exhibit different vibrant colours. They are widely used in the art and automobile industry, in the production of paint that is resistance to high temperature and bad weather conditions. They can also be used in organic semiconductors for OLED displays [225] Organic dyes are also environmentally friendly compared to their inorganic counterparts.

12.1 QUINACRIDONE

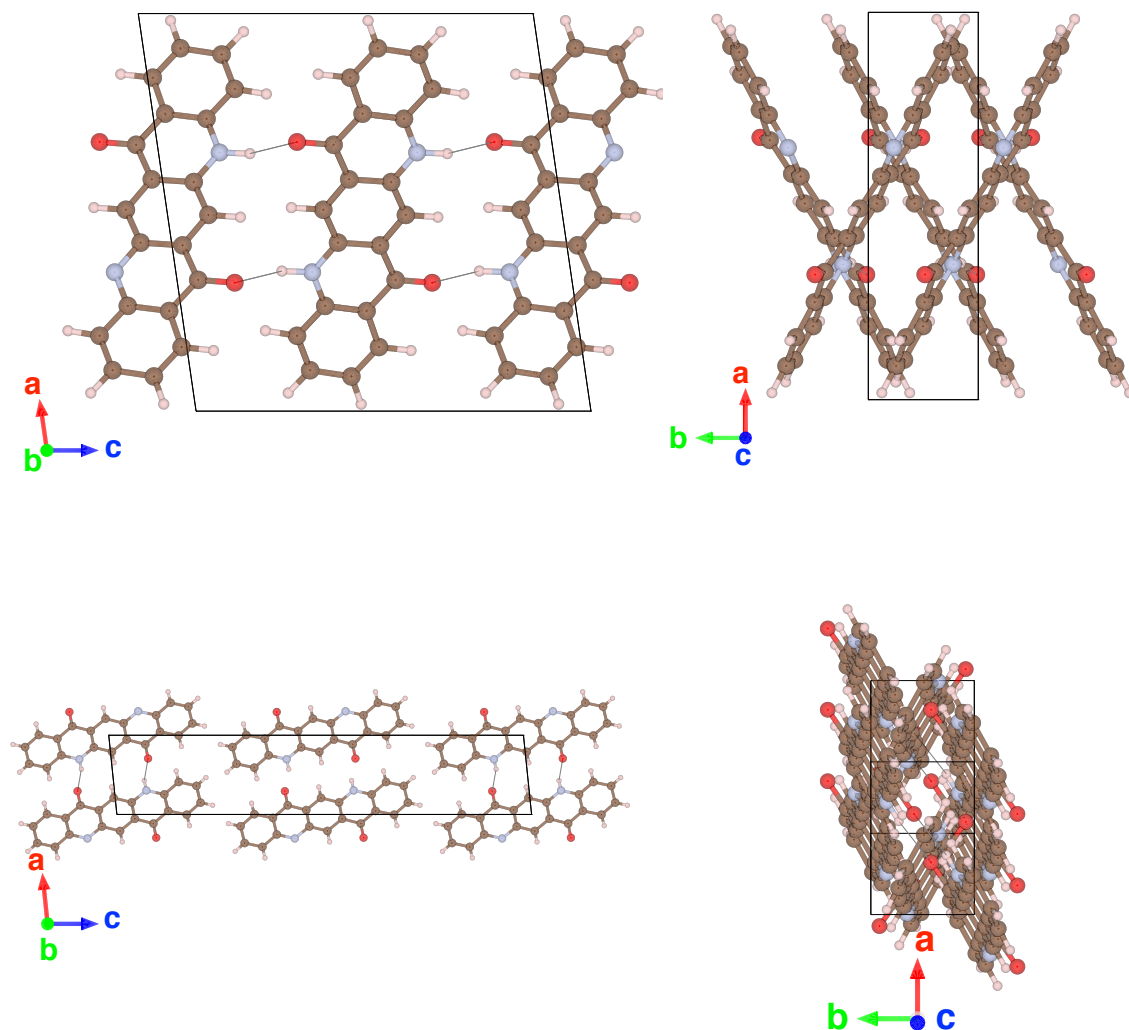


Figure 12.1: Unit cells of (top) γ and (bottom) β quinacridone, visualised using VESTA. Hydrogens are denoted in white, oxygen in red, nitrogen in blue and carbon in brown.

The two quinacridone polymorphs of interest here are the β and γ variants, which are both very stable at standard temperature pressure, and can be purchased commercially. The molecules in the β polymorph are connected to neighbouring molecules via two hydrogen-bonds, and stack along the lattice b vector, whilst the molecules of the γ polymorph form a criss-cross motif. Proper characterisation of the polymorphs is an important stepping stone to understand the conditions needed for their performance in organic electronics.

These have been distinguished (bulk) experimentally through non-destructive techniques such as IR and Raman [226]. Gorelik *et al.* [227] performed electron diffraction experiments to obtain the crystal structure, and beam damage was minimised by systematically moving the electron beam during the measurements so that signals come from clean parts of the sample. The pigments, labelled Hostaperm Red Violet ER02 (β -variant) and Hostaperm Red E5B02 (γ -variant), were provided by the manufacturer Clariant. Since the samples were not grown in house, the quinacridone crystallites are of indeterminable, mixed orientations. Therefore it is important to consider momentum transfer along all lattice vector directions. Figure 12.2 shows the quantum dipole scattering theory evaluated for both quinacridone polymorphs, where the momentum transfer of the inelastically scattered wave is evaluated along all three lattice vectors with a magnitude of $10^{-3} \text{ \AA}^{-1}$.

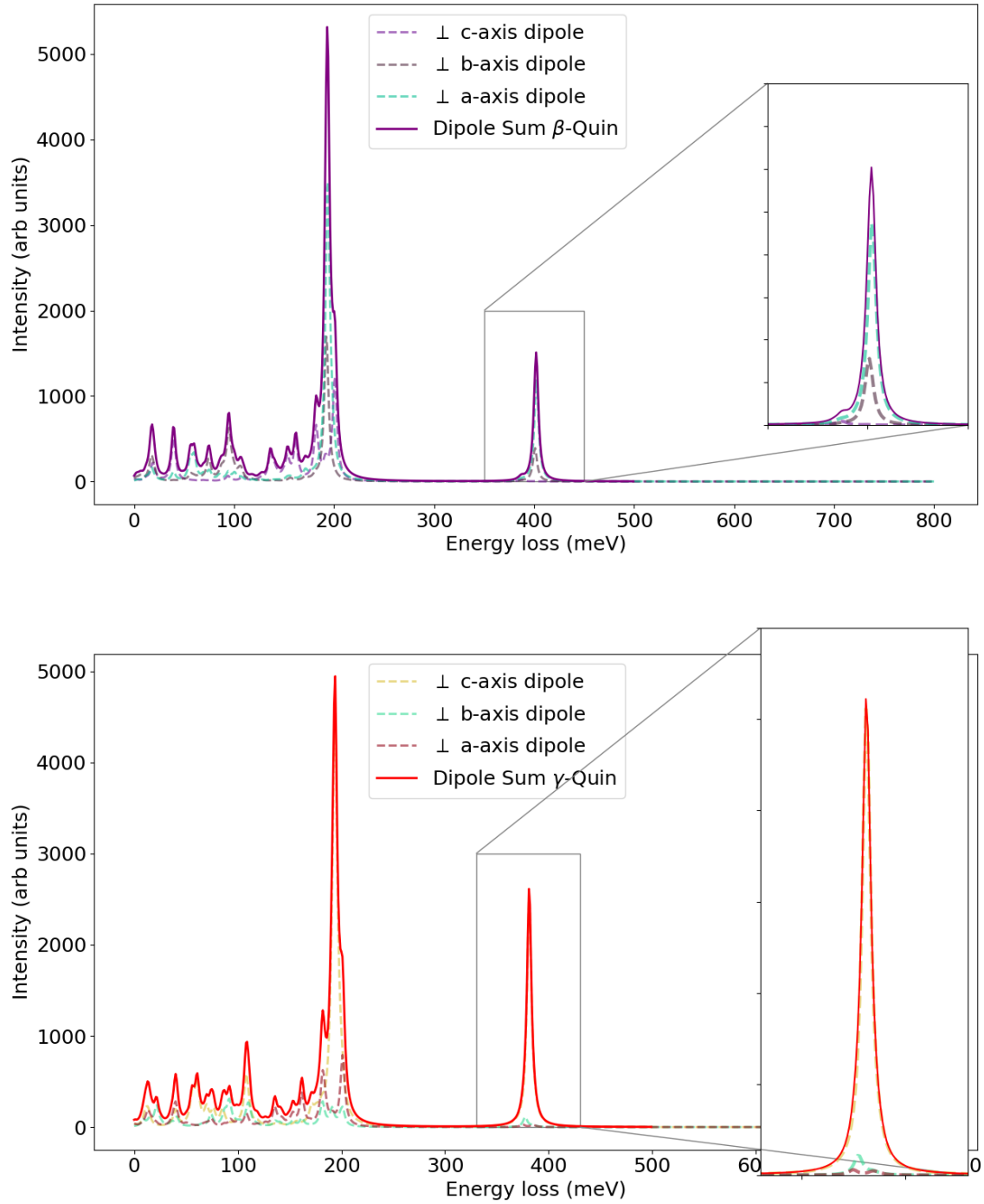


Figure 12.2: Quantum dipole scattering theory applied to (top) β and (bottom) γ -quinacridone. The solid line is the sum of spectra (dashed) calculated for electron beam perpendicular to the a, b and c lattice vectors (hence parallel to the momentum transfers $\vec{k}$). Lorentzian smearing of 5meV is applied.

The optical modes in the vicinity of 200meV are distinctly distinguishable for a beam $\perp b$ -axis, for which there are three distinct peaks for the γ variant and one for β . However, this will unlikely be visibly distinct in experiment if the crystal orientation with respect to the beam is unknown/mixed. A sum over different relative alignments is performed and shows that this area around 200meV may be difficult to distinguish in the EELS spectrum. On the other hand, in the high frequency vibration region ($\sim 400\text{meV}$), there is a clear distinction between the two polymorphs in the case where the signal is summed over all directions. There is one lattice direction that contributes to the majority of the sum in each case. For the major peak at $\sim 400\text{meV}$ (with a small shoulder contributing from the peak $\sim 390\text{meV}$) in the β variant, the major contributor is that from the $\perp a$ -axis, while the major peak at 380meV in the γ variant is ascribed to the $\perp c$ -axis. This is rationalised by referencing the unit cell geometries in Fig. 12.1. The majority of the intramolecular N-H and C-H bonds for β -quinacridone are well aligned with the a -axis, and thus a momentum transfer $\vec{k}$ parallel to this axis will couple well (large dot product overlap) to their stretching mode eigenvectors. Similarly for γ -quinacridone, the same bonds are well aligned with the c -axis.

Since they are theoretically distinguishable, we turn to the experimental challenges of first establishing that they are of the correct morphology, before performing ultra-low loss STEM EELS experiments for comparisons.

Before any ultra-low loss EELS can be done, we need to perform TEM imaging on these powders to confirm that the crystallites are thin enough to obtain a discernible signal (according to the materials' safety data sheet, the particle size is $5.8\mu\text{m}$).

12.1.1 *Crystal characterisation*

We will also use Powder X-ray diffraction to confirm that the bulk behaviour matches that of literature. These were performed on the Rigaku SmartLab Diffractometer stationed at the Rex Richards Building, Department of Materials. Each measurement comprised of a 20 minute scan over the desired angular range, in flat-plate geometry. $Cu_{K\alpha}$ illuminating radiation ($\lambda = 1.5406 \text{ \AA}$) was generated at ambient pressure and temperature.

X-ray diffraction analysis is an elastic scattering method to determine the bulk structure of the material. X-rays illuminated onto a sample produces constructive interference at conditions satisfying Bragg's law $n\lambda = 2d \sin(\theta)$ [228], for integer n , lattice spacing d and grazing angle θ . In a powdered material, the orientations of the crystallites are random. Therefore, by scanning a range of angles (2θ), all plausible lattice diffractions can be obtained. Intensity peaks occur at angle θ when the lattice spacings d are suitable to diffract X-rays. This can provide the bulk behaviour of the crystal.

The powdered pigments from Clariant are used without any modifications. Their XRD analysis are performed for the 2θ range over $5\text{-}60^\circ$ for both polymorphs. The theoretical XRD spectra are generated using CrystalDiffract (and CrystalMaker), using the fully relaxed unit cells provided by the CCDC. The identifiers for the β and γ polymorphs are QNACRDo7 and QNACRDo8 respectively as specified by Salzillo *et al.* [225]. These comparisons are shown in Fig. 12.3 and Fig. 12.4.

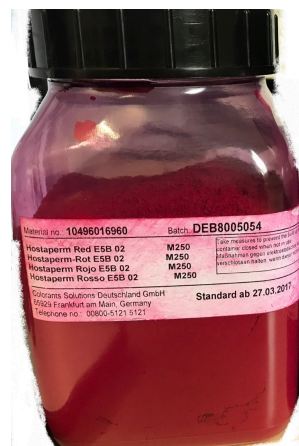
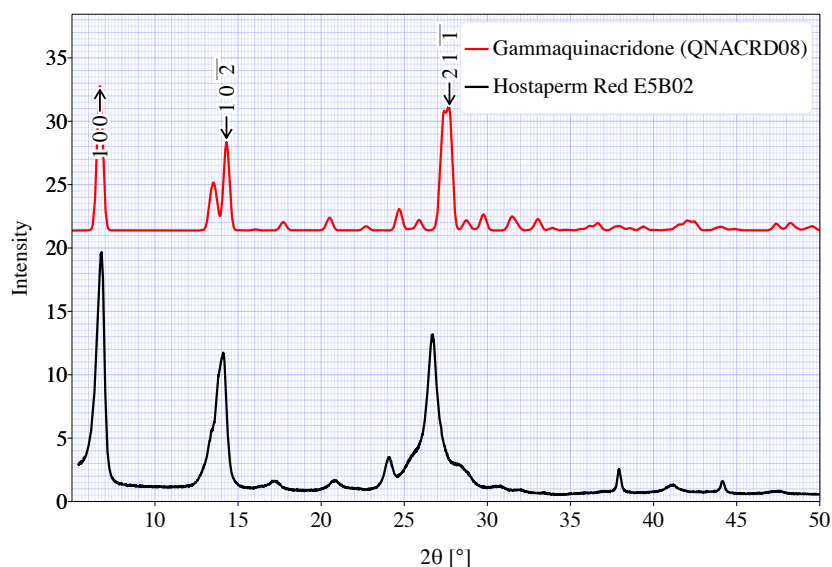


Figure 12.3: (Left) Simulated vs experimental XRD spectrum for Hostaperm Red E5B02 powder, corresponding to the γ polymorph and (right) an image of the powder. The powder X-ray spectroscopy experiments were performed by and credited to John Cattermull and myself.

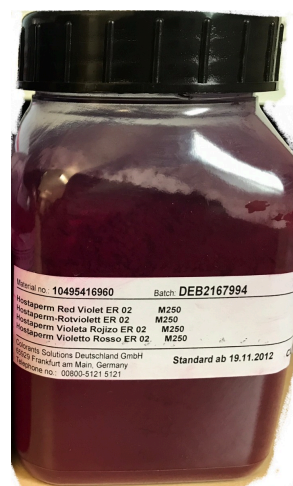
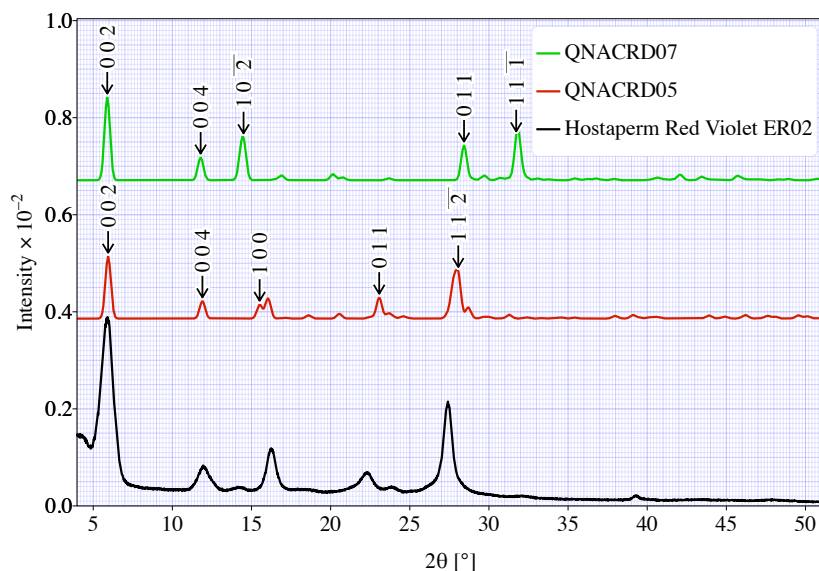


Figure 12.4: (Left) Simulated vs experimental XRD spectrum for Hostaperm Red Violet ER02 powder, corresponding to the β polymorph and (right) an image of the powder.

The experimental peaks have been systematically shifted ($\sim 3^\circ$) such that the largest peak near 5° are aligned to simulations. Systematic shifts can occur from several reasons. For example, specimen displacement errors [229]

occur if the surface of the sample is not flat enough such that it does not coincide with the surface of the sample holder. This will affect the position at which the diverging X-ray beam hits the sample, leading to systematic shifts of the whole spectrum. Any strain/compression in the sample also produces systematic shifts through distortions of the unit cell lattice parameters. If the grains of the sample are not randomly orientated, systematic redistributions in the diffraction peak intensities can occur by a preferred orientation of the crystallites. However, the experimental spectra for both β and γ quinacridone fit that of the simulations very well, as backed up by the XRD experiments performed by Squires *et al.* [230].

There was an initial issue with the β -variant, violet powder in which the experimental spectrum did not match that of the simulated spectrum from the unit cell structure of QNACRD07 (suggested by Salzillo *et al.*). This is evident from the large, missing peak coming from the $11\bar{1}$ plane. This was solved by using the QNACRD05 variant from the CCDC, also identified as the β variant and offers a better match to experiment. The two deposited structures have the same space group but have slightly different lattice parameters and spatial arrangements which gives rise to the difference in their simulated spectra.

Now that the bulk spectra have been corroborated, we need to confirm that the microscopic crystallites are thin enough to perform (S)TEM and are of the correct unit cell structure. This is important as the crystallites are the parts upon which the ultra-low loss EELS experiments will be performed so it is vital to obtain a proper electron diffraction pattern. The instruments involved are the JEOL JEM-2100 and JEM ARM200CF, both based at the David Cockayne Centre for Electron Microscopy at the University of Oxford, Department of Materials. The quinacridone powders are held in either lacey carbon films on Copper or Gold TEM grids provided by Agar Scientific. *Sample preparation was performed by Ruomu Zhang, Alex Sheader and myself.* Figure 12.5 shows

the TEM image of the Hostaperm Violet powder. Images of the red powder are very similar. The grains are composed of crystallites that overlap but are thin enough to produce a reasonable electron diffraction pattern, especially around the edges.

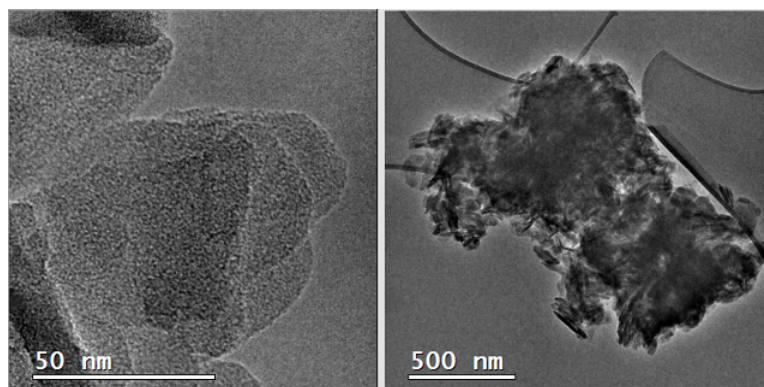


Figure 12.5: TEM images of Hostaperm Red Violet ER02 powder captured using the JEOL JEM-2100. TEM experiments were performed by and credited to Ruomu Zhang.

Electron irradiation damage is a major contributor in limiting high resolution TEM analyses. These can be separated into elastic and inelastic regimes [231]. For a high energy electron beam, elastic scattering can cause atomic displacements, creating defects and breaking down the crystallinity. More severe cases of these knock-on effects result in the ejection of atoms, leaving behind vacancies. At the fixed settings of the microscope (200kV), beam damage via this knock-on effect is very apparent and occurs rapidly. The sample rapidly deteriorates and visibly ‘moves’ when illuminated with the beam, and within seconds the electron diffraction pattern go from crystalline to ring-like. A ring pattern is formed due to either the material being polycrystalline or amorphous, where the diffracting planes are randomly oriented in different directions. The main culprit for organic compound degradation in the inelastic regime is radiolysis. This occurs when the incident beam irreversibly cause electronic excitations and break chemical bonds. It also causes heating and charging effects, leading to secondary emissions, mass loss and further struc-

tural damage. This culminates in the observed fading of spots in the electron diffraction pattern.

Using a very high incident energy results in more elastic knock-on damage. Reducing the energy requires a longer exposure time needed to adequately record the needed information, leading to more inelastic scattering damages. Thus, there is a trade off and it is not enough just to reduce the incident irradiation beam energy. Thus, the best solution here is to limit to dose onto the specimen by maximising the beam size and minimising the aperture of the electron microscope to decelerate the rate of damage until a reasonable diffraction image can be taken.

With the limited information we have on the powders, it was difficult to identify specific zone axes in the diffraction experiment. A zone axis is a direction parallel to the intersection of crystallographic planes. To substantiate the unit cell structure of our powdered samples, we need to match two reciprocal lattice vectors (by finding the appropriate Bragg spots and the $\vec{G}$ -vector connecting them) and their intersecting angle between the experimental diffraction pattern and the simulated diffraction pattern (of a single crystal) of quinacridone using CrystalDiffract. Since the zone-axis is unknown, we manually search around the stereogram until a good fit is found. The results for the red and violet Hostaperm powders are presented in [Fig. 12.6](#).

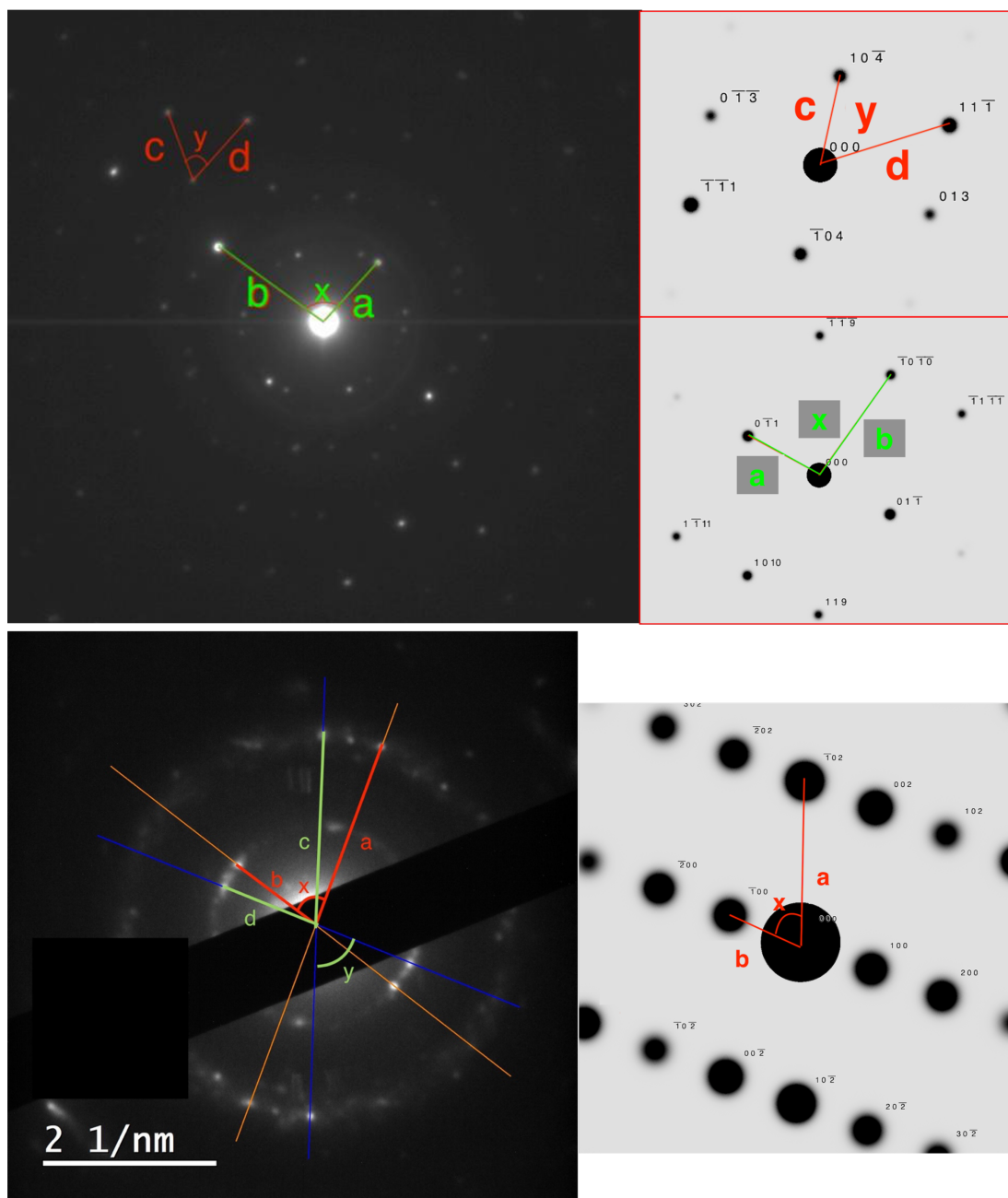


Figure 12.6: Matching two reciprocal lattice vectors and an angle between the experimental and simulated electron diffraction patterns. (Top) γ -quinacridone: The labelled variables in the experimental electron diffraction pattern (left) are $a=0.24$, $b=0.38$, $c=0.21$, $d=0.24$ ($\text{\AA}^{-1}$), $x=96$, $y=62$ ($^\circ$) and (right) $a=0.26$, $b=0.39$, $c=0.21$, $d=0.29$ ($\text{\AA}^{-1}$), $x=97$ and $y=62$ ($^\circ$). (Bottom) β -quinacridone: The labelled variables are (left) $a=0.22$, $b=0.11$, $c=0.22$, $d=0.11$ ($\text{\AA}^{-1}$), $x=72$ and $y=70$ ($^\circ$) and (right) $a=0.17$, $b=0.08$ ($\text{\AA}^{-1}$) and $x=70$ ($^\circ$). Experimental diffraction patterns were performed by and credited to Ruomu Zhang.

The γ polymorph produced a good diffraction pattern, where bright Bragg spots have their corresponding mirror image through the central bright spot. This means it is well aligned with a zone axis. The β -polymorph diffraction pattern on the other hand, was more difficult to identify due to the polycrystalline character of the pattern. Therefore we've identified two identical sets of vectors and their corresponding enclosed angle, which corresponds to the same crystal planes producing diffraction spots that are rotated around the zone-axis.

Finally, we would like to confirm there are no impurities from the manufacturing process. We have performed STEM core-loss EELS experiments on the JEM ARM200CF in attempt determine the elemental composition. However this was not successful in giving a clear signal of any element besides the Carbon K-edge. This is likely because the sample was likely to be already very burnt by the time the EELS signal was acquired and therefore the only visible signal was due to sample damage, or the build up of contamination. Another possibility is that the dosage was too low which prevented higher energy transitions corresponding to the Nitrogen and Oxygen K-edges. Another method of determining the chemical composition is through energy-dispersive X-ray spectroscopy (EDX) (also referred to as EDX or EDXS), which was also available to perform on JEM ARM200CF. This is a characterisation technique that is used for spatial elemental analyses. Upon impact, inner shell electrons ejected from the sample by the incident electron beam leave behind holes, which are then filled by higher energy state electrons. This then emits X-rays whose energies are fingerprints of the specific element. Thus a STEM experiment is able to establish a spatial map of elemental composition in a specific sample area. The EDX mapping was performed using the hyperspy python module and the results for both polymorphs are shown in Fig. 12.7. If the ejected electron creates an initial vacancy in the K shell and the filler electron comes

from the adjacent L shell, this is denoted by the K_{α} subscript. Similarly a filler electron from two shells up (M shell) is denoted by K_{β} . The nomenclature follows naturally for L_{α} , L_{β} , etc. if the initial vacancy occurs in the L shell [232]. The red (purple) pigment was scattered on a lacey Copper (Gold) grid, which explains the Cu (Au) associated peaks in its EDX spectrum. Throughout both samples the main compounds identified are those belonging to the organic molecule (H,C,N and O), but both also include silicon contamination. This is very common in assembly processes, but their EDX peaks are much smaller relative to that of the elements of interest, and are within the tolerance for ultra-low loss EELS experiments to be performed.

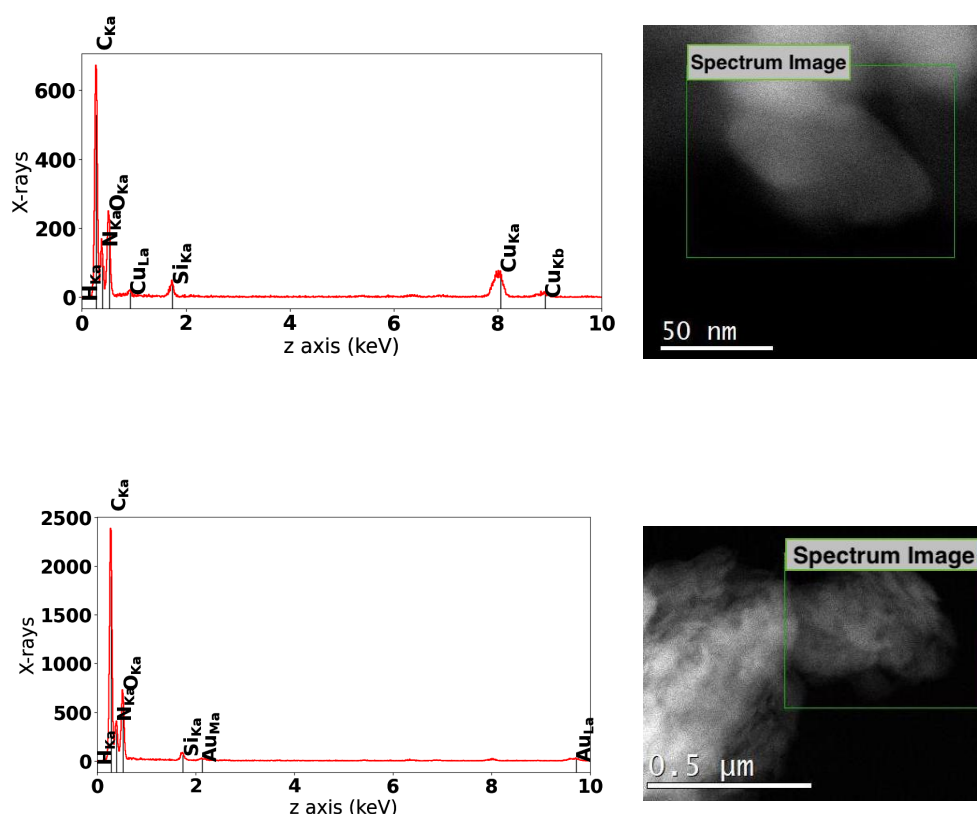


Figure 12.7: (Top left) Red pigment EDX spectrum and its (top right) associated TEM image. (Bottom left) Purple pigment EDX spectrum and its (bottom right) associated TEM image. *EDX experiments were performed by and credited to Ruomu Zhang.*

12.1.2 *Ultra-low Loss EELS experiments vs simulations*

Ultra-low loss EELS experiments were conducted by Prof. Quentin Ramasse (shadowed by Dr. Rebecca Nicholls and myself) on the Nion UltraSTEM100MC, located at SuperSTEM, on SciTech Daresbury Science and Innovation Campus, Warrington, UK. All subsequent figures including experimental spectra for quinacridone are therefore accredited to Prof. Ramasse, Dr. Nicholls and myself. A 60keV convergent electron beam is employed with a 20 mrad collection, a 22 mrad convergence angle and a 1mm entrance aperture. The energy resolution of the microscope is 8meV at minimum, which is ample to resolve the desired vibrational features. The same powdered samples from the previous XRD, TEM and EDS experiments were used. Ordinarily, only background subtraction is needed to separate the desired spectrum from the total EELS signal. However, during the time of experimentation there was an issue with the microscope hardware, giving rise to a systematic ‘spectrum’ even from pure vacuum signals. We circumvent this issue by taking the difference between the background-subtracted EELS signal and that of a pure vacuum taken without any sample nearby. As a result, the peak amplitudes below 100meV can shift (up and down) substantially depending on the choice of ‘system signal’ subtraction. The crystallites also often ‘jump’ due to charging effects as the beam approaches the sample, and these results are discarded.

Figure 12.8 compares the simulated quantum, semi-classical and experimental aloof beam ultra-low loss EELS for the two polymorphs of quinacridone. A Lorentzian smearing of width 11meV is used for all simulations in order to match the general shape of the experimental results and the only horizontal shift in the entire plot occurs when the experimental spectra are aligned to the simulations at the highest peak of $\sim 193\text{meV}$. Visually, we can identify and match several peaks shown in the vertical dashed lines but it is diffi-

cult to distinguish between the polymorphs experimentally in the energy loss range up to $\sim 200\text{meV}$. The experimental shoulder at 182meV is more visibly prominent in the γ variant, and is reflected in the quantum simulations.

The quantum impact and dipole scattering curves are not normalised with respect to each other, confirming the dominance of dipole contributions in the aloof mode. The β variant dipole scattering introduces a major peak at 402meV , and the impact scattering further contributes a peak at 387meV , and their combination explains the left shoulder in the experimental curve. The individual peaks are more difficult to discern for the γ experiment, which could be due to more experimental noise and system signal subtraction. Nonetheless, the relative positions of the highest peaks in this region clearly distinguishes the polymorphs, in both experiment and simulations. As shown previously in Fig. 11.6, dispersion corrections can greatly shift the phonon peak energies up to 20meV , especially in the high frequency range. This can explain the slight misalignment between experimental EELS and simulation in this energy range. However, there is another experimental issue with dispersion. In the EELS spectrometer, lenses are used to deflect and bin the incoming scattered fast electrons according to their corresponding energy. The error associated with this deflection process leads to a horizontal scaling factor (to first order approximations) and hence adds another layer of complication for matching the energy peak positions against simulations. Therefore, a Fourier-transform infrared spectroscopy (FTIR) experiment to measure the infrared absorbance of the two quinacridone powders was carried out in order to identify the severity of the deflection issue from the EELS experiment, also shown in Fig. 12.8. This was performed on the NicoletTM iS20 FTIR Spectrometer, located at the Rex Richards Building, University of Oxford.

This is because the peaks from the EELS and FTIR experiments should match, corresponding the infrared active phonon modes. The baseline sub-

traction for the FTIR spectra uses the method of asymmetric least square smoothing proposed by P. Eilers and H. Boelens [233]. As a result, the FTIR peak positions match that of the simulated peaks better, confirming that the horizontal fast electron deflection issues in the EELS experiment do indeed play a non-negligible role.

Since quinacridone crystallises with a monoclinic unit cell similar to the previously studied β -guanine, the same semi-classical theory is used in the semi-classical (SC) simulations in Fig. 12.8, whereby the relative orientation between the beam and all 3-axes of the sample are summed. The SC theory red-shifts the largest peak at $\sim 193\text{meV}$, and it also incorrectly suggests that the two polymorphs should be distinguishable around 109meV due to their large relative intensity difference.

As a result of increasing the Lorentzian smearing to 11meV , which better describes the experimental resolution, the shoulder at $\sim 200\text{meV}$ which was more prominent in Fig. 12.2 becomes concealed in the smearing process for the quantum theories. However, it is still present in the semi-classical simulations at this smearing width and cannot be explained away as easily. This shoulder is not present in the EELS experiment, but is visible in the FTIR spectrum due to the finer available energy resolution. According to Fig. 12.2, the major momentum transfer contributors to this shoulder are that along the c and a -axes for β and γ -polymorphs respectively. It is also possible that signals along these directions are more suppressed for the chosen crystallite.

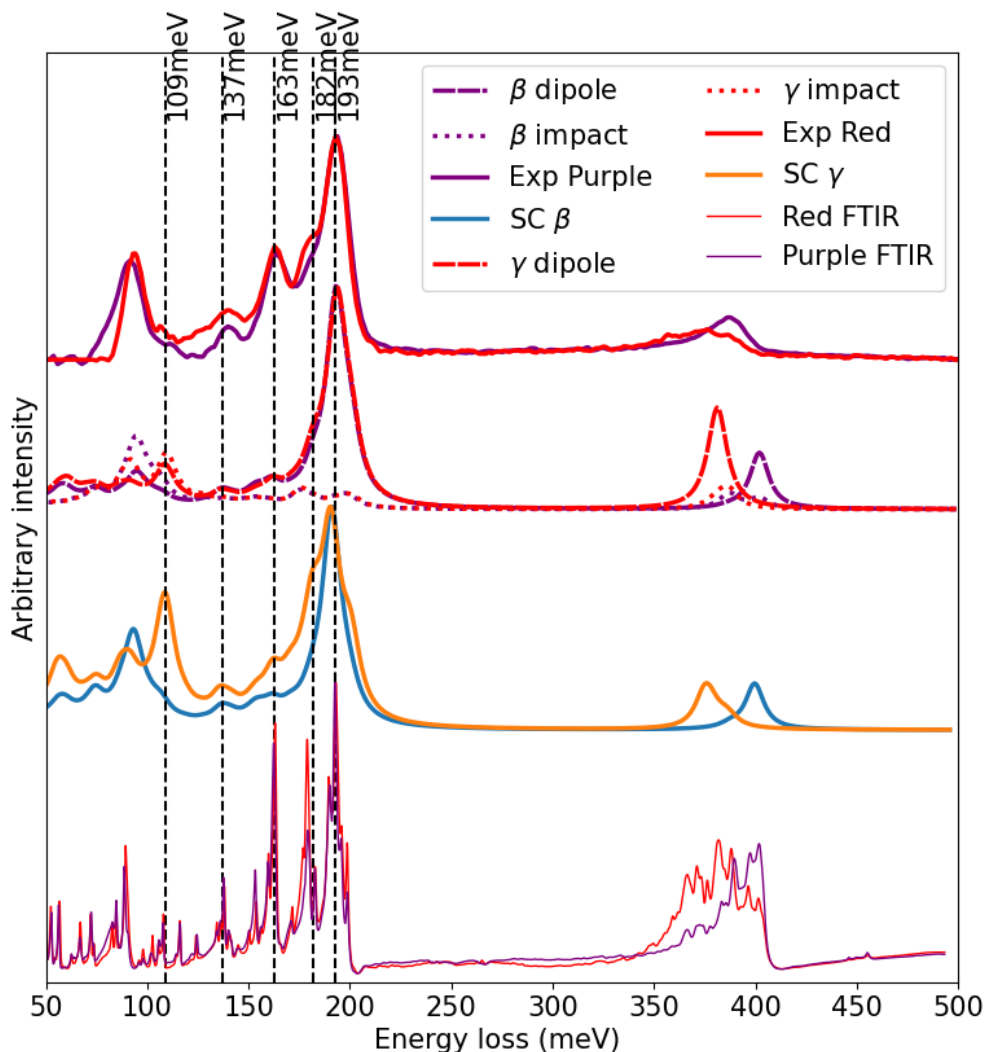


Figure 12.8: Experimental vs simulated ultra-low loss EELS for the β and γ polymorphs of quinacridone. The experimental ‘Exp’ impact parameter for the purple and red powders are 76 and 75nm respectively. ‘SC’ denotes the semi-classical theory, and all simulations are summed over the cases where the beam is perpendicular to all lattice vectors. A Lorentzian broadening of FWHM=11meV is used in all simulations to match the experimental EELS resolution. FTIR experiments results are also displayed, which were carried out and credited to Boruch Epstein and myself.

A spectral series showing the effects changing the electron beam impact parameter is given in Fig. 12.10 for both polymorphs. The results show that the spectral shapes are well preserved even for distances above 300nm. It is interesting to note that the ratio of the intensities between the highest peak $\sim 193\text{meV}$ vs. the first distinctive peak $\sim 93\text{meV}$ does not remain constant with changing impact parameter b (for both variants). As the beam moves away

from the sample edge, the former peak decreases at a faster rate compared to that of the latter. However, according to Fig. 12.8, it is intuitive for the impact theory to contribute less with increasing b , such that the peak $\sim 93\text{meV}$ should decrease faster. Thus, it is important to consider the effect of impact parameter on this apparent incongruity in future work.

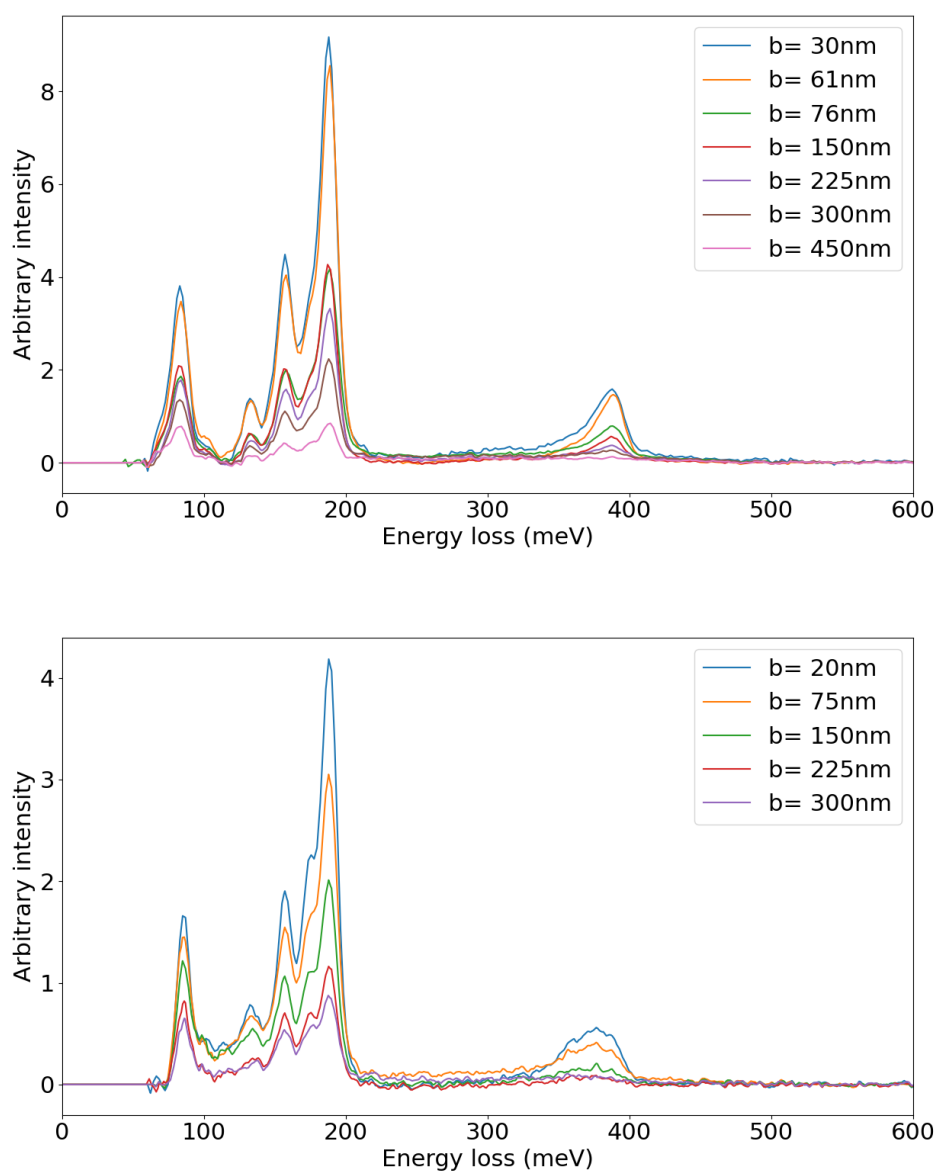


Figure 12.10: Spectral series showing the effect of impact parameter ' b ' on the aloof spectra for (top) β and (bottom) γ quinacridone.

Finally, impact scattering experiments performed on sections of the samples thin enough to retain the energy resolution are scaled and compared to that of the aloof case in Fig. 12.12. Albeit less strong, general features are retained in the impact spectra. Interestingly for β -quinacridone, the experimental shoulder at 387meV becomes more prominent relative to the major peak at $\sim 402\text{meV}$. This is in agreement with an increased contribution from the impact scattering theory in reference to Fig. 12.8. Similarly, an increase in the monopole contribution for the γ variant should result in a broadening of this high frequency peak towards the right. Having said that, this is difficult to discern experimentally, partly due to more difficulties with the erroneous system spectrum.

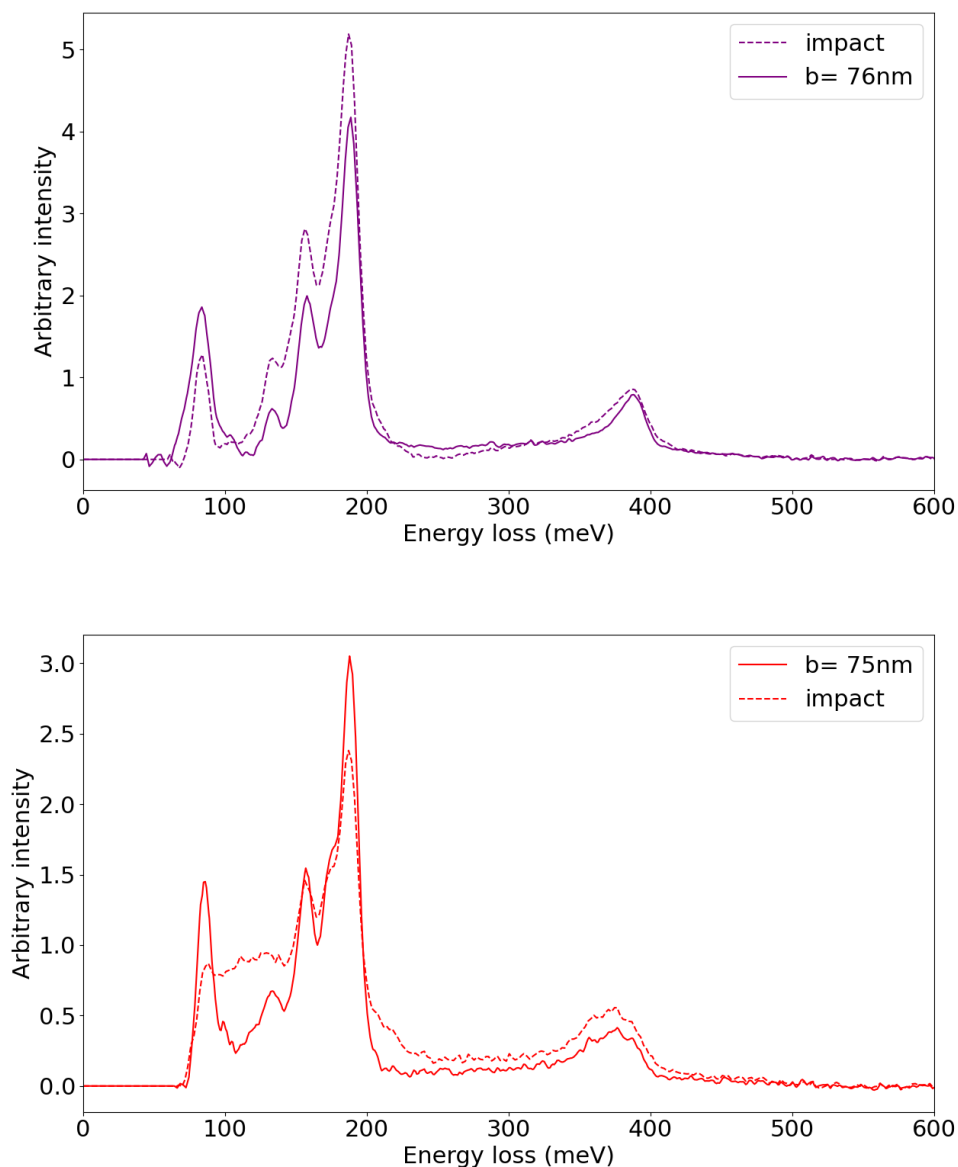


Figure 12.12: Comparisons of experimental impact and aloof energy losses for the (top) β and (bottom) γ polymorphs. No vertical scaling is performed.

12.1.3 Summary

We have successfully distinguished the vibrational signatures of β and γ quinacridone polymorphs using the quantum scattering theories, and com-

pared them against the semi-classical results. The dipole theory dominates over the impact in magnitude, offer better relative intensity predictions, and their synergistic combination help explain experimental features that are not fully present in one or the other. Relative intensities are well predicted and peak positions lie within the margin of error caused by DFT dispersion corrections. We have also demonstrated experimentally (in [Fig. 12.12](#)) that upon impact scattering, the change in shape of the β -quinacridone energy loss spectra at $\sim 387\text{meV}$ can be explained theoretically by increasing in the quantum impact contribution.

One major issue in the experiment was the system signal that pervades all spectra, and was not exactly constant on different days. This introduced for example peaks in the gain-area and an extended arch that stretches up to $\sim 1\text{eV}$. The culprit could be due to charging effects in one of NION's many apertures, such that the intensities of various features can change depending on the apertures' relative positions to each other.

There are several additional experiments that can be done. For example, decreasing the collection and convergence angles can increase the fraction of dipole scattered electrons near the Γ point. In aloof mode, shifting the aperture away from the bright field beam such that more $k = 0$ contributions are blocked out allows for the study of impact scattered electrons with less sample damage, and thus can help evaluate the validity of the impact scattering theory.

12.2 PHARMACEUTICAL MOLECULAR CRYSTALS

It is desirable to identify the emergence of any unwanted polymorphs during drug synthesis and production, as they can greatly impede the intended drug functionality. Thus as a stepping stone towards achieving this goal, we con-

tinue from the satisfactory proof of concept result for Quinacridone, and turn our attention to distinguishing several pharmaceutical drug polymorphs in the following sections by providing their theoretical ultra-low loss EELS spectra. The Lorentzian smearing used from here onwards is set at a FWHM of 11meV to match the average experimental resolution of the NION microscope from the previous quinacridone section.

12.2.1 *Olanzapine*

Olanzapine is widely used as an antipsychotic drug to treat schizophrenia and other related disorders. There has been studies on the solid state characterisation of olanzapine using IR and Raman and several anhydrous forms have been discovered [234–238]. Here, we investigate forms I, II and IV with corresponding unit cell data obtained from the CSD, with identifiers UNOGIN, UNOGIN₀₄ and UNOGIN₀₅ respectively. Their simulated vibrational spectra are presented in Fig. 12.13. In attempt to distinguish the spectra, Form I has a noticeable peak at 85meV which is not as present in the other two, and the conspicuous dipole contribution to the peak at 174meV makes form IV stand out. For potential future experiments, it will be interesting to test if the peaks around 378meV becomes more apparent as the beam approaches to the sample such that the impact scattering/monopole term contributes more weight.

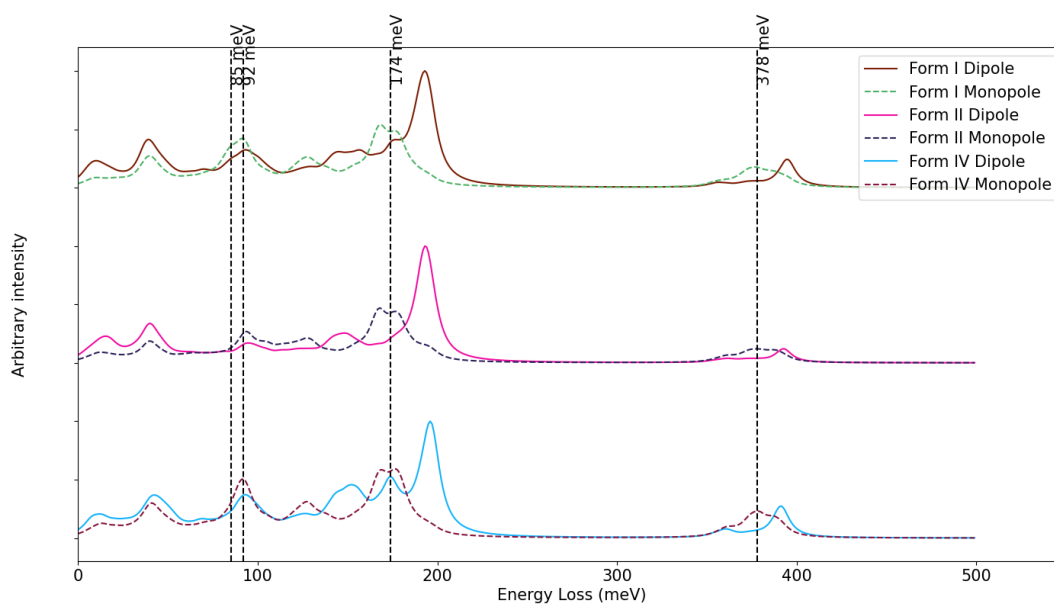


Figure 12.13: Ultra-low loss EELS simulations using the quantum dipole and impact scattering theories for olanzapine, where each spectrum is the cumulative sum over momentum transfer along the three lattice vector directions with magnitude $|k| = 0.001\text{\AA}^{-1}$.

12.2.2 Pyrazinamide

Pyrazinamide is on the WHO Model List of Essential Medicines and is used to treat tuberculosis. Studies have shown promising differences between the IR spectra for the four known polymorphs, α , β , δ and γ [239–241]. The unit cell informations are obtained from the CSD with identifiers PYRZIN, PYRZIN23, PYRZIN16 and PYRZIN20 respectively and the calculated vibrational spectra are shown in Figure 12.14. In the higher energy loss regime, polymorphs α and δ have their largest distinctive peak at 391meV , whilst β and γ variants could potentially be distinguishable by their largest peak at 402.5 and 409.5meV respectively, although their difference falls just below the current experimental resolution. The α polymorph can potentially be distinguished from the δ via a more dominant peak at 177meV .

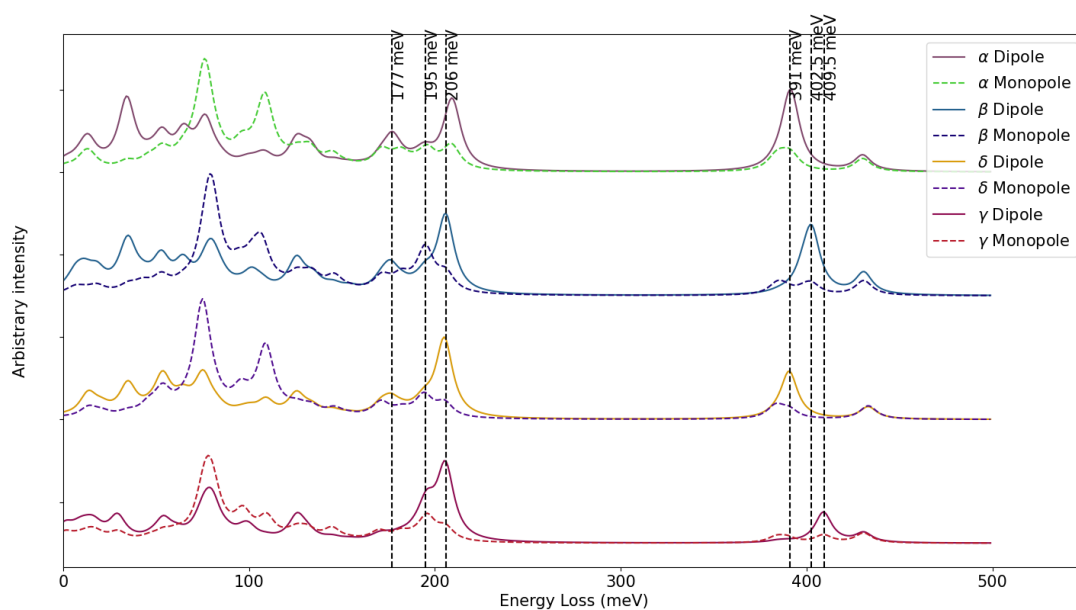


Figure 12.14: Ultra-low loss EELS simulations using the quantum dipole and impact scattering theories for pyrazinamide, where each spectrum is the cumulative sum over momentum transfer along the three lattice vector directions with magnitude $|k| = 0.001 \text{ \AA}^{-1}$.

13.1 BORON SUBPHOSPHATE

$B_{12}P_2$ is a semiconductor material that crystallises in the rhombohedral space group. It displays desirable properties such as high thermal stability and radiation damage resistance. As the unit cell of $B_{12}P_2$ is uniaxial, the dielectric tensor can be written as a purely diagonal matrix with components $\epsilon_{11} = \epsilon_{22} = \epsilon_{\perp}$ and $\epsilon_{33} = \epsilon_{\parallel}$ [242] where the lattice c -vector is the optic axis as shown in Fig. 13.1. Its aloof beam ultra-low loss EELS spectra was studied by Radtke *et al.* [243] experimentally and theoretically using the semi-classical formalism calculated with QUANTUM ESPRESSO. Two orientations were investigated, with the electron beam parallel and perpendicular to the lattice c -axis at an impact parameter of $b \approx 10nm$.

In this section, we simulate the ultra-low loss EELS spectrum for $B_{12}P_2$ using the semi-classical, quantum impact and dipole theories, with CASTEP as the source of DFT parameters. Convergence testing in CASTEP using the PBE functional resulted in an optimised monoclinic unit cell with lattice parameters $c = 11.845\text{\AA}$ and $a = 5.990\text{\AA}$ at a plane-wave cut-off of $1000eV$ and a $8 \times 8 \times 8$ k-point MP grid. These optimised lattice parameters match the QUANTUM ESPRESSO outputs (from Radtke *et al.*) to three decimals. Using the semi-classical theory described in Section 4.2, we generate the dielectric tensor (Fig. 13.2), separated into the $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ which are the two unique eigenvalues of the diagonalised tensor.

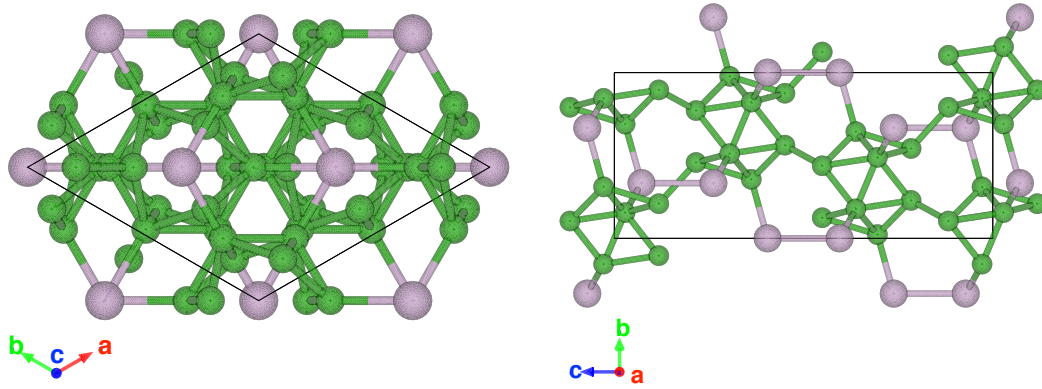


Figure 13.1: Unit cell of $B_{12}P_2$ visualised in VESTA. The initial unit cell structure was obtained from Materials Project with the identifier mp-28395. The green and purple spheres denote Boron and Phosphorous atoms respectively.

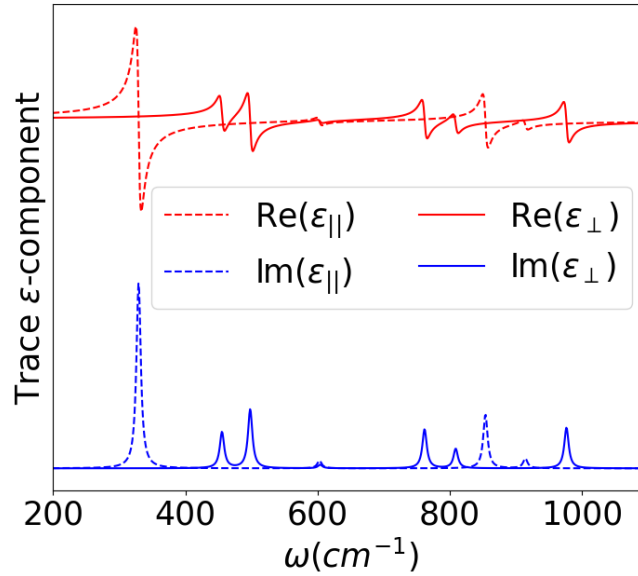


Figure 13.2: Real and imaginary parts of $\epsilon_{\perp}$ and $\epsilon_{\parallel}$ components for the dielectric tensor in the diagonal basis, where the eigenvector for $\epsilon_{\parallel}$ is parallel to the optic crystal c -axis and that for $\epsilon_{\perp}$ is perpendicular to the c -axis.

This sensitivity to direction of the dielectric response manifests in the ultra-low loss spectra of Fig. 13.4. Here we include and compare the semi-classical (calculated using both CASTEP and QUANTUM ESPRESSO), quantum impact and dipole theories (calculated using CASTEP outputs). The peaks line up well in frequency, as the lattice vectors from geometry optimisations for both DFT codes match up to $10^{-4}\text{\AA}$. There are pronounced intensity dif-

ferences between CASTEP and QUANTUM ESPRESSO outputs at modes 74.93, 74.81 and 113.42 meV. This is reflected in the differences in dielectric tensors and is caused by the variations in Born effective charge tensors and phonon eigenvectors.

All simulations are again the amalgamation of momentum transfer along the three lattice vectors, since long range dipole contributions from different part of the crystal provide a mixture of different relative orientations to the beam. When the beam is perpendicular to $\vec{c}$ -lattice vector, $\vec{k} \perp \vec{c}$ contributions are reduced and manually scaled by $\frac{1}{2}$. On the other hand, these contributions are manually doubled when the beam is $\parallel \vec{c}$. Interestingly, Γ -point calculations provide the first peak location at 40.87 meV, but is blue-shifted in experiments. This is accurately captured by the quantum theories due to frequency shifts caused by vibrational calculations performed off- Γ .

There appears to be a collaboration in Fig. 13.4 between the quantum impact and dipole theories such that their combination more suitably matches that of experiment. For example the dipole theory produces the correct relative intensities between peaks at energies 56.52 and 61.81 meV, whereas the impact theory is able to better pick out the peaks around 74, 94 and 100 meV. This is especially prominent for the case where the electron beam $\parallel c$ -vector, whereby the impact scattering intensities at these energies surpasses that of the dipole. This higher relative contribution of the impact theory (compared to dipole) to the total energy loss is reflected in the fact that the impact parameter of $b \approx 10\text{nm}$ in the experimental signals provided by Radtke *et al.* (Fig. 13.4) is very small compared to our experiments on quinacridone in Section 12.1, where the best case was $b \approx 20\text{nm}$. Unsurprisingly, impact contributions are much smaller relative to that from dipole in Fig. 12.8. The plot of momentum transfer exclusively along the $\vec{c}$ -direction shows that it predominantly contributes to the peak at 40.87 meV.

13.1 BORON SUBPHOSPHATE

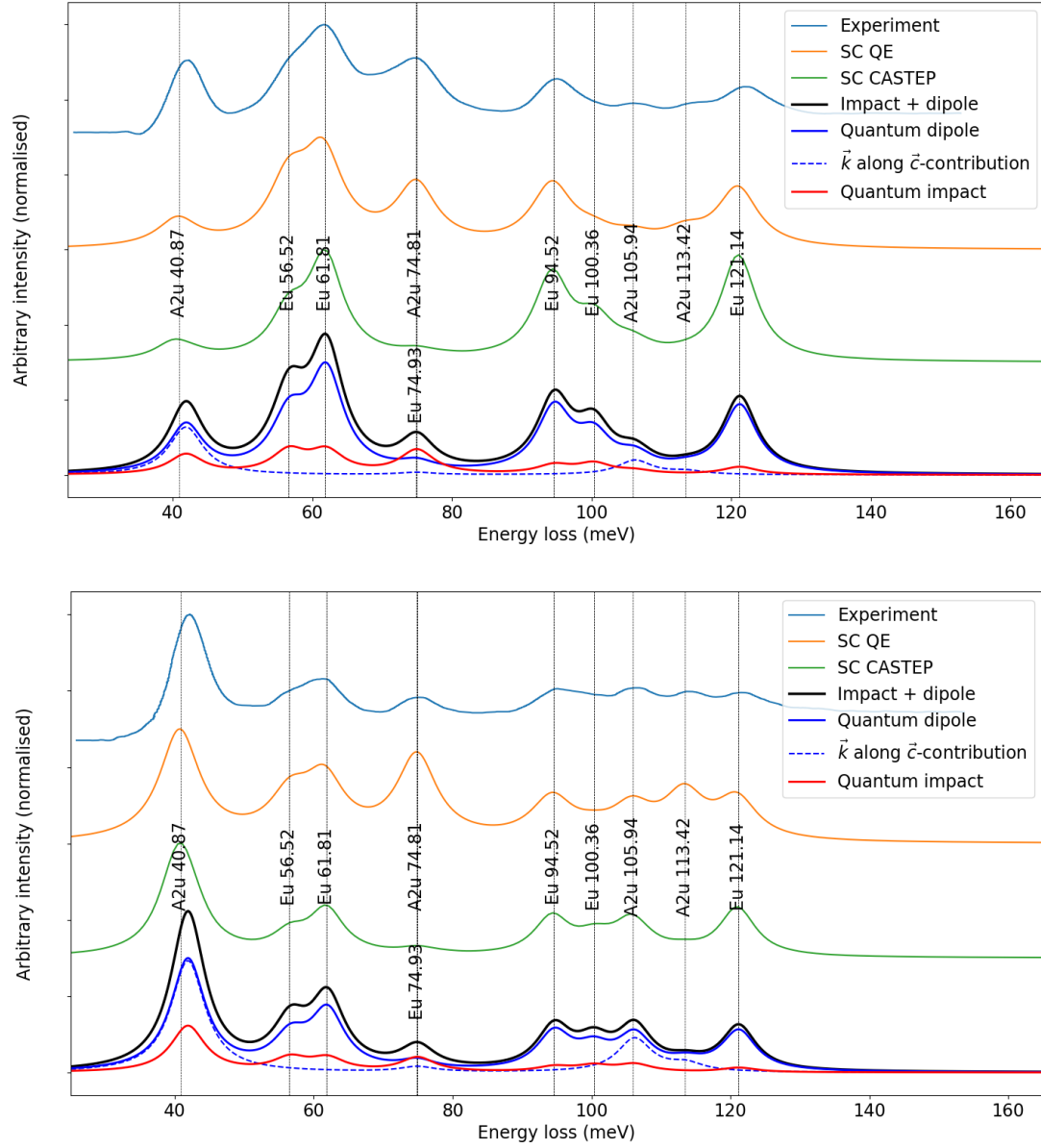


Figure 13.4: Aloof beam Ultra-low loss EELS of $B_{12}P_2$ using semiclassical (SC), quantum impact and dipole theories. The dashed line labelled ' $\vec{c}$ -contribution' denote the case where momentum transfer is solely along the lattice $\vec{c}$ -direction. *Experimental spectra are credited to Radtke et al. [243].* (Top) Electron beam is parallel and (bottom) perpendicular to lattice c -vector. The vertical lines are labelled with the irreducible representations and vibrational energies of the modes corresponding to the visible peaks.

Part V

CONCLUSION

GENERAL CONCLUSION

Practically, despite not having the same superior spatial resolution in the aloof beam mode compared to the more commonly used impact TEM, the former can be used as a complementary technique to tip enhanced IR spectroscopy, which can have resolution down to sub-10nm [244]. Aloof beam EELS are also advantageous because the vibrational spectra can be detected at a large impact parameter, before bringing the beam closer towards to sample where damage becomes non-negligible. As shown theoretically and experimentally throughout the thesis, aloof beam EELS is sensitive to the relative orientation between the beam and sample. This selectivity makes it possible to pick configurations such that specific modes of interest have eigenvectors in alignment with the momentum transfer and hence becoming more prominent in the EELS spectrum.

Part II of this thesis has methodically studied the theoretical origins of the semi-classical and quantum impact inelastic scattering theories used to predict the ultra-low loss vibrational energy spectra of crystals. The semi-classical theory performs decently in predicting aloof beam spectra, but does not take into account the momentum transfer vector as $\epsilon(\omega)$ is evaluated at $k = 0$ momentum transfer. The current quantum impact scattering theory is similar to assuming isolated atoms where long range dipole interactions are neglected because we don't explicitly account for charge redistribution. The way around this was to manually introduce a charge transfer term (such as Mulliken charges), which dominates at low momentum transfer vectors due to the diverging $\frac{1}{k^2}$ component. This work developed a new quantum dipole theory for the aloof configuration tailored to molecular crystals, and is comparable to the impact scattering theory in absolute magnitude. By introducing a

multipole expansion of the charge density to second order, it naturally led to the introduction of dynamic Born/mode effective charges.

[Part III](#) then discusses the criteria and importance of functional and dispersion contributions in predicting accurate *ab initio* DFT calculations. We also performed a systematic benchmark of the rSCAN meta-GGA functional on both the X23 set and a handpicked selection of molecular crystals, demonstrating the success of rSCAN in predicting equilibrium crystal structures without the need of dispersion corrections. The implications of the results on the behaviour of phonons and NMR chemical shifts are also discussed.

In the context of molecular crystals, we restricted ourselves to purely aloof beam mode experiments for comparisons against semi-classical and quantum simulations so that the major contributor to shifts and intensities of energy loss peaks come from DFT treatments, and less from omitted physics such as phonon-polaritons which are beyond the scope of this work. We have performed a basic study of the temperature dependence of phonons (via the Grüneisen parameters) for β -guanine in [Section 11.1.4](#). However, detailed thermal effects/phonon anharmonicity are not thoroughly investigated.

Finally, everything is consolidated in [Part IV](#). As expected, the quantum dipole theory is larger in absolute magnitude than the monopole theory in aloof mode, and demonstrates improved relative intensities compared to the semi-classical case for β -guanine. It also successfully predicts and distinguishes between the intensity spectra for two polymorphs of quinacridone. Finally, the bulk crystal boron subphosphide is considered, where the quantum theories are further endorsed (corroborated by literature experiments) as they correctly blue-shifts the peak intensity at 40.87 meV (from Γ -point calculations).

Theoretically, both quantum and semi-classical treatments require phonon-polaritons considerations, as they can give rise to additional peaks. This was illustrated for boron nitride in [Chapter 10](#), whereby surface polaritons that can shift/cause additional peaks can contribute to the discrepancy between simulation and momentum resolved ultra-low loss EELS experiments. Treatments of bulk and surface polaritons also inevitably leads to the consideration of thickness dependency. Phonon anharmonicity and thermal effects are also not accounted for in the theory, which can become an issue for systems whereby vibrational modes do not follow a harmonic potential well.

The main direction for further improvements to the theory, is to consolidate and provide a quantitative description of the monopole and dipole contributions to energy loss as a function of impact parameter. This is important as their combination appears to work best in predicting the aloof beam spectra, as demonstrated for quinacridone in [Section 12.1](#) and boron subphosphate in [Chapter 13](#). If this is possible, it can explain why in [Fig. 12.10](#) the intensity peaks are not decreasing uniformly with increasing impact parameter. Furthermore, it may become practicable to monitor in real time which bonds are being broken with decreasing impact parameter.

More specifically, the quantum impact scattering theory is more valid when the beam is on sample, whilst the dipole is more valid in the aloof mode when the impact parameter $\gg$ intermolecular separation. However, there will always be dipolar contributions from distant parts of the crystal whether the beam is aloof or on sample. This naturally lead to the question of how to transition between the two ‘extremes’? As the fast electron moves closer to the specimen, the multipole expansion premise breaks down if impact signals dominate. A naive way of uniting the two theories is to introduce a scaling

factor $\eta(\vec{k}, b) \in [0, 1]$ that depends on the momentum transfer and a radius of impact ‘ b ’, such that everything inside (outside) the radius comes from impact (dipole) contributions. This gives the total energy loss as the linear combination

$$\eta(\vec{k}, b) \times \text{Impact energy loss} + (1 - \eta(\vec{k}, b)) \times \text{Dipole energy loss}. \quad (14.1)$$

A simple starting point can be to scale the theories’ contributions based on the relative ratio of sample volumes affected but the exact dependency of η on the impact parameter b and $\vec{k}$ requires a more formal rationalisation.

Another method of achieving this could be to employ the distributed multipole analysis method [245], which is able to describe electrostatic interactions at all distances (not just far away, useful for the conventional multipole expansion used in this thesis). It is a generalisation of Mulliken’s analysis whereby an exact portrayal of the potential outside a molecule is represented. This is a numerical method in which the charge distribution generated from *ab initio* methods is used to describe the multipole moments at several sites in the molecule of interest. Thus, one can employ for example the frozen phonon method [246] to calculate the rate of change of dipole moment needed in the phonon creation process.

Other improvements include better quantification of the effects of DFT dispersion corrections to the phonon peaks for a range of molecular crystals with different degrees of long range intermolecular forces. Van Dyck [199] has published re-parametrisation constants for the gaussian approximations of the electron form factors, and it can be of interest to see if they give non-negligible variations compared to the values used in this thesis (which are obtained from the ITC).

14.1 FUTURE WORK

To conclude, an outlook on the applicability of ultra-low loss EELS for distinguishing between molecular (and bulk) crystals is promising, and as continuous experimental advances steadily improve the resolving power of electron microscopes, it will allow for better directional and spatial determination of crystal compositions.

APPENDIX

In the derivation of the classical electron energy loss (equation 4.39), there is a discrepancy amongst literature of how many 2π s should be in the global constants. Although this dimensionless factor does not affect the resulting intensities due to an absolute scaling which occurs when matching with experimental spectra, this section dedicates itself to reviewing and untangling the origins of such factors in the literature.

In the work of Radtke *et al.*, the energy loss probability is referenced from the works of Taverna [104], Howie [109] and Batson [113]. Taverna derives the electron energy loss spectrum of the aloof beam case where the electron passes by a tube rather than a plane, but the resulting expression is of the same form where the material geometry differences are encapsulated in the polarisability α tensor, defining the dielectric response of the cylinder. The global constant here is $(\frac{1}{2\pi})$. In Howie's work the factor is indeed $\frac{1}{(2\pi)^2}$ and their derivation considered aloof electron trajectories near a cubic specimen. Finally, in Batson's 1983 work, the factor used is 4π and in deriving so, it is self referential to a proceeding in 1981 [114], whereby there is a slight discrepancy in the (global dimensionless constants) formulation of the system's bulk response function $\phi(\omega, q)$.

The discrepancies in the appearances of 2π between different formulations are attributed to the method of how authors conglomerate constants in solving the Poisson/Laplace equations in gaussian or SI units. This, together with the effect of geometries and simplifications of the dielectric tensor components provide motivation for why a thorough derivation of the probabilistic

energy loss is provided in the main text, in order to properly understand the origins of each term.

RELATIONSHIP BETWEEN DOUBLE DIFFERENTIAL CROSS SECTION AND DYNAMICAL STRUCTURE FACTOR

B.1 BORN APPROXIMATION FOR THE DDCS

Here we flesh out the full derivation of the DDCS expression of [Eq. \(5.2\)](#) in [Section 5.2](#) using the Born approximation in the limit of weak scattering. Starting from the general definition of the DDCS as given in [Eq. \(5.1\)](#),

$$\frac{d^2\sigma}{d\Omega dE_1} = \frac{1}{N} \frac{[\vec{j}_1(\vec{r}, \vec{k}_1, E_1) \cdot \hat{r}]r^2}{\vec{j}_0|_z} \quad (\text{B.1})$$

and following the arguments by Sturm [[122](#)]; the term $[\vec{j}_1(\vec{r}, \vec{k}_1, E_1) \cdot \hat{r}]r^2 d\Omega dE_1$ in phase space denotes the total number of scattered particles into a volume d^3k_1 around the reciprocal vector $\vec{k}_1$, i.e. is equivalent to

$$N_0 \sum_{n_0, n_1} P_{n_0} w(n_0, \vec{k}_0 \rightarrow n_1, \vec{k}_1) D(\vec{k}_1) d^3k_1 \quad (\text{B.2})$$

where N_0 denotes the number of particles existing in state $|\vec{k}_0\rangle$, $D(\vec{k}_1)$ is the number density of plane-wave states and w is the transition probability from the initial to final states. For all intents and purposes we consider only periodic boundary conditions so that for a volume V ,

$$D(\vec{k}_1) d^3k_1 = D(E_1) dE_1 = \frac{V}{(2\pi)^3} k_1^2 d\Omega dk_1 \quad (\text{B.3})$$

We now need to find the expression for the transition rate probability using the Born series and first born approximation under the weak scattering limit.

B.1.1 Born series and transition probability

$$w = \frac{2\pi}{\hbar} |\langle \psi_i | V | \psi_f \rangle|^2 \rho() \quad (\text{B.4})$$

for some perturbation V acting on the initial and final eigenstates ψ_i and ψ_f respectively. To solve the scattering problem, we need to know the form of the final wavefunction, ψ_f in the integral

$$\langle \psi_i | V | \psi_f \rangle = \int \psi_i^* V \psi_f d^3r \quad (\text{B.5})$$

We begin from the time-independent Schrödinger equation, of an incident particle with mass m experiencing a potential $V(\vec{r})$ from the target material,

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \psi_{\vec{k}}(\vec{r}) = E \psi_{\vec{k}}(\vec{r}) \quad (\text{B.6})$$

which we can rewrite as

$$(\nabla^2 + k^2) \psi(\vec{r}) = \frac{2m}{\hbar^2} V(\vec{r}) \psi(\vec{r}) \quad (\text{B.7})$$

for $k^2 = \frac{2mE}{\hbar^2}$. The homogenous solution is that of a plane wave and corresponds to the incident wave, $\psi_0(\vec{r})$ of free particle of energy $E_0 = \frac{\hbar^2 k_0^2}{2m}$. For the particular solution, $\psi_1(\vec{r})$, one can introduce a Green's function and transform this into an integral equation, i.e. the Lippmann-Schwinger equation [247–249] where the full solution to the wavefunction satisfies

$$\psi_{\vec{k}}(\vec{r}) = \psi_0(\vec{r}) + \frac{2m}{\hbar^2} \int G(\vec{r} - \vec{r}') V(\vec{r}') \psi'_{\vec{k}}(\vec{r}') \quad (\text{B.8})$$

The Green's function, $G(\vec{r} - \vec{r}')$ will satisfy from a point source of $\delta(\vec{r} - \vec{r}')$

$$(\nabla^2 + k^2) G(\vec{r} - \vec{r}') = \delta(\vec{r} - \vec{r}') \quad (\text{B.9})$$

To find the expression for $G(\vec{r} - \vec{r}')$, we substitute into [Eq. \(B.9\)](#) the fourier transforms of G and the delta function,

$$G(\vec{r} - \vec{r}') = \frac{1}{(2\pi)^3} \int e^{i\vec{q} \cdot (\vec{r} - \vec{r}')} \tilde{G}(\vec{q}) d^3q \quad (\text{B.10})$$

$$\delta(\vec{r} - \vec{r}') = \frac{1}{(2\pi)^3} \int e^{i\vec{q} \cdot (\vec{r} - \vec{r}')} d^3q \quad (\text{B.11})$$

to get $G(\vec{q}) = \frac{1}{k^2 - q^2}$. Plugging this back into its fourier transform gives

$$G(\vec{r} - \vec{r}') = \frac{1}{(2\pi)^3} \int \frac{e^{i\vec{q} \cdot (\vec{r} - \vec{r}')}}{k^2 - q^2} d^3q \quad (\text{B.12})$$

$$= \frac{1}{(2\pi)^3} \int_0^\infty \frac{q^2}{k^2 - q^2} dq \int_0^\pi e^{iq||\vec{r} - \vec{r}'|| \cos(\theta)} \sin(\theta) d\theta \int_0^{2\pi} d\phi \quad (\text{B.13})$$

$$= \frac{1}{(2\pi)^2} \int_0^\infty \frac{q^2}{(iq||\vec{r} - \vec{r}'||)(k^2 - q^2)} (e^{iq||\vec{r} - \vec{r}'||} - e^{-iq||\vec{r} - \vec{r}'||}) \quad (\text{B.14})$$

$$= \frac{1}{4\pi^2 i ||\vec{r} - \vec{r}'||} \int_0^\infty \frac{q}{k^2 - q^2} (e^{iq||\vec{r} - \vec{r}'||} - e^{-iq||\vec{r} - \vec{r}'||}) dq \quad (\text{B.15})$$

$$= -\frac{1}{4\pi^2 i ||\vec{r} - \vec{r}'||} \int_{-\infty}^\infty \frac{q e^{iq||\vec{r} - \vec{r}'||}}{q^2 - k^2} dq \quad (\text{B.16})$$

This integral can be solved using contour integration. If one does not displace the poles, one can follow two different contours shown in [Fig. B.1](#).

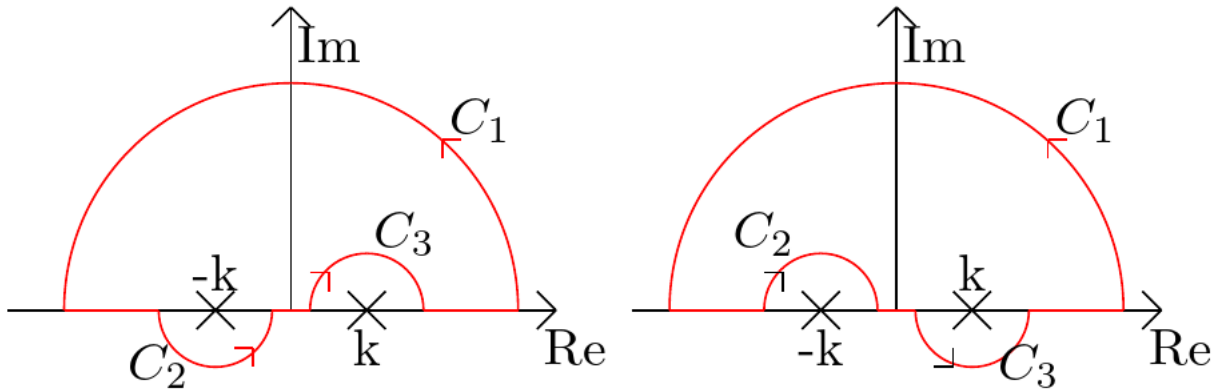


Figure B.1: Two possible routes to take in evaluation of the integral in [Eq. \(B.16\)](#) when transformed into the complex plane.

If we follow Fig. B.1 (b), the contour integral (replacing q in Eq. (B.16) with z) is

$$\begin{aligned} \int_C \frac{ze^{iz|\vec{r}-\vec{r}'|}}{z^2-k^2} dz &= \int_C f(z) dz = 2\pi i \times \text{residue}(f(z=k)) = 2\pi i \times \frac{e^{iz|\vec{r}-\vec{r}'|}}{2} = i\pi e^{iz|\vec{r}-\vec{r}'|} \\ &= \mathcal{P} \int_{-R}^R f(q) dq + \int_{C_1+C_2+C_3} f(z) dz \end{aligned} \quad (\text{B.17})$$

where R is the radius of the largest semicircle in Fig. B.1 The integral over the curves C_1 , C_2 and C_3 vanish as we parameterize C_2 and C_3 with circles $z = -k + re^{i\theta}$ and $z = k + re^{i\theta}$ respectively. This gives

$$\begin{aligned} \int_{C_2+C_3} f(z) dz &= \lim_{r \rightarrow 0} \left[- \int_0^\pi \frac{(-k + re^{i\theta})e^{i|\vec{r}-\vec{r}'||-k+re^{i\theta}|}}{(-k + re^{i\theta})^2 - k^2} ire^{i\theta} d\theta \right. \\ &\quad \left. + \int_\pi^{2\pi} \frac{(k + re^{i\theta})e^{i|\vec{r}-\vec{r}'||k+re^{i\theta}|}}{(k + re^{i\theta})^2 - k^2} ire^{i\theta} d\theta \right] \end{aligned} \quad (\text{B.18})$$

$$= \int_\pi^0 i \frac{e^{i|\vec{r}-\vec{r}'||k|}}{2} + \int_\pi^{2\pi} i \frac{e^{i|k||\vec{r}-\vec{r}'|}}{2} d\theta \quad (\text{B.19})$$

$$= 0 \quad (\text{B.20})$$

and finally, we just have

$$G(\vec{r} - \vec{r}') = - \frac{e^{i|q||\vec{r}-\vec{r}'|}}{4\pi|\vec{r} - \vec{r}'|} \quad (\text{B.21})$$

We can also follow contour (b) and come to the same conclusion. Alternatively, one can also for example displace the poles according to Fig. B.2 and obtain the same integral result

$$\int_{-\infty}^{\infty} \frac{q e^{i|q||\vec{r}-\vec{r}'|}}{q^2 - k^2} dq = \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{q e^{i|q||\vec{r}-\vec{r}'|}}{q^2 - (k + i\epsilon)^2} dq \quad (\text{B.22})$$

$$= 2\pi i \lim_{\epsilon \rightarrow 0^+} \text{Res} \left[\frac{q e^{i|q||\vec{r}-\vec{r}'|}}{(q - (k + i\epsilon))(q - (-k - i\epsilon))} \right]_{q=k+i\epsilon} \quad (\text{B.23})$$

$$= 2\pi i \times \left(\frac{1}{2} e^{i|k||\vec{r}-\vec{r}'|} \right) \quad (\text{B.24})$$

$$= \pi i e^{i|k||\vec{r}-\vec{r}'|} \quad (\text{B.25})$$

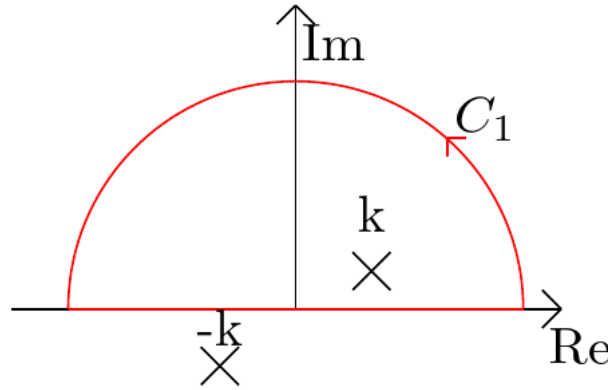


Figure B.2: Solving Eq. (B.16) by displacing poles.

Finally, the total wavefunction using the Green's function solution method is

$$\psi_{\vec{k}}(\vec{r}) = \psi_0(\vec{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{i|k||\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} V(\vec{r}') \psi(\vec{r}') d^3\vec{r}' \quad (\text{B.26})$$

$$\approx \psi_0(\vec{r}) - \frac{m}{2\pi\hbar^2} \int \frac{e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}} e^{-i\vec{k}\cdot\vec{r}'}}{r} V(\vec{r}') d^3\vec{r}' \quad (\text{B.27})$$

$$= \psi_0(\vec{r}) + f \frac{e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}}{r} \quad (\text{B.28})$$

where $\frac{1}{|\vec{r}-\vec{r}'|}$ is simplified to $\frac{1}{r}$ because in the scattering experiment, the size of the target material is much smaller than the distance from the detector, i.e. $r \ll r'$. We have also employed the first Born approximation by replacing $\psi(\vec{r}')$ with the incident wave $\psi_0(\vec{r}') = e^{i\vec{k}_0 \cdot \vec{r}'}$. This is because we assume that the interaction hamiltonian (potential) is weak enough to only slightly change the incident wave, such that the scattered wave is approximated by a plane wave. We define the term $f = -\frac{m}{2\pi\hbar^2} \int e^{-i\vec{k} \cdot \vec{r}'} V(\vec{r}') d^3r'$ as the scattering amplitude f , which is equivalent to the differential cross section per unit solid angle measured in experiments. This separation of the scatterer and system (scattered wavefunction same form as incident, with difference in momentum) using the first Born approximation is used in the derivation of the EELS double differential cross section treated in section [Section 5.2](#).

Finally, combining [Eq. \(B.1\)](#), [Eq. \(B.2\)](#), [Eq. \(B.3\)](#) and the expression of the incident beam current density $j_0|_z = \frac{N_0}{V} \frac{\hbar k_0}{m}$, we arrive at [Eq. \(5.2\)](#) in the main text,

$$d\sigma^2 = \frac{1}{N} \frac{\sum_{n_0, n_1} P_{n_0} \frac{2\pi}{\hbar} |\langle n_1, k_1 | H_{\text{int}} | n_0, k_0 \rangle|^2 \delta(E_{n_0} + E_0 - E_{n_1} - E_1) \frac{V}{(2\pi)^3} \frac{mk_1}{\hbar^2} d\Omega dE}{\frac{\hbar k_0}{mV}} \quad (\text{B.29})$$

$$= \frac{k_1}{Nk_0} \frac{m^2 V^2}{\hbar^4 (2\pi)^2} \sum_{n_0, n_1} P_{n_0} |\langle n_0, k_0 | H_{\text{int}} | n_1, k_1 \rangle|^2 \delta(E_{n_0} + E_0 - E_{n_1} - E_1) d\Omega dE \quad (\text{B.30})$$

Note that here for the incident and scattered free electron, $E = \frac{\hbar^2 k^2}{2m}$, so that $dE = \frac{\hbar^2 k}{m} dk$

Starting from the general DDOS Eq. (B.30), we plug in the interacting hamiltonian for the impact scattering case, $H_{int} = \frac{Z_j e^2}{4\pi\epsilon_0} \sum_j \frac{1}{|\vec{r} - \vec{r}_j|}$, such that

$$\langle n_1, \vec{k}_1 | \frac{e^2}{4\pi\epsilon_0} \sum_j \frac{Z_j}{|\vec{r} - \vec{r}_j|} | n_0, \vec{k}_0 \rangle = \frac{e^2}{4\pi\epsilon_0 V} \langle n_0 | \sum_j \int_{\mathcal{R}^3} Z_k \frac{e^{-i\vec{k}_0 \cdot \vec{r}} e^{i\vec{k}_1 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} dV | n_1 \rangle \quad (\text{B.31})$$

Let $\vec{k} = \vec{k}_0 - \vec{k}_1$, we focus on the integral in the bracket sandwich:

$$\sum_j \int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} = \sum_j \int_{\mathcal{R}^3} \frac{e^{-i\vec{k} \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} dV \quad (\text{B.32})$$

$$= \sum_j \int_{\mathcal{R}^3} \frac{e^{i\vec{k} \cdot \vec{r}_j} e^{i\vec{k} \cdot (\vec{r} - \vec{r}_j)}}{|\vec{r} - \vec{r}_j|} d^3(\vec{r} - \vec{r}_j) \quad (\text{B.33})$$

Now we let $\vec{r} - \vec{r}_j = \vec{r}^*$ such that $d\vec{r}^* = d\vec{r}$.

$$\sum_j \int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} = \sum_j \int_0^{2\pi} d\phi \int_0^\pi \int_0^\infty \frac{e^{i\vec{k} \cdot \vec{r}_j} e^{ikr^* \cos(\theta)} r^{*2} \sin(\theta)}{|\vec{r}^*|} dr^* d\theta \quad (\text{B.34})$$

Let $t = \cos(\theta)$ s.t. $dt = -\sin(\theta)d\theta$ and we have

$$\sum_j \int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} = \sum_j \int 2\pi e^{i\vec{k} \cdot \vec{r}_j} \int_{-1}^1 dt \int_0^\infty e^{ikr^* t} r^* dr^* \quad (\text{B.35})$$

$$= \sum_j \int 2\pi e^{i\vec{k} \cdot \vec{r}_j} \int_0^\infty \frac{1}{ikr^*} r^* [e^{ikr^*} - e^{-ikr^*}] dr^* \quad (\text{B.36})$$

Now let's introduce an attenuation factor $e^{-\lambda r^*}$ such that we have

$$\sum_j \int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} \quad (\text{B.37})$$

$$= \sum_j \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \int_0^\infty [e^{ikr^* - \lambda r^*} - e^{-ikr^* - \lambda r^*}] dr^* \quad (\text{B.38})$$

$$= \lim_{\lambda \rightarrow 0} \sum_j \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \left(\frac{e^{ikr^* - \lambda r^*}}{ik - \lambda} - \frac{e^{-ikr^* - \lambda r^*}}{-ik - \lambda} \right)_0^\infty \quad (\text{B.39})$$

$$= \lim_{\lambda \rightarrow 0} \sum_j \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \left(\frac{e^{ikr^* - \lambda r^*} (-ik - \lambda)}{k^2 + \lambda^2} + \frac{e^{-ikr^* - \lambda r^*} (-ik + \lambda)}{k^2 + \lambda^2} \right)_0^\infty \quad (\text{B.40})$$

$$= \lim_{\lambda \rightarrow 0} \sum_j \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \left(\frac{ik + \lambda + ik - \lambda}{k^2 + \lambda^2} \right) \quad (\text{B.41})$$

$$= \sum_j \frac{4\pi e^{i\vec{k} \cdot \vec{r}_j}}{k^2} \quad (\text{B.42})$$

Thus B.31 squared becomes

$$\frac{e^4 (4\pi)^2}{\epsilon_0^2 k^4 V^2 (4\pi)^2} |\langle n_0 | \sum_j Z_j e^{i\vec{k} \cdot \vec{r}_j} | n_1 \rangle|^2 \quad (\text{B.43})$$

Inserting B.43 into B.30, and converting $k_1^2 dk_1 = \frac{mk_1}{\hbar^2} dE_1$ we get the DDSCS for impact scattered EELS as

$$\frac{d^2\sigma}{d\Omega dE_1} = \frac{2\pi e^4 \delta(E_{n_0} - E_{n_1} + \hbar\omega) V^2 m \sum_{n_0, n_1} P_{n_0} |\langle n_0 | \sum_j e^{i\vec{k} \cdot \vec{r}_j} | n_1 \rangle|^2 m^2 k_1}{\epsilon_0^2 k^4 \hbar^4 k_0 (2\pi)^3 N V^2} \quad (\text{B.44})$$

$$= \frac{m^2 e^4}{\hbar^4 k^4 4\pi^2} \frac{k_1}{k_0} \frac{1}{N} \sum_{n_0, n_1} P_{n_0} |\langle n_0 | \sum_j Z_j e^{i\vec{k} \cdot \vec{r}_j} | n_1 \rangle|^2 \delta(E_{n_0} - E_{n_1} + \hbar\omega) \quad (\text{B.45})$$

And we can identify the Rutherford cross-section for scattering of charged particles as $\left(\frac{d\sigma}{d\Omega}\right) = \frac{4m^2e^4}{\hbar^4k^4}$, resulting in same expression as that by Sturm [122]. Finally, we re-write this expression to relate to the structure factor via

$$\begin{aligned}
 \frac{d\sigma^2}{d\Omega dE} &= \frac{m^2e^4}{\hbar^4k^44\pi^2} \frac{k_1}{k_0} \frac{1}{N} \sum_{n_0, n_1} P_{n_0} |\langle n_0 | \sum_j Z_j e^{i\vec{k} \cdot \vec{r}_j} | n_1 \rangle|^2 \delta(E_{n_0} - E_{n_1} + \hbar\omega) \\
 &= \frac{m^2e^4}{\hbar^4k^44\pi^2} \frac{k_1}{k_0} \frac{1}{N} \frac{1}{2\pi\hbar} \int dt e^{-\omega t} \sum_{n_0, n_1} P_{n_0} \langle n_0 | \sum_j Z_j e^{i\vec{k} \cdot \vec{r}_j} e^{iE_{n_0}t/\hbar} | n_1 \rangle \\
 &\quad \times \langle n_1 | \sum_{j'} Z_{j'} e^{-iE_{n_1}t/\hbar} \sum_{j'} e^{-i\vec{k} \cdot \vec{r}_{j'}} | n_0 \rangle \\
 &= \frac{m^2e^2}{\hbar^4k^44\pi^2} \frac{k_1}{k_0} \frac{1}{N} \frac{1}{2\pi\hbar} \int dt e^{-\omega t} \sum_{n_0} \langle n_0 | \sum_j Z_j e^{i\vec{k} \cdot \vec{r}_j} e^{iHt/\hbar} \sum_{j'} e^{-i\vec{k} \cdot \vec{r}_{j'}} Z_{j'} e^{-iHt/\hbar} | n_0 \rangle \\
 &= \frac{m^2e^2}{\hbar^4k^44\pi^2} \frac{k_1}{k_0} \frac{1}{N} \frac{1}{2\pi\hbar} \int dt e^{-\omega t} \sum_{n_0} P_{n_0} \langle n_0 | \rho(\vec{k}, t=0) \rho(-\vec{k}, t) | n_0 \rangle \\
 &= \frac{m^2e^2}{\hbar^4k^44\pi^2} \frac{k_1}{k_0} \frac{1}{N} S(\omega, \vec{k}) \tag{B.46}
 \end{aligned}$$

using the relationships $\delta(E_{n_0} - E_{n_1} + \hbar\omega) = \frac{1}{2\pi\hbar} \int dt e^{-i\omega t} e^{i(E_{n_1} - E_{n_0})t/\hbar}$, $\sum_{n_1} |n_1\rangle \langle n_1| = 1$ and $e^{-iE_{n_1}t/\hbar} |n_1\rangle = e^{-iHt/\hbar} |n_1\rangle$. Here, $\sum_j e^{i\vec{k} \cdot \vec{r}_j}$ is the point charge density of the material in fourier space, since in real space, $\rho(\vec{r}) = \sum_j Z_j \delta(\vec{r} - \vec{r}_j)$ such that it's fourier transform is $\sum_j Z_j e^{i\vec{k} \cdot \vec{r}_j}$

DIPOLE CENTRE OF CHARGE TIME DEPENDENCE

We would like to investigate the contribution of the term $e^{-i\vec{k}\cdot\vec{r}_d(t)}$ in the charge density correlation function of Eq. (6.35). First, we can e.g. represent the dipole's position as the centre of mass, $e^{-i\vec{k}\cdot\vec{r}_d(t)} = e^{-i\vec{k}\cdot\frac{(\sum_{\kappa}\vec{u}_{\kappa}^d(t)m_{\kappa})}{\sum_{\kappa}m_{\kappa}}}$. We can thus expand the dipole correlation as

$$\begin{aligned}
& \langle \hat{\rho}_{dip}(\vec{k}, 0) \hat{\rho}_{dip}(-\vec{k}, t) \rangle \\
&= \left\langle \sum_{dd'} e^{-i\vec{k}\cdot(\vec{l}_d - \vec{l}_{d'})} \left(\left((\vec{\mu}_{d,0} + \sum_{\kappa} Z_{\kappa}^* \vec{u}_{\kappa}^d(0)) \cdot \vec{k} \right) e^{-i\vec{k}\cdot\vec{r}_d(0)} \left((\vec{\mu}_{d',0} + \sum_{\kappa'} Z_{\kappa'}^* \vec{u}_{\kappa'}^{d'}(t)) \cdot \vec{k} \right) e^{i\vec{k}\cdot\vec{r}_{d'}(t)} \right) \right\rangle \\
&= \left\langle \sum_{dd'} e^{i\vec{k}\cdot(\vec{l}_d - \vec{l}_{d'})} \left(\left((\vec{\mu}_{d,0} + \sum_{\kappa} Z_{\kappa}^* \left[\sum_s \vec{e}_s c_{s,\kappa} (a_s e^{i\vec{q}_s \cdot \vec{b}} + a_s^{\dagger} e^{-i\vec{q}_s \cdot \vec{b}}) \right] \cdot \vec{k} \right) e^{\sum_{\kappa\alpha} \frac{-i\vec{k}\cdot\vec{u}_{\kappa\alpha}^d(0)m_{\kappa\alpha}}{\sum_{\kappa\alpha} m_{\kappa\alpha}}} \right. \right. \\
&\quad \left. \left((\vec{\mu}_{d',0} + \sum_{\kappa'} Z_{\kappa'}^* \left[\sum_{s'} \vec{e}_{s'} c_{s',\kappa'} (a_{s'} e^{i\vec{q}_{s'} \cdot \vec{b}'} e^{-i\omega_{s'} t} + a_{s'}^{\dagger} e^{-i\vec{q}_{s'} \cdot \vec{b}'} e^{i\omega_{s'} t}) \right] \cdot \vec{k} \right) e^{\sum_{\kappa'\alpha} \frac{i\vec{k}\cdot\vec{u}_{\kappa'\alpha}^{d'}(t)m_{\kappa'\alpha}}{\sum_{\kappa'\alpha} m_{\kappa'\alpha}}} \right) \right\rangle \\
&= \left\langle \sum_{dd'} e^{i\vec{k}\cdot(\vec{l}_d - \vec{l}_{d'})} \left((\vec{\mu}_{d,0} \cdot \vec{k}) e^{\sum_{\kappa\alpha} \frac{-i\vec{k}\cdot\vec{u}_{\kappa\alpha}^d(0)m_{\kappa\alpha}}{\sum_{\kappa\alpha} m_{\kappa\alpha}}} (\vec{\mu}_{d',0} \cdot \vec{k}) e^{\sum_{\kappa'\alpha} \frac{i\vec{k}\cdot\vec{u}_{\kappa'\alpha}^{d'}(t)m_{\kappa'\alpha}}{\sum_{\kappa'\alpha} m_{\kappa'\alpha}}} \textcircled{1} + \right. \\
&\quad \left. (\vec{\mu}_{d,0} \cdot \vec{k}) e^{\sum_{\kappa\alpha} \frac{-i\vec{k}\cdot\vec{u}_{\kappa\alpha}^d(0)m_{\kappa\alpha}}{\sum_{\kappa\alpha} m_{\kappa\alpha}}} \sum_{\kappa'} Z_{\kappa'}^* \left[\sum_{s'} (\vec{e}_{s'} \cdot \vec{k}) c_{s',\kappa'} (a_{s'} e^{i\vec{q}_{s'} \cdot \vec{b}'} e^{-i\omega_{s'} t} + a_{s'}^{\dagger} e^{-i\vec{q}_{s'} \cdot \vec{b}'} e^{i\omega_{s'} t}) \right] \right. \\
&\quad \times e^{\sum_{\kappa'\alpha} \frac{i\vec{k}\cdot\vec{u}_{\kappa'\alpha}^{d'}(t)m_{\kappa'\alpha}}{\sum_{\kappa'\alpha} m_{\kappa'\alpha}}} \textcircled{2} + \sum_{\kappa} Z_{\kappa}^* \left[\sum_s (\vec{e}_s \cdot \vec{k}) c_{s,\kappa} (a_s e^{i\vec{q}_s \cdot \vec{b}} + a_s^{\dagger} e^{-i\vec{q}_s \cdot \vec{b}}) \right] e^{\sum_{\kappa\alpha} \frac{-i\vec{k}\cdot\vec{u}_{\kappa\alpha}^d(0)m_{\kappa\alpha}}{\sum_{\kappa\alpha} m_{\kappa\alpha}}} (\vec{\mu}_{d',0} \cdot \vec{k}) \\
&\quad \times e^{\sum_{\kappa'\alpha} \frac{i\vec{k}\cdot\vec{u}_{\kappa'\alpha}^{d'}(t)m_{\kappa'\alpha}}{\sum_{\kappa'\alpha} m_{\kappa'\alpha}}} \textcircled{3} + \sum_{\kappa} Z_{\kappa}^* \left[\sum_s (\vec{e}_s \cdot \vec{k}) c_{s,\kappa} (a_s e^{i\vec{q}_s \cdot \vec{b}} + a_s^{\dagger} e^{-i\vec{q}_s \cdot \vec{b}}) \right] e^{\sum_{\kappa\alpha} \frac{-i\vec{k}\cdot\vec{u}_{\kappa\alpha}^d(0)m_{\kappa\alpha}}{\sum_{\kappa\alpha} m_{\kappa\alpha}}} \\
&\quad \times \sum_{\kappa'} Z_{\kappa'}^* \left[\sum_{s'} (\vec{e}_{s'} \cdot \vec{k}) c_{s',\kappa'} (a_{s'} e^{i\vec{q}_{s'} \cdot \vec{b}'} e^{-i\omega_{s'} t} + a_{s'}^{\dagger} e^{-i\vec{q}_{s'} \cdot \vec{b}'} e^{i\omega_{s'} t}) \right] e^{\sum_{\kappa'\alpha} \frac{i\vec{k}\cdot\vec{u}_{\kappa'\alpha}^{d'}(t)m_{\kappa'\alpha}}{\sum_{\kappa'\alpha} m_{\kappa'\alpha}}} \textcircled{4} \Bigg\rangle \\
\end{aligned} \tag{C.1}$$

Now let's look at each of the final 4 terms separately. For the first term, $\sum_{\kappa\alpha} m_{\kappa\alpha} = M_d = M$ and $\sum_{\kappa'\alpha} m_{\kappa'\alpha} = M_d = M$ since all dipoles have the same mass. Because there are no extra a or $a^{\dagger}$'s we can use Baker Hausdorff's theo-

rem, i.e. $e^{\hat{A}}e^{\hat{B}} = e^{\hat{A}+\hat{B}+\frac{1}{2}[\hat{A},\hat{B}]}$, where the higher order terms of commutators in the exponential vanish because commutators of a and $a^\dagger$ are just scalars.

$$\begin{aligned}
 \textcircled{1} &= \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) e^{\sum_{\kappa^\alpha} \frac{-i\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{\sum_{\kappa^\alpha} m_{\kappa^\alpha}}} e^{\sum_{\kappa'^\alpha} \frac{i\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{\sum_{\kappa'^\alpha} m_{\kappa'^\alpha}}} \right\rangle \\
 &= \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) \exp \left(\sum_{\kappa^\alpha} \frac{-i\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} + \sum_{\kappa'^\alpha} \frac{i\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right. \\
 &\quad \left. \times \exp \left(\frac{1}{2} \left[\sum_{\kappa^\alpha} \frac{-i\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}, \sum_{\kappa'^\alpha} \frac{i\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right] \right) \right\rangle \quad (\text{C.2})
 \end{aligned}$$

From here we can pull out the last exponential term from the expectation value as it is a factor, and we need to treat the term highlighted in red using $\langle e^{\hat{A}} \rangle = e^{\frac{1}{2}\langle \hat{A}^2 \rangle}$

$$\begin{aligned}
 &\left\langle \exp \left(\sum_{\kappa^\alpha} -i\vec{k} \cdot \left(\frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} - \sum_{\kappa'^\alpha} \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right) \right\rangle \\
 &= \exp \left(\frac{1}{2} \left\langle \left(\sum_{\kappa^\alpha} -i\vec{k} \cdot \left(\frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} - \sum_{\kappa'^\alpha} \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right)^2 \right\rangle \right) \\
 &= \exp \left(\left\langle \sum_{\kappa^\alpha, \kappa'^\beta} -\frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\beta}^d(0)m_{\kappa'^\beta}}{M}) \right. \right. \\
 &\quad \left. - \sum_{\kappa'^\alpha, \kappa'^\beta} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\beta}^{d'}(t)m_{\kappa'^\beta}}{M}) \right. \\
 &\quad \left. + \sum_{\kappa^\alpha, \kappa'^\alpha} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) + \sum_{\kappa^\alpha, \kappa'^\alpha} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}) \right\rangle \right) \quad (\text{C.3})
 \end{aligned}$$

Thus putting this together with Eq. (C.2), we have

$$\begin{aligned}
 \textcircled{1} &= \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) \exp \left(\left\langle \sum_{\kappa^\alpha, \kappa^\beta} -\frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa^\beta}^d(0)m_{\kappa^\beta}}{M}) \right. \right. \right. \\
 &\quad - \sum_{\kappa'^\alpha, \kappa'^\beta} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\beta}^{d'}(t)m_{\kappa'^\beta}}{M}) \\
 &\quad + \sum_{\kappa^\alpha, \kappa'^\alpha} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) \\
 &\quad \left. \left. + \sum_{\kappa^\alpha, \kappa'^\alpha} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) \cancel{(\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M})} \right) \right) \right\rangle \\
 &\quad \left\langle \exp \left(\frac{1}{2} \left(\sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \right) \left(\frac{\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right) \right. \\
 &\quad \left. \times \exp \left(-\frac{1}{2} \left(\vec{k} \cdot \sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \cancel{(\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M})} \right) \right) \right\rangle \\
 &= \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) \exp \left(\left\langle \sum_{\kappa^\alpha, \kappa^\beta} -\frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa^\beta}^d(0)m_{\kappa^\beta}}{M}) \right. \right. \right. \\
 &\quad - \sum_{\kappa'^\alpha, \kappa'^\beta} \frac{1}{2} (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M}) (\vec{k} \cdot \frac{\vec{u}_{\kappa'^\beta}^{d'}(t)m_{\kappa'^\beta}}{M}) + \left(\sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \right) \left(\frac{\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \left. \right) \right) \right\rangle \\
 &\hspace{15cm} \text{(C.4)}
 \end{aligned}$$

We can rewrite this as

$$\begin{aligned}
 \textcircled{1} &= \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) \exp \left(\left\langle \sum_{\kappa^\alpha} -\frac{1}{2} \left(\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \right)^2 \right\rangle \right) \right. \\
 &\quad \times \exp \left(\left\langle \sum_{\kappa'^\alpha} -\frac{1}{2} \left(\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right)^2 \right\rangle \right) \\
 &\quad \times \exp \left(\left\langle \sum_{\kappa^\alpha \neq \kappa^\beta} -\frac{1}{2} \left(\vec{k} \cdot \frac{\vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \right) \left(\vec{k} \cdot \frac{\vec{u}_{\kappa^\beta}^d(0)m_{\kappa^\beta}}{M} \right) \right\rangle \right) \\
 &\quad \exp \left(\left\langle - \sum_{\kappa'^\alpha \neq \kappa'^\beta} \frac{1}{2} \left(\vec{k} \cdot \frac{\vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \left(\vec{k} \cdot \frac{\vec{u}_{\kappa'^\beta}^{d'}(t)m_{\kappa'^\beta}}{M} \right) \right\rangle \right) \\
 &\quad \times \exp \left(\sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \left(\frac{\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right) \Bigg\rangle \\
 &= \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) \prod_{\kappa} \exp \left(-\frac{2W_{\kappa}m_{\kappa}^2}{M^2} \right) \prod_{\kappa^\alpha \neq \kappa^\beta} \right. \\
 &\quad \left[\exp \left(\left(\frac{\hbar(m_{\kappa^\alpha}m_{\kappa^\beta})^{\frac{1}{2}}}{2NM^2} \right) \sum_s \frac{(\vec{k} \cdot \vec{e}_{s,\kappa^\alpha}^d)(\vec{k} \cdot \vec{e}_{s,\kappa^\beta}^{d*})}{\omega_s} e^{i\vec{q}_s \cdot (\vec{b}-\vec{b})} \right) \right] \\
 &\quad \times \exp \left(\left\langle \left(\sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \right) \left(\frac{\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right\rangle \right) \Bigg\rangle \\
 &\approx \left\langle (\vec{\mu}_{d,0} \cdot \vec{k})(\vec{\mu}_{d',0} \cdot \vec{k}) \prod_{\kappa} \exp \left(-\frac{2W_{\kappa}m_{\kappa}^2}{M^2} \right) \prod_{\kappa^\alpha \neq \kappa^\beta} \right. \\
 &\quad \left[\exp \left(\left(\frac{\hbar(m_{\kappa^\alpha}m_{\kappa^\beta})^{\frac{1}{2}}}{2NM^2} \right) \sum_s \frac{(\vec{k} \cdot \vec{e}_{s,\kappa^\alpha}^d)(\vec{k} \cdot \vec{e}_{s,\kappa^\beta}^{d*})}{\omega_s} e^{i\vec{q}_s \cdot (\vec{b}-\vec{b})} \right) \right] \\
 &\quad \times \left(1 + \left\langle \left(\sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0)m_{\kappa^\alpha}}{M} \right) \left(\frac{\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t)m_{\kappa'^\alpha}}{M} \right) \right\rangle \right) \tag{C.5}
 \end{aligned}$$

where W is the Debye-Waller factor. The 1 in the last taylor expansion term does not correspond to any phonon generation so we're interested in the final correlation term in C.5 in orange.

$$\begin{aligned}
 & \left\langle \left(\sum_{\kappa^\alpha, \kappa'^\alpha} \frac{\vec{k} \cdot \vec{u}_{\kappa^\alpha}^d(0) m_{\kappa^\alpha}}{M} \right) \left(\frac{\vec{k} \cdot \vec{u}_{\kappa'^\alpha}^{d'}(t) m_{\kappa'^\alpha}}{M} \right) \right\rangle \\
 &= \left\langle \sum_{\kappa^\alpha, \kappa'^\alpha} \sum_{s, s'} \left(\frac{c_{s, \kappa^\alpha} c_{s', \kappa'^\alpha} m_{\kappa^\alpha} m_{\kappa'^\alpha}}{M^2} \vec{k} \cdot (\vec{e}_{\kappa^\alpha, s}^d a_s e^{i\vec{q}_s \cdot \vec{b}} + \vec{e}_{\kappa^\alpha, s}^{d*} a_s^\dagger e^{-i\vec{q}_s \cdot \vec{b}}) \right. \right. \\
 & \quad \times \left. \left. \vec{k} \cdot (\vec{e}_{\kappa'^\alpha, s'}^{d'} a_{s'} e^{i\vec{q}_{s'} \cdot \vec{b}'} e^{-i\omega_{s'} t} + \vec{e}_{\kappa'^\alpha, s'}^{d'*} a_{s'}^\dagger e^{-i\vec{q}_{s'} \cdot \vec{b}'} e^{i\omega_{s'} t}) \right) \right\rangle \\
 &= \sum_{\kappa^\alpha, \kappa'^\alpha} \sum_s \frac{c_{s, \kappa^\alpha} c_{s, \kappa'^\alpha} m_{\kappa^\alpha} m_{\kappa'^\alpha}}{M^2} \left[(\vec{k} \cdot \vec{e}_{\kappa^\alpha, s}^d) (\vec{k} \cdot \vec{e}_{\kappa'^\alpha, s}^{d'*}) e^{i\vec{q}_s \cdot (\vec{b} - \vec{b}')} e^{i\omega_s t} \langle n_s + 1 \rangle \right. \\
 & \quad \left. + (\vec{k} \cdot \vec{e}_{\kappa^\alpha, s}^{d*}) (\vec{k} \cdot \vec{e}_{\kappa'^\alpha, s}^{d'}) e^{-i\vec{q}_s \cdot (\vec{b} + \vec{b}')} e^{-i\omega_s t} \langle n_s \rangle \right] \quad (C.6)
 \end{aligned}$$

Where again we only keep the $aa^\dagger$ and $a^\dagger a$ terms which give physical meaning. The first term is what we're after (containing $\langle n_s + 1 \rangle$). Hence,

$$\begin{aligned}
 \textcircled{1} &= (\vec{\mu}_{d,0} \cdot \vec{k}) (\vec{\mu}_{d',0} \cdot \vec{k}) \prod_{\kappa} \exp\left(-\frac{2W_{\kappa} m_{\kappa}^2}{M^2}\right) \\
 &\times \prod_{\kappa^\alpha \neq \kappa^\beta} \left[\exp\left(\left(\frac{\hbar(m_{\kappa^\alpha} m_{\kappa^\beta})^{\frac{1}{2}}}{2NM^2}\right) \sum_s \frac{(\vec{k} \cdot \vec{e}_{s, \kappa^\alpha}^d) (\vec{k} \cdot \vec{e}_{s, \kappa^\beta}^{d*})}{\omega_s}\right) \right] \\
 &\times \sum_{\kappa^\alpha, \kappa'^\alpha} \frac{c_{s, \kappa^\alpha} c_{s, \kappa'^\alpha} m_{\kappa^\alpha} m_{\kappa'^\alpha}}{M^2} \sum_s (\vec{k} \cdot \vec{e}_{\kappa^\alpha, s}^d) (\vec{k} \cdot \vec{e}_{\kappa'^\alpha, s}^{d'*}) e^{i\vec{q}_s \cdot (\vec{b} - \vec{b}')} e^{i\omega_s t} \langle n_s + 1 \rangle \quad (C.7)
 \end{aligned}$$

For $\textcircled{2}$ and $\textcircled{3}$ in C.1, we will have an odd number of phonon ladder operators (e.g. $aa^\dagger$, which means there won't be any relevant terms to the phonon creation process.) For term $\textcircled{4}$ in C.1, if we approximate the exponential operators as 1 (as done in thesis), we arrive back at the result in Eq. (6.38) with a $\frac{1}{k^2}$ dependence. On the other hand if we expand the exponential operator to keep the $\vec{k} \cdot \vec{e}_d$ term, it will result in three, four, and more phonon ladder operators, which will contribute to multiple phonon creation/annihilation processes (i.e. contributing e.g. $\langle n_s + 1 \rangle^2 e^{i(\omega_{s1} + \omega_{s2})t}$ and when integrated with $\int dt e^{-i\omega t}$ will give $\delta(\omega - \omega_{s1} - \omega_{s2})$, which is ignored. Finally, term $\textcircled{1}$ has a k^4 dependence, which should cancel the $\frac{1}{k^4}$ term. This is much smaller

in comparison with the $\frac{1}{k^2}$ (since $k \ll 0$) dependence we obtain from letting $e^{-i\vec{k}\cdot\vec{r}_d(t)} = 1$, which is done in the thesis. Hence, we confirm the dominant term for ultra-low loss EELS is the largest of (4).

It may also be feasible to replace the dipole's displacement from it's equilibrium position, $\vec{r}_d(t)$ with

$$\frac{1}{2} \left[\frac{\sum_{\kappa^{\alpha+}} \delta q_{\kappa^{\alpha+}}(t) \vec{u}_{\kappa^{\alpha+}}^d(t)}{\sum_{\kappa^{\alpha+}} q_{\kappa^{\alpha+}}(t)} + \frac{\sum_{\kappa^{\alpha-}} \delta q_{\kappa^{\alpha-}}(t) \vec{u}_{\kappa^{\alpha-}}^d(t)}{\sum_{\kappa^{\alpha-}} \delta q_{\kappa^{\alpha-}}(t)} \right] \quad (\text{C.8})$$

where the $\kappa^{\alpha+}, \kappa^{\alpha-}$ denotes the atoms κ^{α} that carry partially positive and negative charges respectively, and $\vec{u}_{\kappa^{\alpha\pm}}^s(t)$ are the still the atomic displacement vectors from equilibrium. Without re-writting the full derivation, it is clear that any additional terms arising from the first order taylor expansion of $e^{-i\vec{k}\cdot\vec{r}_d(t)}$ will again either contribute three or more phonon operators, or contribute terms that are dependent on $\vec{k}^4$, similar to using the centre of mass case.

MISCELLANEOUS DERIVATIONS

D.1 FOURIER TRANSFORM OF ELECTRIC POTENTIAL ALONG ONE AXIS

We can use contour integration to compute

$$I = \int_{-\infty}^{\infty} \frac{e^{ik_z|z-b|}}{k_x^2 + k_y^2 + k_z^2} dk_z \quad (\text{D.1})$$

Let $k_x^2 + k_y^2$ be K^2 and compressing the variable $|z - b|$ to Z , we pick the contour of the upper half semicircle depicted in [Fig. D.1](#), which encloses the pole at iK . Thus the integral is equal to $2\pi i \text{Res}(k_z = iK)$, where

$$\frac{e^{ik_z|z-b|}}{K^2 + k_z^2} = \frac{e^{ik_z|z-b|}}{2iK(k_z - iK)} - \frac{e^{ik_z|z-b|}}{2iK(k_z + iK)} \quad (\text{D.2})$$

and so $\text{Res}(k_z = iK) = \frac{e^{-K|z-b|}}{2iK}$ and finally

$$I = 2\pi i \times \left(\frac{e^{-K|z-b|}}{2iK} \right) = \frac{\pi \exp(-\sqrt{k_x^2 + k_y^2}|z - b|)}{\sqrt{k_x^2 + k_y^2}} \quad (\text{D.3})$$

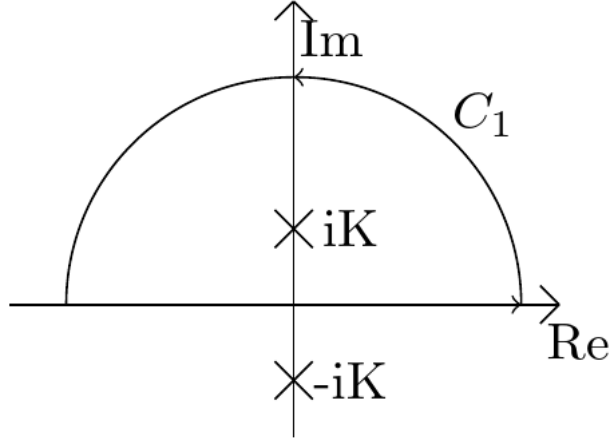


Figure D.1: Contour integral over semi-circle enclosing the pole $z = iK$.

D.2 THERMAL AVERAGE OF SPACE TIME CORRELATION FOR QUANTUM
IMPACT SCATTERING THEORY

We want to calculate the full structure factor for the impact scattering case given by Eq. (5.11). We have approximated the thermal average of Eq. (5.14) by a first order truncation of the exponential taylor expansion and now must write out the latter term more fully. Using the phonon displacement operators given by Eq. (5.12), we have

$$\sum_{\alpha,\beta} k_\alpha k_\beta \langle \vec{u}_{l,\alpha,i}(0) \vec{u}_{l',\beta,i'}(t) \rangle \quad (D.4)$$

$$= \frac{\hbar}{2N \sqrt{m_i m_{i'} \omega_{q0,j} \omega_{q1,i}}} \sum_{q0,j} \sum_{q1,j'} \sum_{\alpha,\beta} k_\alpha k_\beta e_{i,\alpha}(q0,j) e_{i',\beta}^*(q1,j') \quad (D.5)$$

$$(\alpha_{q0,j} e^{i\vec{q}_0 \cdot \vec{l}} + \alpha_{q0,j}^\dagger e^{-i\vec{q}_0 \cdot \vec{l}})(\alpha_{q1,j'} e^{-i\omega_{q1,j'} t} e^{i\vec{q}_1 \cdot \vec{l}'} + \alpha_{q1,j'}^\dagger e^{i\omega_{q1,j'} t} e^{-i\vec{q}_1 \cdot \vec{l}'})] \rangle \quad (D.6)$$

Here we can pick out $q_0 = q_1, j = j'$ due to orthogonality. We also pick out only the terms with $\alpha\alpha^\dagger$ (=1+number operator) and $\alpha^\dagger\alpha$ (number operator). Since we sum over $\sum_{i,i'}$ eventually, they give the same result. Thus this gives

$$\sum_{\alpha,\beta} k_\alpha k_\beta \langle u_{l,\alpha,i}(0) u_{l',\beta,i'}(t) \rangle \quad (\text{D.7})$$

$$= \frac{\hbar}{2N\sqrt{m_i m_{i'}} \omega_{q_0,j}} \sum_{\alpha,\beta} k_\alpha k_\beta \sum_{q_0,j} e_{i,\alpha}(q_0,j) e_{i',\beta}^*(q_0,j) [\langle n_{q_0,j} \rangle e^{-i\omega_{q_0,j}t} e^{-i\vec{q}_0 \cdot (\vec{l} - \vec{l}')} + \langle n_{q_0,j} + 1 \rangle e^{i\omega_{q_0,j}t} e^{i\vec{q}_0 \cdot (\vec{l} - \vec{l}')}]$$

$$= \sum_{q_0,j} \frac{\hbar}{2\omega_{q_0,j}} \left| \frac{1}{\sqrt{m_i}} \vec{k} \cdot \vec{e}_i(q_0,j) \right|^2 [\langle n_{q_0,j} \rangle e^{-i\omega_{q_0,j}t} e^{-i\vec{q}_0 \cdot (\vec{l} - \vec{l}')} + \langle n_{q_0,j} + 1 \rangle e^{i\omega_{q_0,j}t} e^{i\vec{q}_0 \cdot (\vec{l} - \vec{l}')}]$$

$$(\text{D.9})$$

Plug this back into the expression for structure factor, using the relationships

$$\int_{-\infty}^{\infty} e^{-i\omega t} dt = 2\pi\delta(\omega), \quad \sum_l e^{i\vec{k} \cdot \vec{l}} = \frac{L^3}{(2\pi)^3} \sum_{\vec{G}} \delta(\vec{k} - \vec{G}),$$

$$\sum_{ll'} e^{-i(\vec{k} - \vec{q}_0) \cdot (\vec{l} - \vec{l}')} = \left(\sum_l e^{-i(\vec{k} - \vec{q}_0) \cdot \vec{l}} \right) \left(\sum_{l'} e^{i(\vec{k} - \vec{q}_0) \cdot \vec{l}'} \right) = \frac{L^6}{(2\pi)^6} \sum_{\vec{G}} \delta(\vec{k} - \vec{q}_0 - \vec{G}) \sum_{\vec{G}'} \delta(\vec{k} - \vec{q}_0 - \vec{G}')$$

$$(\text{D.10})$$

, and rearranging gives

D.3 FOURIER TRANSFORM OF MONOPOLE POTENTIAL

$$\begin{aligned}
S(\vec{k}, \omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} e^2 \sum_i e^{-i\vec{k} \cdot \vec{R}_i} \sum_{i'} e^{i\vec{k} \cdot \vec{R}_{i'}} \sum_{l'l'} e^{-i\vec{k} \cdot (\vec{l} - \vec{l}')} \\
&\quad [Z_i - f_i(\vec{q})][Z_{i'} - f_{i'}(\vec{q}_1)]^* \\
&\quad \times e^{-2W_i} \left(1 + \sum_{q_0,j} \frac{\hbar}{2m_i \omega_{q_0,j}} |\vec{k} \cdot \vec{e}_i(q_0, j)|^2 [\langle n_{q_0,j} \rangle e^{-i\omega_{q_0,j} t} e^{-i\vec{q}_0 \cdot (\vec{l} - \vec{l}')} \right. \\
&\quad \left. + \langle n_{q_0,j} + 1 \rangle e^{i\omega_{q_0,j} t} e^{i\vec{q}_0 \cdot (\vec{l} - \vec{l}')}] \right) \\
&= \frac{e^2}{2\pi\hbar} \left| \sum_i e^{-i\vec{k} \cdot \vec{R}_i} (Z_i - f_i(\vec{k})) \right|^2 e^{-2W_i} \\
&\quad (\delta(\omega) \frac{L^6}{(2\pi)^6} \sum_{\vec{G}} \delta(\vec{k} - \vec{G}) + \frac{\hbar}{2m_i \omega_{q_0,j}} |\vec{k} \cdot \vec{e}_i(\vec{q}_0, j)|^2 \\
&\quad \times \sum_{q_0,j} \sum_{l'l'} [\langle n_{q_0,j} \rangle \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{-i\omega_{q_0,j} t} e^{-i(\vec{q}_0 + \vec{k}) \cdot (\vec{l} - \vec{l}')} \\
&\quad + \langle n_{q_0,j} + 1 \rangle \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{i\omega_{q_0,j} t} e^{i(\vec{q}_0 - \vec{k}) \cdot (\vec{l} - \vec{l}')}]) \\
&= \frac{e^2}{2\pi\hbar} \left| \sum_i e^{-i\vec{k} \cdot \vec{R}_i} (Z_i - f_i(\vec{k})) \right|^2 e^{-2W_i} \\
&\quad (\delta(\omega) \frac{L^6}{(2\pi)^6} \sum_{\vec{G}} \delta(\vec{k} - \vec{G}) + \frac{\hbar}{2m_i \omega_{q_0,j}} \sum_{q_0,j} |\vec{k} \cdot \vec{e}_i(\vec{q}_0, j)|^2 \\
&\quad \times [\langle n_{q_0,j} \rangle \delta(\omega + \omega_{q_0}) \frac{L^6}{(2\pi)^6} \times \sum_{\vec{G}} \delta(\vec{k} + \vec{q}_0 - \vec{G}) \\
&\quad + \langle n_{q_0,j} + 1 \rangle \delta(\omega - \omega_{q_0}) \times \sum_{\vec{G}} \frac{L^6}{(2\pi)^6} \delta(\vec{k} - \vec{q}_0 - \vec{G})]) \tag{D.11}
\end{aligned}$$

D.3 FOURIER TRANSFORM OF MONOPOLE POTENTIAL

For a point charge located at $\vec{r}_j$, the fourier transform of the monopole charge density is

$$\int_{\mathcal{R}^3} \frac{e^{-i\vec{k} \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} dV = \int_{\mathcal{R}^3} \frac{e^{i\vec{k} \cdot \vec{r}_j} e^{i\vec{k} \cdot (\vec{r} - \vec{r}_j)}}{|\vec{r} - \vec{r}_j|} d^3(\vec{r} - \vec{r}_j) \tag{D.12}$$

Now we let $\vec{r} - \vec{r}_j = \vec{r}^*$ such that $d\vec{r}^* = d\vec{r}$.

$$\int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} = \int_0^{2\pi} d\phi \int_0^\pi \int_0^\infty \frac{e^{i\vec{k} \cdot \vec{r}_j} e^{ikr^* \cos(\theta)} r^{*2} \sin(\theta)}{|\vec{r}^*|} dr^* d\theta \quad (\text{D.13})$$

Let $t = \cos(\theta)$ s.t. $dt = -\sin(\theta)d\theta$ and we have

$$\int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} = \int 2\pi e^{i\vec{k} \cdot \vec{r}_j} \int_{-1}^1 dt \int_0^\infty e^{ikr^* t} r^* dr^* \quad (\text{D.14})$$

$$= \int 2\pi e^{i\vec{k} \cdot \vec{r}_j} \int_0^\infty \frac{1}{ikr^*} r^* [e^{ikr^*} - e^{-ikr^*}] dr^* \quad (\text{D.15})$$

Now lets introduce an attenuation factor $e^{-\lambda r^*}$ such that we have

$$\int_{\mathcal{R}^3} \frac{e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\vec{k}_0 \cdot \vec{r}}}{|\vec{r} - \vec{r}_j|} = \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \int_0^\infty [e^{ikr^* - \lambda r^*} - e^{-ikr^* - \lambda r^*}] dr^* \quad (\text{D.16})$$

$$= \lim_{\lambda \rightarrow 0} \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \left(\frac{e^{ikr^* - \lambda r^*}}{ik - \lambda} - \frac{e^{-ikr^* - \lambda r^*}}{-ik - \lambda} \right)_0^\infty \quad (\text{D.17})$$

$$= \lim_{\lambda \rightarrow 0} \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \left(\frac{e^{ikr^* - \lambda r^*} (-ik - \lambda)}{k^2 + \lambda^2} + \frac{e^{-ikr^* - \lambda r^*} (-ik + \lambda)}{k^2 + \lambda^2} \right)_0^\infty \quad (\text{D.18})$$

$$= \lim_{\lambda \rightarrow 0} \frac{2\pi e^{i\vec{k} \cdot \vec{r}_j}}{ik} \left(\frac{ik + \lambda + ik - \lambda}{k^2 + \lambda^2} \right) \quad (\text{D.19})$$

$$= \frac{4\pi e^{i\vec{k} \cdot \vec{r}_j}}{k^2} \quad (\text{D.20})$$

The monopole and dipole potentials in real space are $\phi_{\text{mono}} = -\frac{Ze}{4\pi\epsilon_0} \frac{1}{r}$ and $\phi_{\text{dip}} = -\frac{Ze}{4\pi\epsilon_0} \frac{\vec{\mu} \cdot \vec{r}}{r^3}$ respectively. They can be related via

$$(\vec{\mu} \cdot \nabla) \phi_{\text{mono}}(\vec{r}) = (\vec{\mu} \cdot \nabla) \left(-\frac{1}{r} \right) \quad (\text{D.21})$$

$$= \vec{\mu} \cdot (\partial_x \vec{i} + \partial_y \vec{j} + \partial_z \vec{k}) \left(-\frac{1}{\sqrt{x^2 + y^2 + z^2}} \right) \quad (\text{D.22})$$

$$= \frac{\vec{\mu} \cdot \vec{r}}{r^3} \quad (\text{D.23})$$

$$= \phi_{\text{dip}}(\vec{r}) \quad (\text{D.24})$$

The fourier tranform of [Eq. \(D.24\)](#) is

$$\phi_{\text{dip}}(\vec{k}) = (i\vec{\mu} \cdot \vec{k}) \phi_{\text{mono}}(\vec{k}) \quad (\text{D.25})$$

In fourier space, the potential of a point charge at position $\vec{r}_i$ is given by (see [Appendix D.3](#))

$$\int_{\mathcal{R}^3} \frac{e^{-i\vec{k} \cdot \vec{r}}}{|\vec{r} - \vec{r}_i|} dV = \frac{4\pi e^{i\vec{k} \cdot \vec{r}_i}}{k^2}. \quad (\text{D.26})$$

Thus for a dipole potential centered at the origin ($\vec{r}_d = \vec{0}$), the fourier transform becomes

$$\phi(\vec{k})_{\text{dip}} = \int_{\mathcal{R}} \frac{e^{-i\vec{k} \cdot \vec{r}} \vec{\mu} \cdot \vec{r}}{r^3} dV = (i\vec{\mu} \cdot \vec{k}) \frac{4\pi e^{i\vec{k} \cdot \vec{0}}}{k^2} = 4\pi \frac{i\vec{\mu} \cdot \vec{k}}{k^2} \quad (\text{D.27})$$

For the case of $\vec{r}_d \neq \vec{0}$, we would have $\phi(\vec{k})_{\text{dip}} = 4\pi \frac{i\vec{\mu} \cdot \vec{k}}{k^2} e^{i\vec{k} \cdot \vec{r}_d}$

D.5 CHARGE DENSITY OF POINT DIPOLE

Poisson's equation allows us to relate the potential $\phi(\vec{r})$ with an effective charge distribution $\rho(\vec{r})$.

$$\nabla^2 \phi(\vec{r}) = -\frac{\rho(\vec{r})}{\epsilon_0} \quad (\text{D.28})$$

Fleshing out the potential as a multipole expansion gives

$$\frac{1}{4\pi\epsilon_0} \nabla^2 \left[\frac{q}{r} + \frac{\vec{\mu} \cdot \vec{r}}{r^3} + \dots \right] = -\frac{\rho(\vec{r})}{\epsilon_0} \quad (\text{D.29})$$

The first term becomes (given $r = \sqrt{x^2 + y^2 + z^2}$)

$$\nabla^2 \frac{1}{r} = \nabla \cdot \left(\nabla \frac{1}{r} \right) = \nabla \cdot \left(-\frac{x\vec{i} + y\vec{j} + z\vec{k}}{r^3} \right) = \nabla \cdot \left(-\frac{\vec{r}}{r^3} \right) = 0 \quad (\text{D.30})$$

for $r \neq 0$. However, integrating and using Gauss' theorem gives

$$\int \int \int_{V_{\text{sphere}}} \nabla^2 \frac{1}{r} dV = \int \int_{S_{\text{sphere}}} -\frac{\vec{r}}{r^3} \cdot d\vec{S} = \int_0^\pi \int_0^{2\pi} -\frac{\vec{r}}{r^3} r^2 \sin \theta d\phi d\theta = -4\pi \quad (\text{D.31})$$

Thus for any volume containing the origin, the integral becomes -4π and thus we have $\nabla^2 \frac{1}{r} = -4\pi\delta(\vec{r})$. For the second term, we have

$$\nabla^2 \frac{\vec{\mu} \cdot \vec{r}}{r^3} = \nabla \cdot \nabla \left(\frac{\vec{\mu} \cdot \vec{r}}{r^3} \right) \quad (\text{D.32})$$

$$= \vec{\mu} \cdot \nabla \cdot \nabla \left(-\nabla \frac{1}{r} \right) \quad (\text{D.33})$$

$$= -\vec{\mu} \cdot \nabla \left(\nabla^2 \frac{1}{r} \right) \quad (\text{D.34})$$

$$= \vec{\mu} \cdot \nabla (4\pi\delta(\vec{r})) \quad (\text{D.35})$$

$$= 4\pi\vec{\mu} \cdot \nabla \delta(\vec{r}) \quad (\text{D.36})$$

and so poisson's equation becomes

$$\frac{1}{4\pi\epsilon_0} \nabla^2 \left[\frac{\vec{q}}{r} + \frac{\vec{\mu} \cdot \vec{r}}{r^3} + \dots \right] = \frac{1}{4\pi\epsilon_0} \left[-4\pi\delta(\vec{r}) + 4\pi\vec{\mu} \cdot \nabla\delta(\vec{r}) + \dots \right] = -\frac{\rho(\vec{r})}{\epsilon_0} \quad (\text{D.37})$$

For a charge distribution, equation D.37 gives the charge density expanded as

$$\rho(\vec{r}) = \delta(\vec{r}) - \vec{\mu} \cdot \nabla\delta(\vec{r}) + \dots \quad (\text{D.38})$$

Finally, if the charge distribution is centred around $\vec{r}_d$, the dipole contribution becomes $-\vec{\mu} \cdot \nabla\delta(\vec{r} - \vec{r}_d)$.

BASIC GROUP THEORY DISCUSSION

Consider a molecule of N atoms, it belongs to a symmetry group and thus has a set of symmetry operations that when applied, leaves the molecule invariant. There are $3N$ degrees of freedom, and this can be represented as a reducible representation Γ_{total} , describing how the molecule transforms under its symmetry group. This representation can be decomposed into its irreducible representations (irreps) where each mode belongs to an irrep. An irrep is a representation of the same symmetry group, but it does not contain any subspaces where the symmetry operations are non-trivial.

Going back to the transition matrix element,

$$\int dV \phi_{\nu'}^* \mu_i \phi_{\nu''} \quad (\text{E.1})$$

where $i \in \{x, y, z\}$, ν' and ν'' are the initial and final states of the wavefunction. Since these integrals occur over the entire space spanned by possible configurations of the molecule, they cannot change under a symmetry operation of the original symmetry group of the molecule. Using this fact and the little orthogonality theorem, one can show that the wavefunction for mode and dipole moment must have at least one irreducible representation in common in order for Eq. (E.1) not to vanish [60] (see pages 159-162 in reference). The irreducible representations of the dipole moment transforms in the same way as that of the cartesian vectors x, y , or z does. Hence, for a mode to be IR active, it must contain irreps that also transform along at least one of these cartesian directions. This is a general rule and thus for the mode to be Raman active, it must contain irreps that contain terms such as x^2 , y^2 , xy , etc. and linear combinations thereof.

CONVERGENCE TEST FOR URACIL AND X₂₃ DATASET INFORMATION

F.O.1 *X₂₃ and handpicked molecular crystal dataset dataset geometries, phonons
and NMR*

X ₂₃	
Name	CCDC/COD identifier
Acetic acid	ACETACo7
Adamantane	ADAMANo8
Anthracene	ANTCENo9
Benzene	BENZENo1
Carbon dioxide	1010498
Cyanamide	CYANAMo1
Cyclohexanedione	CYHEXO
Cytosine	CYTSINo1
Ethyl-carbamate	ECARBMo1
Formamide	FORMAMo2
Hexamine	HXMTAM10
Imidazole	IMAZOLo4
Naphthalene	NAPHTA31
Oxalic acid (α polymorph)	OXALACo3
Oxalic acid (β polymorph)	OXALACo4
Pyrazine	PYRAZIo1
Pyrazole	PYRZOLo5
Succinic acid	4116141
Triazine	TRIZIN
Trioxane	TROXAN11
Uracil	URACIL
Urea	UREAXXo2

Table F.1: Molecular crystal names and identifiers of the X₂₃ dataset, whose CIF files are obtained either from the CCDC or COD.

Handpicked Molecular Crystal set	
Name	CCDC/COD identifier
Formic acid	FORMACo1
Acetic acid	ACETACo7
Propionic acid	PRONAC
Butyric acid	BUTRAC
Valeric acid	VALRAC
Hexanoic acid	ISENID
Heptanoic acid	ISENOJ
Octanoic acid	ISENUP
Nonanoic acid	ISEPAX
Decanoic acid	ISEPEB
α -Glycine	GLYCIN86
L-Alanine	LALNIN24
L-Valine	LVALIN05
L-Isoleucine	LISLEU02
L-Glutamine	GLUTAM02
L-Methionine	LMETON02
L-serine	LSERIN20
L-Threonine	LTHREO03
L-Tyrosine	LTYROS10
L-Cysteine	LCYSTN22

Table F.2: Molecular crystal names and identifiers of the handpicked dataset, whose CIF files are obtained either from the CCDC or COD.

Table F.3: Unit cell volumetric percentage deviations from experiments of the X23 crystal data set, optimised with varying XC functionals. This is then summarised by the mean relative deviation (MRD) and mean absolute relative deviation (MARD). A bare PBE functional used for the X23 set acts as a reminder of the substantial over-expansion molecular systems undergo when subject to the pure functional.

X23 CRYSTALS				
Crystal	PBE	PBE+TS	rSCAN	rSCAN+MBD*
Acetic acid	22.06	-1.77	-0.73	-5.20
Adamantane	26.05	-6.58	0.92	-6.75
Ammonia	4.75	-9.28	-8.82	-12.10
Anthracene	31.18	-1.66	4.15	-2.72
Benzene	34.53	-2.82	1.69	-4.85
Carbon Dioxide	22.83	8.71	-4.04	-6.59
Cyanamide	14.76	0.56	-2.81	-5.53
Cyclo-hexanedione	27.57	-2.16	-0.82	-5.96
Cytosine	35.17	-2.78	-0.47	-4.78
Ethyl carbamate	19.27	-4.69	-3.17	-8.29
Formamide	36.63	-1.77	-2.15	-6.16
Hexamine	20.82	0.52	3.19	-3.44
Imidazole	32.88	-2.49	2.18	-4.58
Naphthalene	32.99	-0.60	4.63	-2.18
Oxalic acid α	13.33	0.08	-4.69	-6.98
Oxalic acid β	21.16	0.74	-4.25	-7.37
Pyrazine	28.31	-4.40	0.95	-4.98
Pyrazole	37.08	1.32	4.29	-2.62
Succinic acid	24.38	0.34	-1.90	-5.38
Triazine	20.44	-5.53	-3.27	-7.80
Trioxane	17.12	-1.98	-1.20	-5.91
Uracil	23.03	-2.85	-1.07	-4.96
Urea	8.58	-0.11	-1.24	-3.90
MRD	24.13	²¹³ -1.71	-0.81	-5.61
MARD	24.13	2.77	2.72	5.61

Table F.4: Unit cell volumetric percentage deviations from experiments of the manually chosen MC molecular crystal data sets optimised with varying XC functionals. The two datasets are summarised by the mean relative deviation (MRD) and mean absolute relative deviation (MARD).

MC CRYSTALS				
Crystal	PBE+TS	PBE+MBD*	rSCAN	rSCAN+MBD*
α -glycine	2.28	1.27	-0.74	-3.45
α -alanine	-0.16	-0.13	-0.57	-3.36
Butyric acid	-6.39	-8.35	-3.10	-9.19
Decanoic acid	-6.68	-7.51	-0.16	-8.13
Formic acid	2.48	4.26	-1.11	-5.24
Heptanoic acid	-9.07	-7.89	-2.53	-9.60
Glutamine	-1.12	-1.61	-1.70	-3.79
Isoleucine	-2.64	-5.17	-0.29	-5.52
Methionine	-0.99	-2.32	0.92	-3.82
Serine	1.22	-0.53	-1.39	-3.70
Threonine	0.26	-0.02	0.16	-2.82
Valine	-4.74	-6.64	-2.16	-7.09
Nonanoic acid	-11.08	-12.20	-3.94	-13.52
Octanoic acid	-6.89	-7.88	-0.63	-8.60
Cysteine	0.76	0.38	0.41	-1.75
Propionic acid	-4.89	-5.24	-3.67	-9.14
Valeric acid	-5.40	-7.63	-2.53	-9.34
Hexanoic acid	-9.40	-9.97	-3.91	-11.53
Tyrosine	-1.47	-2.70	-0.77	-3.79
MRD	-3.28	-4.08	-1.41	-6.42
MARD	4.10	4.83	1.62	6.42

GUANINE

The α polymorph was obtained from the CCDC with identifiers KEMDOW. Figure G.1 shows the convergence analysis performed for α -guanine in terms of bond length convergence with cut-off energy and k-spacing.

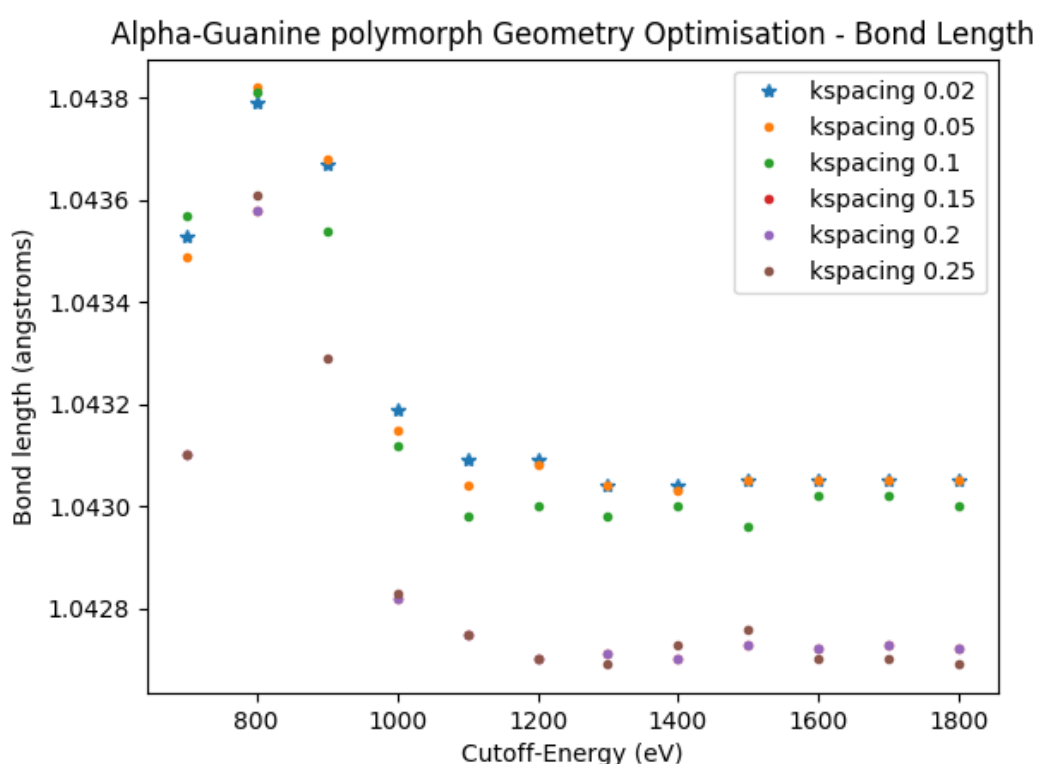


Figure G.1: Convergence test with respect to k-spacing and energy cut-off performed on α -guanine to obtain reasonable input parameters for phonon calculations.

As k-spacing continually decreased towards $0.02 \text{ \AA}^{-1}$ the bond lengths stabilised (no more jumps such as that from k-spacing of $0.15 \rightarrow 0.1 \text{ \AA}^{-1}$). The cut-off energy needed for stability occurs 1200 keV . The initial phonon calculations were problematic because the maximum forces on the atoms exceeded that of the force tolerance. This was solved by reducing the *ELEC_ENERGY_TOL*

and *ELEC_FORCE_TOL*, which is the difference in forces between successive SCF cycles (not to be confused with *GEOM_FORCE_TOL* which is the force tolerance for the ground state electron densities).

Figure G.2 shows the percentage deviation of the intramolecular bond lengths between α guanine and that of the synchrotron study in literature [1]. Notice that the bonds involving hydrogen deviate wildly from experiment. This is because hydrogen is too light of an element and scatter X-rays very weakly, meaning they are difficult to accurately locate.

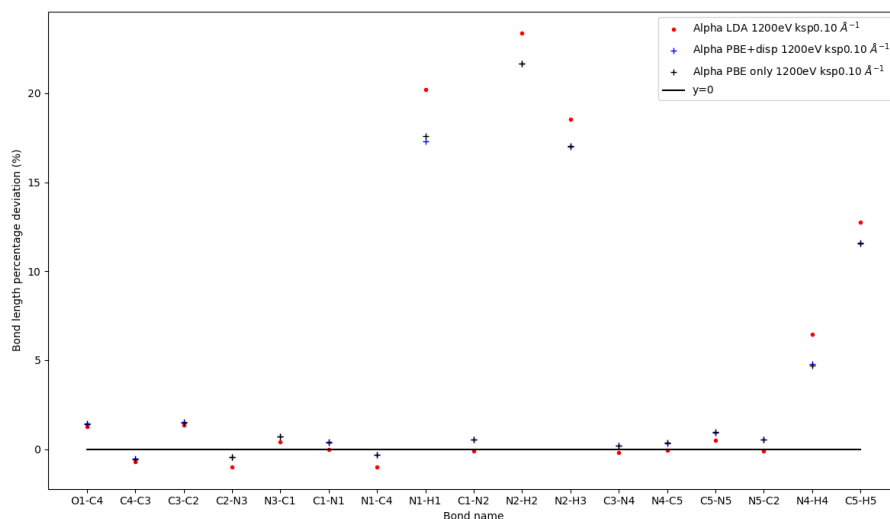


Figure G.2: Percentage deviation of guanine intramolecular bond lengths from experimental literature [1].

Finally, the lattice parameters from several literature experimental, theoretical sources together with our calculations are summarised in Table G.1. This shows as predicted, LDA overbinds and underestimates the lattice parameters. PBE grossly overestimates and pushes atoms apart, but is much more reliable when dispersion corrections are included. We will also focus on using PBE with dispersion corrections instead of rSCAN as the latter is not yet operational with DFPT for phonon calculations and thus is a hindrance as not

β polymorph	a	b	c	Angle(°)
Literature sim VASP (PBE+TS) [209]	3.59	9.72	18.34	119.5
Literature Exp Hirsch <i>et al.</i> [209]	3.629	9.813	18.427	118.04
Literature sim ESPRESSO (PBE only) [55]	4.321	9.836	18.646	115.77
Literature sim ESPRESSO (PBE+ D2) [55]	3.496	9.684	18.447	118.33
CASTEP PBE only	4.41	9.85	18.68	115.0
CASTEP PBE+TS	3.62	9.76	18.45	119.2
CASTEP PBE+Go6	3.50	9.70	18.48	118.47

Table G.1: Comparison of β -guanine lattice parameters optimisation between CASTEP vs literature simulations and experiments.

only does require much more computational power, but make calculations of e.g. BEC very difficult.

G.0.1 QUANTUM ESPRESSO DFT calculations for semi-classical DDCS

The QUANTUM ESPRESSO inputs also used the PBE+Grimme dispersion scheme, a $6 \times 2 \times 1$ k-point grid and ultrasoft pseudopotentials with cut-off energies for plane-waves and charge-densities as 60 ($\sim 800eV$) and 600 ($\sim 8000eV$) Rydbergs respectively. The resulting energy loss spectra are plotted in Fig. G.3, which looks very similar to that of Fig. 11.3 which is redrawn here for reference.

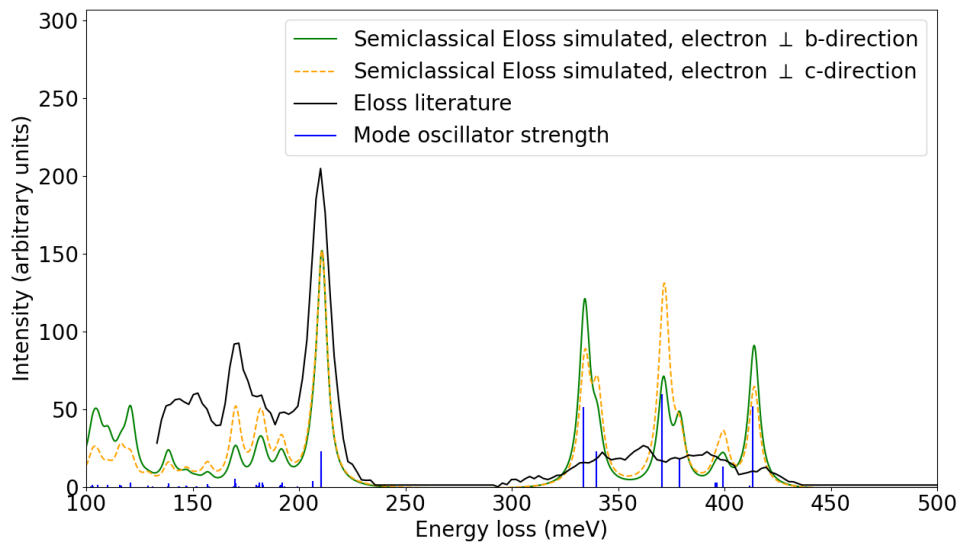


Figure G.3: Using QUANTUM ESPRESSO instead of CASTEP for simulating the semi-classical β -guanine energy loss spectra *vs* experiment (labelled Eloss literature). This is done for two different relative orientations between the beam and sample geometry. Lorentzian smearing with a FWHM of 5meV has been applied and the mode oscillator strength intensities are shown in blue.

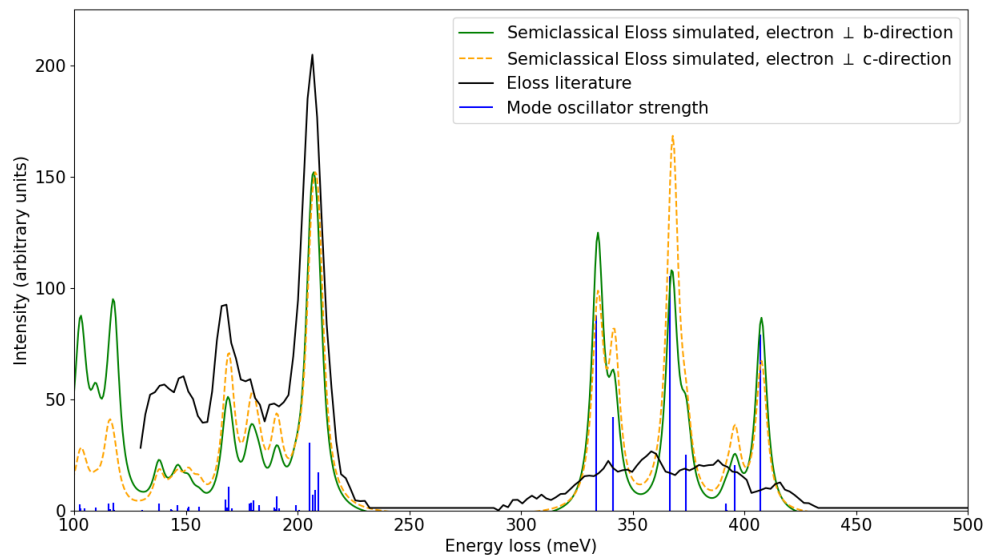


Figure G.4: Figure 11.3 is re-plotted here for comparison.

MISCELLANEOUS RESULTS

H.1 BORON NITRIDE - QUANTUM IMPACT SCATTERING HIRSH AND BORN STATIC CHARGES

A figure similar to [Fig. 10.2](#) is presented in [Fig. H.o](#) whereby the quantum impact scattering theory is used to simulate the energy loss for hBN and cBN, showing the effects of using Hirshfeld and Born effective charge trace amplitude (denoted BECTA, defined as $\frac{1}{3}Tr(Born)$) as the static charge transfers in [Eq. \(10.10\)](#).

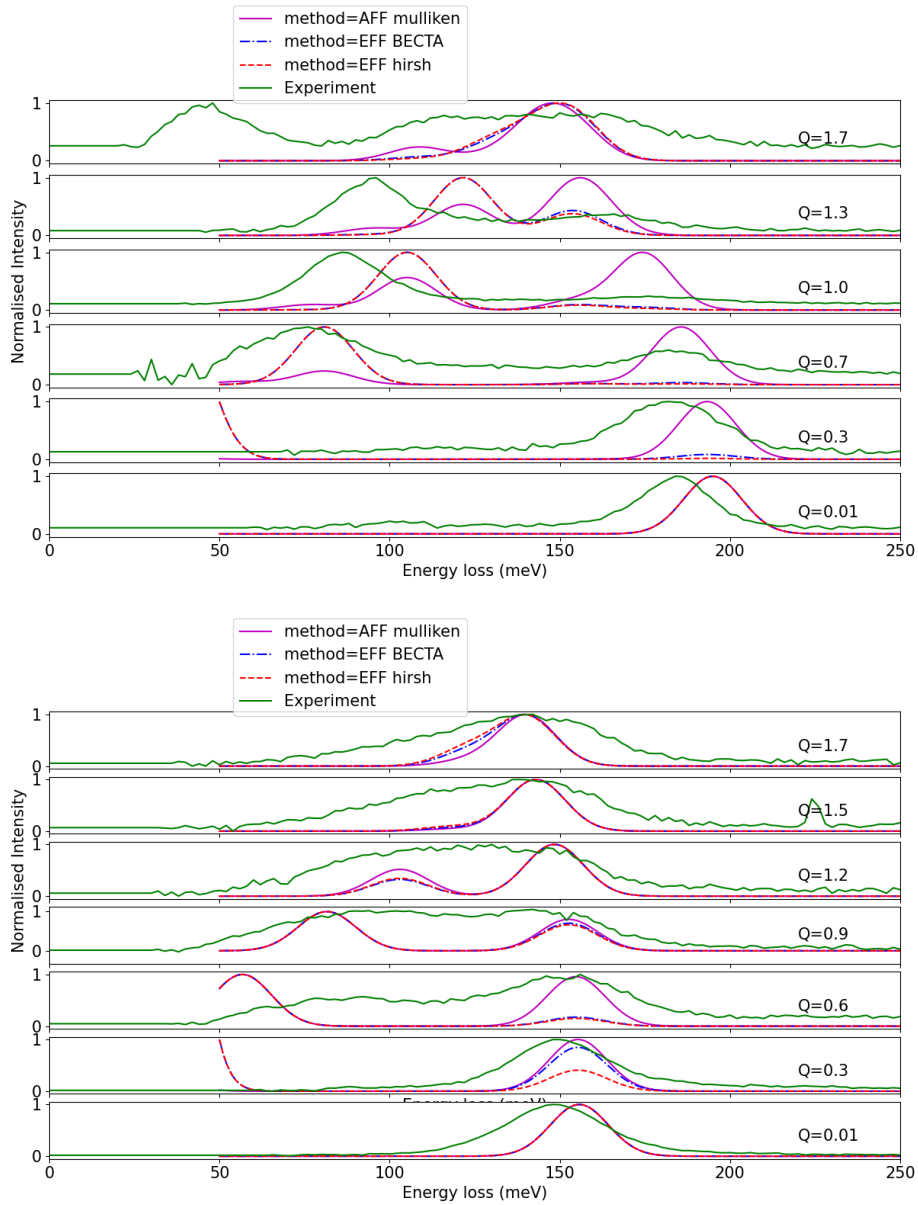


Figure H.o: Momentum resolved ultra-low loss EELS simulation of (top) hBN along $\Gamma - K$ and (bottom) cBN along $\Gamma - X$ momentum resolved ultra-low loss EELS spectra. The quantum impact scattering theory is used for all simulations. Q denotes the magnitude of the imparted momentum. *The experimental data obtained by Nicholls et al. are presented with permission from the authors.* The experimental spectra are shown in green and all plots are normalised.

BIBLIOGRAPHY

- [1] Kathy Guille and William Clegg. Anhydrous guanine: a synchrotron study. *Acta Crystallographica Section C: Crystal Structure Communications*, 62(8):0515–0517, 2006.
- [2] Ondrej L Krivanek, Tracy C Lovejoy, Matthew F Murfitt, Gwyn Skone, Philip E Batson, and Niklas Dellby. Towards sub-10 meV energy resolution STEM-EELS. In *Journal of Physics: Conference Series*, volume 522, page 012023. IOP Publishing, 2014.
- [3] Ondrej L Krivanek, Jonathan P Ursin, Neil J Bacon, George J Corbin, Niklas Dellby, Petr Hrnčirik, Matthew F Murfitt, Christopher S Own, and Zoltan S Szilagyi. High-energy-resolution monochromator for aberration-corrected scanning transmission electron microscopy/electron energy-loss spectroscopy. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 367(1903):3683–3697, 2009.
- [4] Riccardo Deidda, Pierre-Yves Sacre, Matthieu Clavaud, Laureen Coïc, Hermene Avohou, Philippe Hubert, and Eric Ziemons. Vibrational spectroscopy in analysis of pharmaceuticals: Critical review of innovative portable and handheld NIR and Raman spectrophotometers. *TrAC Trends in Analytical Chemistry*, 114:251–259, 2019.
- [5] Lee Brammer and GR Desiraju. Crystal design: structure and function. *Perspectives in Supramolecular Chemistry*, ed. GR Desiraju, Wiley, Chichester, 7:1, 2003.

BIBLIOGRAPHY

- [6] Wojciech Czernicki and Malgorzata Baranska. Carbamazepine polymorphs: Theoretical and experimental vibrational spectroscopy studies. *Vibrational Spectroscopy*, 65:12–23, 2013.
- [7] Rolf Hilfiker and Von Markus. *Polymorphism in the pharmaceutical industry*, volume 2. Wiley Online Library, 2006.
- [8] Lynne S Taylor and George Zografi. The quantitative analysis of crystallinity using ft-raman spectroscopy. *Pharmaceutical research*, 15(5):755–761, 1998.
- [9] Jörg Breitenbach, Wolfgang Schrof, and Jörg Neumann. Confocal raman-spectroscopy: analytical approach to solid dispersions and mapping of drugs. *Pharmaceutical research*, 16(7):1109–1113, 1999.
- [10] Ethan L Crowell, Zbigniew A Dreger, and Yogendra M Gupta. High-pressure polymorphism of acetylsalicylic acid (aspirin): Raman spectroscopy. *Journal of Molecular Structure*, 1082:29–37, 2015.
- [11] Martin E Auer, Ulrich J Griesser, and Juergen Sawatzki. Qualitative and quantitative study of polymorphic forms in drug formulations by near infrared ft-raman spectroscopy. *Journal of molecular structure*, 661:307–317, 2003.
- [12] S Farquharsan. Pharmaceutical applications of raman spectroscopy. *Amer Pharm Rev*, 2014.
- [13] Matthew R Ryder, Bartolomeo Civalleri, Thomas D Bennett, Sebastian Henke, Svemir Rudić, Gianfelice Cinque, Felix Fernandez-Alonso, and Jin-Chong Tan. Identifying the role of terahertz vibrations in metal-organic frameworks: from gate-opening phenomenon to shear-driven structural destabilization. *Physical review letters*, 113(21):215502, 2014.

- [14] Shuo Lin, Yufeng Zhao, and Yeoung-Sang Yun. Highly effective removal of nonsteroidal anti-inflammatory pharmaceuticals from water by zr (iv)-based metal–organic framework: adsorption performance and mechanisms. *ACS applied materials & interfaces*, 10(33):28076–28085, 2018.
- [15] Markus Kubin, Jan Kern, Meiyuan Guo, Erik Källman, Rolf Mitzner, Vital K Yachandra, Marcus Lundberg, Junko Yano, and Philippe Wernet. X-ray-induced sample damage at the mn l-edge: a case study for soft x-ray spectroscopy of transition metal complexes in solution. *Physical Chemistry Chemical Physics*, 20(24):16817–16827, 2018.
- [16] Richard Henderson. The potential and limitations of neutrons, electrons and x-rays for atomic resolution microscopy of unstained biological molecules. *Quarterly reviews of biophysics*, 28(2):171–193, 1995.
- [17] Arno Rehn, Mikhail Mikerov, Sascha Preu, Martin Koch, and Jan C Balzer. Enhancing the performance of thz quasi time-domain spectroscopy systems by low duty cycle laser operation. *Optics express*, 26(25):32758–32764, 2018.
- [18] A Giles Davies, Andrew D Burnett, Wenhui Fan, Edmund H Linfield, and John E Cunningham. Terahertz spectroscopy of explosives and drugs. *Materials today*, 11(3):18–26, 2008.
- [19] SS Dhillon, MS Vitiello, EH Linfield, AG Davies, Matthias C Hoffmann, John Booske, Claudio Paoloni, M Gensch, Peter Weightman, GP Williams, et al. The 2017 terahertz science and technology roadmap. *Journal of Physics D: Applied Physics*, 50(4):043001, 2017.
- [20] Philip F Taday, IV Bradley, DD Arnone, and Michael Pepper. Using terahertz pulse spectroscopy to study the crystalline structure of a drug:

BIBLIOGRAPHY

- A case study of the polymorphs of ranitidine hydrochloride. *Journal of pharmaceutical sciences*, 92(4):831–838, 2003.
- [21] Clare J Strachan, Philip F Taday, David A Newnham, Keith C Gordon, J Axel Zeitler, Michael Pepper, and Thomas Rades. Using terahertz pulsed spectroscopy to quantify pharmaceutical polymorphism and crystallinity. *Journal of Pharmaceutical Sciences*, 94(4):837–846, 2005.
- [22] Ido Azuri, Anna Hirsch, Anthony M Reilly, Alexandre Tkatchenko, Shai Kendler, Oded Hod, and Leeor Kronik. Terahertz spectroscopy of 2, 4, 6-trinitrotoluene molecular solids from first principles. *Beilstein journal of organic chemistry*, 14(1):381–388, 2018.
- [23] Norman Colthup. *Introduction to infrared and Raman spectroscopy*. Elsevier, 2012.
- [24] Etienne Balan, A Marco Saitta, Francesco Mauri, and Georges Calas. First-principles modeling of the infrared spectrum of kaolinite. *American Mineralogist*, 86(11-12):1321–1330, 2001.
- [25] M Krisch and F Sette. Inelastic x-ray scattering with very high resolution at the esrf. *Crystallography Reports*, 62(1):1–12, 2017.
- [26] Lyle H Schwartz and Jerome B Cohen. *Diffraction from materials*. Springer Science & Business Media, 2013.
- [27] James Hillier and RF Baker. Microanalysis by means of electrons. *Journal of Applied Physics*, 15(9):663–675, 1944.
- [28] Ferdinand Hofer, Franz-Philipp Schmidt, Werner Grogger, and Gerald Kothleitner. Fundamentals of electron energy-loss spectroscopy. In *IOP Conference Series: Materials Science and Engineering*, volume 109, page 012007. IOP Publishing, 2016.

- [29] R F Egerton. Electron energy-loss spectroscopy in the TEM. *Reports on Progress in Physics*, 72:016502, dec 2008.
- [30] Yimei Zhu and Hermann Durr. The future of electron microscopy. *Physics Today*, 68(BNL-108108-2015-JA), 2015.
- [31] Harald Ibach and Douglas L Mills. *Electron energy loss spectroscopy and surface vibrations*. Academic press, 2013.
- [32] Sample requirements eels. <https://www.eels.info/how/getting-started/sample-requirements>. Accessed: 2019-06-19.
- [33] Paula MB Piccoli, Thomas F Koetzle, and Arthur J Schultz. Single crystal neutron diffraction for the inorganic chemist—a practical guide. *Comments on Inorganic Chemistry*, 28(1-2):3–38, 2007.
- [34] Philip E Batson, Niklas Dellby, and Ondrej L Krivanek. Sub-ångstrom resolution using aberration corrected electron optics. *Nature*, 418(6898):617, 2002.
- [35] Peter D Nellist, Matthew F Chisholm, N Dellby, OL Krivanek, MF Murfitt, ZS Szilagyi, Andrew R Lupini, A Borisevich, WH Sides, and Stephen J Pennycook. Direct sub-angstrom imaging of a crystal lattice. *Science*, 305(5691):1741–1741, 2004.
- [36] DA Muller, L Fitting Kourkoutis, M Murfitt, JH Song, HY Hwang, J Silcox, N Dellby, and OL Krivanek. Atomic-scale chemical imaging of composition and bonding by aberration-corrected microscopy. *Science*, 319(5866):1073–1076, 2008.
- [37] Christian Dwyer, T Aoki, Peter Rez, SLY Chang, TC Lovejoy, and OL Krivanek. Electron-beam mapping of vibrational modes with nanometer spatial resolution. *Physical review letters*, 117(25):256101, 2016.

BIBLIOGRAPHY

- [38] FJ García De Abajo. Optical excitations in electron microscopy. *Reviews of modern physics*, 82(1):209, 2010.
- [39] RF Egerton. Limits to the spatial, energy and momentum resolution of electron energy-loss spectroscopy. *Ultramicroscopy*, 107(8):575–586, 2007.
- [40] Ray F Egerton. *Electron energy-loss spectroscopy in the electron microscope*. Springer Science & Business Media, 2011.
- [41] HA Brink, MMG Barfels, RP Burgner, and BN Edwards. A sub-50 mev spectrometer and energy filter for use in combination with 200 kv monochromated (s) tems. *Ultramicroscopy*, 96(3-4):367–384, 2003.
- [42] Ondrej L Krivanek, Tracy C Lovejoy, Niklas Dellby, and RW Carpenter. Monochromated stem with a 30 mev-wide, atom-sized electron probe. *Microscopy*, 62(1):3–21, 2013.
- [43] TC Lovejoy, GC Corbin, N Dellby, MV Hoffman, and OL Krivanek. Advances in ultra-high energy resolution stem-eels. *Microscopy and Microanalysis*, 24(S1):446–447, 2018.
- [44] CE Kuyatt and J Arol Simpson. Electron monochromator design. *Review of Scientific Instruments*, 38(1):103–111, 1967.
- [45] Ondrej L Krivanek, Tracy C Lovejoy, Niklas Dellby, Toshihiro Aoki, RW Carpenter, Peter Rez, Emmanuel Soignard, Jiangtao Zhu, Philip E Batson, Maureen J Lagos, et al. Vibrational spectroscopy in the electron microscope. *Nature*, 514(7521):209, 2014.
- [46] HR Daniels, R Brydson, A Brown, and B Rand. Quantitative valence plasmon mapping in the tem: viewing physical properties at the nanoscale. *Ultramicroscopy*, 96(3-4):547–558, 2003.

- [47] LAJ Garvie, Peter Rez, JR Alvarez, and PR Buseck. Interband transitions of crystalline and amorphous SiO_2 : An electron energy-loss spectroscopy (EELS) study of the low-loss region. *Solid State Communications*, 106(5):303–307, 1998.
- [48] RJ Nicholls, FS Hage, DG McCulloch, QM Ramasse, Keith Refson, and JR Yates. Theory of momentum-resolved phonon spectroscopy in the electron microscope. *Physical Review B*, 99(9):094105, 2019.
- [49] Danna Qian, Cheng Ma, Karren L More, Ying Shirley Meng, and Miao-fang Chi. Advanced analytical electron microscopy for lithium-ion batteries. *NPG Asia Materials*, 7(6):e193, 2015.
- [50] H Cohen, T Maniv, R Tenne, Y Rosenfeld Hachon, O Stephan, and C Colliex. Near-field electron energy loss spectroscopy of nanoparticles. *Physical review letters*, 80(4):782, 1998.
- [51] Søren Raza, Shima Kadkhodazadeh, Thomas Christensen, Marcel Di Vece, Martijn Wubs, N Asger Mortensen, and Nicolas Stenger. Multipole plasmons and their disappearance in few-nanometre silver nanoparticles. *Nature communications*, 6:8788, 2015.
- [52] Jacob R Jokisaari, Jordan A Hachtel, Xuan Hu, Arijita Mukherjee, Canhui Wang, Andrea Konecna, Tracy C Lovejoy, Niklas Dellby, Javier Aizpurua, Ondrej L Krivanek, et al. Vibrational spectroscopy of water with high spatial resolution. *Advanced Materials*, 30(36):1802702, 2018.
- [53] Jordan A Hachtel, Jingsong Huang, Ilja Popovs, Santa Jansone-Popova, Jacek Jakowski, and Juan Carlos Idrobo. Seeing site-specific isotopic labeling of amino acids with vibrational spectroscopy in the electron microscope. *arXiv preprint arXiv:1808.02794*, 2018.

BIBLIOGRAPHY

- [54] Peter Rez, Toshihiro Aoki, Katia March, Dvir Gur, Ondrej L Krivanek, Niklas Dellby, Tracy C Lovejoy, Sharon G Wolf, and Hagai Cohen. Damage-free vibrational spectroscopy of biological materials in the electron microscope. *Nature communications*, 7(1):1–8, 2016.
- [55] G Radtke, D Taverna, M Lazzeri, and E Balan. First-principles vibrational electron energy loss spectroscopy of β -guanine. *Physical Review Letters*, 119(2):027402, 2017.
- [56] Alexander A Govyadinov, Andrea Konečná, Andrey Chuvilin, Saül Vélez, Irene Dolado, Alexey Y Nikitin, Sergei Lopatin, Fèlix Casanova, Luis E Hueso, Javier Aizpurua, et al. Probing low-energy hyperbolic polaritons in van der waals crystals with an electron microscope. *Nature communications*, 8(1):95, 2017.
- [57] M Litinskaya. Polaritons. 2016.
- [58] David Tong. Scattering theory, accessed 27/03/2019.
- [59] K Sturm. Dynamic structure factor: An introduction. *Zeitschrift für Naturforschung A*, 48(1-2):233–242, 1993.
- [60] Edgar Bright Wilson, John Courtney Decius, and Paul C Cross. *Molecular vibrations: the theory of infrared and Raman vibrational spectra*. Courier Corporation, 1980.
- [61] Channing C Ahn. *Transmission electron energy loss spectrometry in materials science and the EELS atlas*. John Wiley & Sons, 2006.
- [62] Stefano Baroni, Stefano De Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. *Reviews of modern Physics*, 73(2):515, 2001.

- [63] BD Forbes, AV Martin, SD Findlay, AJ D'Alfonso, and LJ Allen. Quantum mechanical model for phonon excitation in electron diffraction and imaging using a born-oppenheimer approximation. *Physical Review B*, 82(10):104103, 2010.
- [64] Feliciano Giustino. Electron-phonon interactions from first principles. *Reviews of Modern Physics*, 89(1):015003, 2017.
- [65] Xavier Gonze and Changyol Lee. Dynamical matrices, born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Physical Review B*, 55(16):10355, 1997.
- [66] Jozef T Devreese, Victor E Van Doren, and Piet E Van Camp. *Ab initio calculation of phonon spectra*. Springer Science & Business Media, 2012.
- [67] Tao Sun and Philip B Allen. Lattice thermal conductivity: Computations and theory of the high-temperature breakdown of the phonon-gas model. *Physical Review B*, 82(22):224305, 2010.
- [68] Yu-Ning Wu, Wissam A Saidi, Jeffrey K Wuenschell, Terumasa Tadano, Paul Ohodnicki, Benjamin Chorpening, and Yuhua Duan. Anharmonicity explains temperature renormalization effects of the band gap in sr-tio3. *The Journal of Physical Chemistry Letters*, 11(7):2518–2523, 2020.
- [69] Rufus H Ritchie. Plasma losses by fast electrons in thin films. *Physical review*, 106(5):874, 1957.
- [70] FJ Garcia De Abajo and A Howie. Retarded field calculation of electron energy loss in inhomogeneous dielectrics. *Physical Review B*, 65(11):115418, 2002.

BIBLIOGRAPHY

- [71] Viktor Myroshnychenko, Jessica Rodríguez-Fernández, Isabel Pastoriza-Santos, Alison M Funston, Carolina Novo, Paul Mulvaney, Luis M Liz-Marzan, and F Javier García de Abajo. Modelling the optical response of gold nanoparticles. *Chemical Society Reviews*, 37(9):1792–1805, 2008.
- [72] PM Echenique, J Bausells, and A Rivacoba. Energy-loss probability in electron microscopy. *Physical Review B*, 35(4):1521, 1987.
- [73] RH Ritchie and A Howie. Inelastic scattering probabilities in scanning transmission electron microscopy. *Philosophical Magazine A*, 58(5):753–767, 1988.
- [74] AA Lucas, E Kartheuser, and RG Badro. Electron-phonon interaction in dielectric films. application to electron energy loss and gain spectra. *Physical Review B*, 2(7):2488, 1970.
- [75] E Evans and DL Mills. Theory of inelastic scattering of slow electrons by long-wavelength surface optical phonons. *Physical Review B*, 5(10):4126, 1972.
- [76] AA Lucas and JP Vigneron. Theory of electron energy loss spectroscopy from surfaces of anisotropic materials. *Solid state communications*, 49(4):327–330, 1984.
- [77] BD Forbes and LJ Allen. Modeling energy-loss spectra due to phonon excitation. *Physical Review B*, 94(1):014110, 2016.
- [78] R Durman, P Favre, UA Jayasooriya, and SFA Kettle. Longitudinal optical-transverse optical (lo-to) splitting on internal modes in the raman spectra of noncentric crystals. *Journal of crystallographic and spectroscopic research*, 17(4):431–484, 1987.

- [79] Peter Y Yu and Manuel Cardona. *Fundamentals of semiconductors: physics and materials properties*. Springer, 2010.
- [80] Walter Kohn. Nobel lecture: Electronic structure of matter—wave functions and density functionals. *Reviews of Modern Physics*, 71(5):1253, 1999.
- [81] Vladimir Fock. Näherungsmethode zur lösung des quantenmechanischen mehrkörperproblems. *Zeitschrift für Physik*, 61(1):126–148, 1930.
- [82] Pablo Echenique and José Luis Alonso. A mathematical and computational review of hartree–fock scf methods in quantum chemistry. *Molecular Physics*, 105(23-24):3057–3098, 2007.
- [83] Feliciano Giustino. *Materials modelling using density functional theory: properties and predictions*. Oxford University Press, 2014.
- [84] John C Slater. The theory of complex spectra. *Physical Review*, 34(10):1293, 1929.
- [85] Tom Ziegler. A chronicle about the development of electronic structure theories for transition metal complexes. In *Molecular Electronic Structures of Transition Metal Complexes II*, pages 1–38. Springer, 2011.
- [86] Axel D Becke. Real-space post-hartree–fock correlation models. *The Journal of chemical physics*, 122(6):064101, 2005.
- [87] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Physical review*, 136(3B):B864, 1964.
- [88] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Physical review*, 140(4A):A1133, 1965.
- [89] Kieron Burke. Perspective on density functional theory. *The Journal of chemical physics*, 136(15):150901, 2012.

BIBLIOGRAPHY

- [90] John P Perdew and Karla Schmidt. Jacob’s ladder of density functional approximations for the exchange-correlation energy. In *AIP Conference Proceedings*, volume 577, pages 1–20. American Institute of Physics, 2001.
- [91] John P Perdew, Kieron Burke, and Yue Wang. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Physical review B*, 54(23):16533, 1996.
- [92] Sérgio Filipe Sousa, Pedro Alexandrino Fernandes, and Maria Joao Ramos. General performance of density functionals. *The Journal of Physical Chemistry A*, 111(42):10439–10452, 2007.
- [93] Albert P Bartók and Jonathan R Yates. Regularized scan functional. *The Journal of chemical physics*, 150(16):161101, 2019.
- [94] DR Hamann, M Schlüter, and C Chiang. Norm-conserving pseudopotentials. *Physical Review Letters*, 43(20):1494, 1979.
- [95] David Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical review B*, 41(11):7892, 1990.
- [96] Jonathan H Lloyd-Williams and Bartomeu Monserrat. Lattice dynamics and electron-phonon coupling calculations using nondiagonal supercells. *Physical Review B*, 92(18):184301, 2015.
- [97] RM Sternheimer. Electronic polarizabilities of ions from the hartree-fock wave functions. *Physical Review*, 96(4):951, 1954.
- [98] Alberto Ambrosetti, Anthony M Reilly, Robert A DiStasio Jr, and Alexandre Tkatchenko. Long-range correlation energy calculated from coupled atomic response functions. *The Journal of chemical physics*, 140(18):18A508, 2014.

- [99] Michele Lazzeri, Claudio Attaccalite, Ludger Wirtz, and Francesco Mauri. Impact of the electron-electron correlation on phonon dispersion: Failure of lda and gga dft functionals in graphene and graphite. *Physical Review B*, 78(8):081406, 2008.
- [100] Sarah L Price. From crystal structure prediction to polymorph prediction: interpreting the crystal energy landscape. *Physical Chemistry Chemical Physics*, 10(15):1996–2009, 2008.
- [101] Jiří Klimeš and Angelos Michaelides. Perspective: Advances and challenges in treating van der waals dispersion forces in density functional theory. *The Journal of chemical physics*, 137(12):120901, 2012.
- [102] A Otero-De-La-Roza and Erin R Johnson. A benchmark for non-covalent interactions in solids. *The Journal of chemical physics*, 137(5):054103, 2012.
- [103] Alberto Eljarrat and Christoph T Koch. Design and application of a relativistic kramers–kronig analysis algorithm. *Ultramicroscopy*, 206:112825, 2019.
- [104] D Taverna, M Kociak, V Charbois, and L Henrard. Electron energy-loss spectrum of an electron passing near a locally anisotropic nanotube. *Physical Review B*, 66(23):235419, 2002.
- [105] R Garcia-Molina, A Gras-Marti, A Howie, and RH Ritchie. Retardation effects in the interaction of charged particle beams with bounded condensed media. *Journal of Physics C: Solid State Physics*, 18(27):5335, 1985.
- [106] Ondrej L Krivanek, Niklas Dellby, Jordan A Hachtel, J-C Idrobo, MT Hotz, Ben Plotkin-Swing, Neil J Bacon, Andrew L Bleloch, George J Corbin, Matthew V Hoffman, et al. Progress in ultrahigh energy resolution eels. *Ultramicroscopy*, 203:60–67, 2019.

BIBLIOGRAPHY

- [107] Diane M Haiber and Peter A Crozier. Nanoscale probing of local hydrogen heterogeneity in disordered carbon nitrides with vibrational electron energy-loss spectroscopy. *ACS nano*, 12(6):5463–5472, 2018.
- [108] Kartik Venkatraman. *Towards High Spatial Resolution Vibrational Spectroscopy in a Scanning Transmission Electron Microscope*. PhD thesis, Arizona State University, 2020.
- [109] A Howie. Surface reactions and excitations. *Ultramicroscopy*, 11(2-3):141–148, 1983.
- [110] Judy J Cha, Zongfu Yu, Eric Smith, Martin Couillard, Shanhui Fan, and David A Muller. Mapping local optical densities of states in silicon photonic structures with nanoscale electron spectroscopy. *Physical Review B*, 81(11):113102, 2010.
- [111] Enrico Fermi. The ionization loss of energy in gases and in condensed materials. *Physical Review*, 57(6):485, 1940.
- [112] HA Kramers. The stopping power of a metal for alpha-particles. *Physica*, 13(6-7):401–412, 1947.
- [113] PE Batson. Surface plasmon scattering on flat surfaces at grazing incidence. *Ultramicroscopy*, 11(4):299–302, 1983.
- [114] PE Batson. Spatial resolution in electron energy loss spectroscopy. *Ultramicroscopy*, 47(1-3):133–144, 1992.
- [115] DE Newbury, RL Myklebust, and RH Geiss. P.e. batson in: *Analytical electron microscopy*, 1981.
- [116] AP Ramirez, MA Subramanian, M Gardel, G Blumberg, D Li, T Vogt, and SM Shapiro. Giant dielectric constant response in a copper-titanate. *Solid state communications*, 115(5):217–220, 2000.

- [117] Herbert Fröhlich. *Theory of dielectrics: dielectric constant and dielectric loss*. Clarendon Press, 1949.
- [118] AA Ward. Dielectric materials for advanced applications. *National Research Center Publisher, Egypt*, 2016.
- [119] Russell H Lyddane, RG Sachs, and E Teller. On the polar vibrations of alkali halides. *Physical Review*, 59(8):673, 1941.
- [120] Léon Van Hove. Correlations in space and time and born approximation scattering in systems of interacting particles. *Physical Review*, 95(1):249, 1954.
- [121] Sunil K Sinha. Theory of inelastic x-ray scattering from condensed matter. *Journal of Physics: Condensed Matter*, 13(34):7511, 2001.
- [122] K Sturm. Dynamic structure factor: An introduction. *Zeitschrift für Naturforschung A*, 48(1-2):233–242, 1993.
- [123] John H Hubbell. Radiation physics. 2003.
- [124] Gordon Leslie Squires. *Introduction to the theory of thermal neutron scattering*. Courier Corporation, 1996.
- [125] Wulf Rossmann. *Lie groups: an introduction through linear groups*, volume 5. Oxford University Press on Demand, 2006.
- [126] Fernando D Vila, JJ Rehr, HH Rossner, and HJ Krappe. Theoretical x-ray absorption debye-waller factors. *Physical Review B*, 76(1):014301, 2007.
- [127] John David Jackson. Classical electrodynamics, 1999.
- [128] Roger E Raab and Owen L De Lange. *Multipole theory in electromagnetism: classical, quantum, and symmetry aspects, with applications*, volume 128. OUP Oxford, 2004.

BIBLIOGRAPHY

- [129] Martin T Dove and Martin T Dove. *Introduction to lattice dynamics*. Cambridge university press, 1993.
- [130] Dirk Porezag and Mark R Pederson. Infrared intensities and raman-scattering activities within density-functional theory. *Physical Review B*, 54(11):7830, 1996.
- [131] Joseph David Everett. *Illustrations of the CGS System of Units: With Tables of Physical Constants*. Macmillan and Company, limited, 1902.
- [132] Christian Dwyer. Localization of high-energy electron scattering from atomic vibrations. *Physical Review B*, 89(5):054103, 2014.
- [133] Christian Dwyer. Prospects of spatial resolution in vibrational electron energy loss spectroscopy: Implications of dipolar scattering. *Physical Review B*, 96(22):224102, 2017.
- [134] LJ Allen, HG Brown, SD Findlay, and BD Forbes. A quantum mechanical exploration of phonon energy-loss spectroscopy using electrons in the aloof beam geometry. *Microscopy*, 67(suppl_1):i24–i29, 2018.
- [135] Ryosuke Senga, Kazu Suenaga, Paolo Barone, Shigeyuki Morishita, Francesco Mauri, and Thomas Pichler. Position and momentum mapping of vibrations in graphene nanostructures. *Nature*, 573(7773):247–250, 2019.
- [136] William L Barnes. Surface plasmon–polariton length scales: a route to sub-wavelength optics. *Journal of optics A: pure and applied optics*, 8(4):S87, 2006.
- [137] Kiyoshi Yamamoto and Akio Masui. To-lo splitting in infrared spectra of thin films. *Applied spectroscopy*, 50(6):759–763, 1996.

- [138] VA Yakovlev, VG Nazin, and GN Zhizhin. The surface polariton splitting due to thin surface film lo vibrations. *Optics Communications*, 15(2):293–295, 1975.
- [139] Padma Kumar and Dominik Marx. Quantum corrections to classical time-correlation functions: Hydrogen bonding and anharmonic floppy modes. *J. Chem. Phys*, 121:9, 2004.
- [140] Mehrdad Khatami, Hajar Q Alijani, and Iraj Sharifi. Biosynthesis of bimetallic and core–shell nanoparticles: their biomedical applications—a review. *IET nanobiotechnology*, 12(7):879–887, 2018.
- [141] Felix Bloch. Über die quantenmechanik der elektronen in kristallgittern. *Zeitschrift für physik*, 52(7):555–600, 1929.
- [142] Hendrik J Monkhorst and James D Pack. Special points for brillouin-zone integrations. *Physical review B*, 13(12):5188, 1976.
- [143] RA Evarestov and VP Smirnov. Special points of the brillouin zone and their use in the solid state theory. *physica status solidi (b)*, 119(1):9–40, 1983.
- [144] Stewart J Clark, Matthew D Segall, Chris J Pickard, Phil J Hasnip, Matt IJ Probert, Keith Refson, and Mike C Payne. First principles methods using castep. *Zeitschrift für kristallographie-crystalline materials*, 220(5-6):567–570, 2005.
- [145] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *Journal of physics: Condensed matter*, 21(39):395502, 2009.

BIBLIOGRAPHY

- [146] Paolo Giannozzi, Oliviero Andreussi, Thomas Brumme, Oana Bunau, M Buongiorno Nardelli, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Matteo Cococcioni, et al. Advanced capabilities for materials modelling with quantum espresso. *Journal of physics: Condensed matter*, 29(46):465901, 2017.
- [147] Lu Hua Li and Ying Chen. Atomically thin boron nitride: unique properties and applications. *Advanced Functional Materials*, 26(16):2594–2608, 2016.
- [148] Jianwei Sun, Adrienn Ruzsinszky, and John P Perdew. Strongly constrained and appropriately normed semilocal density functional. *Physical review letters*, 115(3):036402, 2015.
- [149] John P Perdew, Jianwei Sun, Richard M Martin, and Bernard Delley. Semilocal density functionals and constraint satisfaction. *International Journal of Quantum Chemistry*, 116(11):847–851, 2016.
- [150] Mohan Chen, Hsin-Yu Ko, Richard C Remsing, Marcos F Calegari Andrade, Biswajit Santra, Zhaoru Sun, Annabella Selloni, Roberto Car, Michael L Klein, John P Perdew, et al. Ab initio theory and modeling of water. *Proceedings of the National Academy of Sciences*, 114(41):10846–10851, 2017.
- [151] Richard C Remsing, Michael L Klein, and Jianwei Sun. Dependence of the structure and dynamics of liquid silicon on the choice of density functional approximation. *Physical Review B*, 96(2):024203, 2017.
- [152] Alexandre Tkatchenko and Matthias Scheffler. Accurate molecular van der waals interactions from ground-state electron density and free-atom reference data. *Physical review letters*, 102(7):073005, 2009.

- [153] Alexandre Tkatchenko, Robert A DiStasio Jr, Roberto Car, and Matthias Scheffler. Accurate and efficient method for many-body van der waals interactions. *Physical review letters*, 108(23):236402, 2012.
- [154] James W Furness, Aaron D Kaplan, Jinliang Ning, John P Perdew, and Jianwei Sun. Accurate and numerically efficient r2scan meta-generalized gradient approximation. *The journal of physical chemistry letters*, 11(19):8208–8215, 2020.
- [155] Anthony M Reilly and Alexandre Tkatchenko. Understanding the role of vibrations, exact exchange, and many-body van der waals interactions in the cohesive properties of molecular crystals. *The Journal of chemical physics*, 139(2):024705, 2013.
- [156] Jeffrey C Grossman, Lubos Mitas, and Krishnan Raghavachari. Structure and stability of molecular carbon: importance of electron correlation. *Physical review letters*, 75(21):3870, 1995.
- [157] A Van de Walle and G Ceder. Correcting overbinding in local-density-approximation calculations. *Physical Review B*, 59(23):14992, 1999.
- [158] Viktor N Staroverov, Gustavo E Scuseria, Jianmin Tao, and John P Perdew. Tests of a ladder of density functionals for bulk solids and surfaces. *Physical Review B*, 69(7):075102, 2004.
- [159] Philipp Haas, Fabien Tran, and Peter Blaha. Calculation of the lattice constant of solids with semilocal functionals. *Physical Review B*, 79(8):085104, 2009.
- [160] Gábor I Csonka, John P Perdew, Adrienn Ruzsinszky, Pier HT Philipsen, Sébastien Lebègue, Joachim Paier, Oleg A Vydrov, and János G Ángyán. Assessing the performance of recent density functionals for bulk solids. *Physical Review B*, 79(15):155107, 2009.

BIBLIOGRAPHY

- [161] Laurids Schimka, Judith Harl, and Georg Kresse. Improved hybrid functional for solids: The hsesol functional. *The Journal of Chemical Physics*, 134(2):024116, 2011.
- [162] JW Linnett. The force constants of some ch, nh and related bonds. *Transactions of the Faraday Society*, 41:223–232, 1945.
- [163] Jeffrey T Burke. Ir spectroscopy or hooke’s law at the molecular level-a joint freshman physics-chemistry experience. *Journal of chemical education*, 74(10):1213, 1997.
- [164] Anna Hirsch, Ido Azuri, Lia Addadi, Stephen Weiner, Kesong Yang, Stefano Curtarolo, and Leeor Kronik. Infrared absorption spectrum of brushite from first principles. *Chemistry of Materials*, 26(9):2934–2942, 2014.
- [165] K Ramesh Babu and G Vaitheeswaran. Ab-initio study of structural and vibrational properties of kn₃ under pressure. *Chemical Physics Letters*, 533:35–39, 2012.
- [166] James Keeler. *Understanding NMR spectroscopy*. John Wiley & Sons, 2011.
- [167] Jochen Autschbach. Relativistic effects on nmr parameters. In *Science and Technology of Atomic, Molecular, Condensed Matter & Biological Systems*, volume 3, pages 69–117. Elsevier, 2013.
- [168] Chris J Pickard and Francesco Mauri. All-electron magnetic response with pseudopotentials: Nmr chemical shifts. *Physical Review B*, 63(24):245101, 2001.
- [169] Jonathan R Yates, Chris J Pickard, and Francesco Mauri. Calculation of nmr chemical shifts for extended systems using ultrasoft pseudopotentials. *Physical Review B*, 76(2):024401, 2007.

- [170] MH Cohen and F Reif. Quadrupole effects in nuclear magnetic resonance studies of solids. In *Solid state physics*, volume 5, pages 321–438. Elsevier, 1957.
- [171] Jérôme Cuny, Jonathan R Yates, Régis Gautier, Eric Furet, Eric Le Fur, and Laurent Le Pollès. Electric field gradient calculations in paramagnetic compounds using the paw approach. application to ^{23}Na nmr in layered vanadium phosphates. *Magnetic Resonance in Chemistry*, 48(S1):S171–S175, 2010.
- [172] Mark Strohmeier, Dirk Stueber, and David M Grant. Accurate ^{13}C and ^{15}N chemical shift and ^{14}N quadrupolar coupling constant calculations in amino acid crystals: zwitterionic, hydrogen-bonded systems. *The Journal of Physical Chemistry A*, 107(38):7629–7642, 2003.
- [173] Chaohui Ye, Riqiang Fu, Jianzhi Hu, Lei Hou, and Shangwu Ding. Carbon-13 chemical shift anisotropies of solid amino acids. *Magnetic resonance in chemistry*, 31(8):699–704, 1993.
- [174] V Lemaitre, ME Smith, and A Watts. A review of oxygen-17 solid-state nmr of organic materials—towards biological applications. *Solid state nuclear magnetic resonance*, 26(3-4):215–235, 2004.
- [175] Kazuhiko Yamada, Takahiro Nemoto, Miwako Asanuma, Hisashi Honda, Toshio Yamazaki, and Hiroshi Hirota. Both experimental and theoretical investigations of solid-state ^{17}O nmr for l-valine and l-isoleucine. *Solid State Nuclear Magnetic Resonance*, 30(3-4):182–191, 2006.
- [176] Christel Gervais, Ray Dupree, Kevin J Pike, Christian Bonhomme, Mickaël Profeta, Chris J Pickard, and Francesco Mauri. Combined first-principles computational and experimental multinuclear solid-state

BIBLIOGRAPHY

- nmr investigation of amino acids. *The Journal of Physical Chemistry A*, 109(31):6960–6969, 2005.
- [177] Kazuhiko Yamada, Tadashi Shimizu, Yoshida Mitsuru, Miwako Asanuma, Masataka Tansho, and Takahiro Nemoto. Solid-state ^{17}O nmr study of small biological compounds. *Zeitschrift für Naturforschung B*, 62(11):1422–1432, 2007.
- [178] ER Andrew. Magic angle spinning. *International Reviews in Physical Chemistry*, 1(2):195–224, 1981.
- [179] DB Chesnut and CG Phung. Nuclear magnetic resonance chemical shifts using optimized geometries. *The Journal of chemical physics*, 91(10):6238–6245, 1989.
- [180] Roderick E Wasylishen, Sandra Mooibroek, and J Bruce Macdonald. A more reliable oxygen- ^{17}O absolute chemical shielding scale. *The Journal of chemical physics*, 81(3):1057–1059, 1984.
- [181] Gang Wu, Shuan Dong, Ramsey Ida, and Nitin Reen. A solid-state ^{17}O nuclear magnetic resonance study of nucleic acid bases. *Journal of the American Chemical Society*, 124(8):1768–1777, 2002.
- [182] Miri Zilka, Simone Sturniolo, Steven P Brown, and Jonathan R Yates. Visualising crystal packing interactions in solid-state nmr: Concepts and applications. *The Journal of Chemical Physics*, 147(14):144203, 2017.
- [183] Peter W Atkins and Ronald S Friedman. *Molecular quantum mechanics*. Oxford university press, 2011.
- [184] Zeng-hui Yang, Haowei Peng, Jianwei Sun, and John P Perdew. More realistic band gaps from meta-generalized gradient approximations: Only

- in a generalized kohn-sham scheme. *Physical review B*, 93(20):205205, 2016.
- [185] Nicola A Spaldin. A beginner’s guide to the modern theory of polarization. *Journal of Solid State Chemistry*, 195:2–10, 2012.
- [186] David Vanderbilt. *Berry phases in electronic structure theory: electric polarization, orbital magnetization and topological insulators*. Cambridge University Press, 2018.
- [187] Robert S Mulliken. Electronic population analysis on lcao–mo molecular wave functions. i. *The Journal of Chemical Physics*, 23(10):1833–1840, 1955.
- [188] Daniel Sanchez-Portal, Emilio Artacho, and Jose M Soler. Projection of plane-wave calculations into atomic orbitals. *Solid State Communications*, 95(10):685–690, 1995.
- [189] Bernard T Thole and Petrus Th van Duijnen. A general population analysis preserving the dipole moment. *Theoretica chimica acta*, 63(3):209–221, 1983.
- [190] Richard FW Bader and TT Nguyen-Dang. Quantum theory of atoms in molecules–dalton revisited. In *Advances in Quantum Chemistry*, volume 14, pages 63–124. Elsevier, 1981.
- [191] Richard FW Bader. The zero-flux surface and the topological and quantum definitions of an atom in a molecule. *Theoretical chemistry accounts*, 105(4):276–283, 2001.
- [192] W Tang, E Sanville, and G Henkelman. A grid-based bader analysis algorithm without lattice bias. *Journal of Physics: Condensed Matter*, 21(8):084204, 2009.

BIBLIOGRAPHY

- [193] Fred L Hirshfeld. Bonded-atom fragments for describing molecular charge densities. *Theoretica chimica acta*, 44(2):129–138, 1977.
- [194] Tian Lu and Feiwu Chen. Atomic dipole moment corrected hirshfeld population method. *Journal of Theoretical and Computational Chemistry*, 11(01):163–183, 2012.
- [195] Edward Prince. *International Tables for Crystallography, Volume C: Mathematical, physical and chemical tables, Chapter 6.1*. Springer Science & Business Media, 2004.
- [196] Nevill Francis Mott. The scattering of electrons by atoms. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 127(806):658–665, 1930.
- [197] JA Ibers. Atomic scattering amplitudes for electrons. *Acta Crystallographica*, 11(3):178–183, 1958.
- [198] DAVID Rez, PETER Rez, and I Grant. Dirac–fock calculations of x-ray scattering factors and contributions to the mean inner potential for electron scattering. *Acta Crystallographica Section A: Foundations of Crystallography*, 50(4):481–497, 1994.
- [199] I Lobato and D Van Dyck. An accurate parameterization for scattering factors, electron densities and electrostatic potentials for neutral atoms that obey all physical constraints. *Acta Crystallographica Section A: Foundations and Advances*, 70(6):636–649, 2014.
- [200] Jian Min Zuo and John CH Spence. *Advanced transmission electron microscopy*. Springer, 2017.
- [201] L-M Peng. Electron atomic scattering factors and scattering potentials of crystals. *Micron*, 30(6):625–648, 1999.

- [202] Juan Carlos Idrobo, Andrew R Lupini, Tianli Feng, Raymond R Unocic, Franklin S Walden, Daniel S Gardiner, Tracy C Lovejoy, Niklas Dellby, Sokrates T Pantelides, and Ondrej L Krivanek. Temperature measurement by a nanoscale electron probe using energy gain and loss spectroscopy. *Physical review letters*, 120(9):095901, 2018.
- [203] Carlos Maciel-Escudero, Andrea Konečná, Rainer Hillenbrand, and Javier Aizpurua. Probing and steering bulk and surface phonon polaritons in uniaxial materials using fast electrons: hexagonal boron nitride. *Physical Review B*, 102(11):115431, 2020.
- [204] Andrea Konecna, Fadil Iyikanat, and F Javier Garcia de Abajo. Theory of atomic-scale vibrational mapping and isotope identification with electron beams. *ACS nano*, 15(6):9890–9899, 2021.
- [205] EP Wigner and J Von-Neumann. Über merkwürdige eigenwerte. *Z. Phys*, 30:467, 1929.
- [206] Gregory J Hatton. The noncrossing rule and spurious avoided crossings. *Physical Review A*, 14(3):901, 1976.
- [207] KN Trueblood, H-B Bürgi, H Burzlaff, JD Dunitz, CM Gramaccioli, HH Schulz, U Shmueli, and SC Abrahams. Atomic displacement parameter nomenclature. report of a subcommittee on atomic displacement parameter nomenclature. *Acta Crystallographica Section A: Foundations of Crystallography*, 52(5):770–781, 1996.
- [208] Arash A Mostofi, Jonathan R Yates, Giovanni Pizzi, Young-Su Lee, Ivo Souza, David Vanderbilt, and Nicola Marzari. An updated version of wannier90: A tool for obtaining maximally-localised wannier functions. *Computer Physics Communications*, 185(8):2309–2310, 2014.

BIBLIOGRAPHY

- [209] Anna Hirsch, Dvir Gur, Iryna Polishchuk, Davide Levy, Boaz Pokroy, Aurora J Cruz-Cabeza, Lia Addadi, Leeor Kronik, and Leslie Leiserowitz. “guanigma”: The revised structure of biogenic anhydrous guanine. *Chemistry of Materials*, 27(24):8289–8297, 2015.
- [210] Stefan Grimme. Semiempirical gga-type density functional constructed with a long-range dispersion correction. *Journal of computational chemistry*, 27(15):1787–1799, 2006.
- [211] Matthieu Bugnet, Guillaume Radtke, Steffi Y Woo, Guo-zhen Zhu, and Gianluigi A Botton. Temperature-dependent high energy-resolution x-rays of ferroelectric and paraelectric bismuth phases. *Physical Review B*, 93(2):020102, 2016.
- [212] Damien Manuel, Delphine Cabaret, Ch Brouder, Ph Saintavrit, Amélie Bordage, and Nicolas Trcera. Experimental evidence of thermal fluctuations on the x-ray absorption near-edge structure at the aluminum k edge. *Physical Review B*, 85(22):224108, 2012.
- [213] Ray L Frost and Matt L Weier. Raman spectroscopy of natural oxalates at 298 and 77 k. *Journal of Raman Spectroscopy*, 34(10):776–785, 2003.
- [214] In private communication with professor guillaume radtke, 2021.
- [215] Berhane Temelso and George C Shields. The role of anharmonicity in hydrogen-bonded systems: The case of water clusters. *Journal of chemical theory and computation*, 7(9):2804–2817, 2011.
- [216] NL Vočadlo and Geoffrey D Price. The grüneisen parameter—computer calculations via lattice dynamics. *Physics of the earth and planetary interiors*, 82(3-4):261–270, 1994.

- [217] Yingchun Ding and Bing Xiao. Thermal expansion tensors, grüneisen parameters and phonon velocities of bulk MnTe ($m = \text{w}$ and mo ; $t = \text{s}$ and se) from first principles calculations. *Rsc Advances*, 5(24):18391–18400, 2015.
- [218] Paolo G. Radaelli. Lecture 9 in crystal structure and dynamics, 2013.
- [219] THK Barron. Grüneisen parameters for the equation of state of solids. *Annals of Physics*, 1(1):77–90, 1957.
- [220] Chris Ablitt, Sarah Craddock, Mark S Senn, Arash A Mostofi, and Nicholas C Bristowe. The origin of uniaxial negative thermal expansion in layered perovskites. *npj Computational Materials*, 3(1):1–8, 2017.
- [221] Ethan T Ritz, Sabrina J Li, and Nicole A Benedek. Thermal expansion in insulating solids from first principles. *Journal of Applied Physics*, 126(17):171102, 2019.
- [222] Francis Birch. Finite elastic strain of cubic crystals. *Physical review*, 71(11):809, 1947.
- [223] Francis Dominic Murnaghan. The compressibility of media under extreme pressures. *Proceedings of the National Academy of Sciences*, 30(9):244–247, 1944.
- [224] Kyle R Cochrane, Michael Desjarlais, and Thomas R Mattsson. Density functional theory (dft) simulations of polyethylene: Principal hugoniot, specific heats, compression and release isentropes. In *AIP Conference Proceedings*, volume 1426, pages 1271–1274. American Institute of Physics, 2012.
- [225] Tommaso Salzillo, Arianna Rivalta, Nicola Castagnetti, Simone D’Agostino, Matteo Masino, Fabrizia Grepioni, Elisabetta Venuti,

BIBLIOGRAPHY

- Aldo Brillante, and Alberto Girlando. Spectroscopic identification of quinacridone polymorphs for organic electronics. *CrystEngComm*, 21(24):3702–3708, 2019.
- [226] Erich F Paulus, Frank JJ Leusen, and Martin U Schmidt. Crystal structures of quinacridones. *CrystEngComm*, 9(2):131–143, 2007.
- [227] TE Gorelik, C Czech, SM Hammer, and MU Schmidt. Crystal structure of disordered nanocrystalline α ii-quinacridone determined by electron diffraction. *CrystEngComm*, 18(4):529–535, 2016.
- [228] Bernard Dennis Cullity. *Elements of X-ray Diffraction*. Addison-Wesley Publishing, 1956.
- [229] JR Connolly. Sample preparation and systematic diffractometer errors, 2009.
- [230] AD Squires, RA Lewis, Adam J Zaczek, and Timothy M Korter. Distinguishing quinacridone pigments via terahertz spectroscopy: absorption experiments and solid-state density functional theory simulations. *The Journal of Physical Chemistry A*, 121(18):3423–3429, 2017.
- [231] RF Egerton, P Li, and M Malac. Radiation damage in the tem and sem. *Micron*, 35(6):399–409, 2004.
- [232] Daisuke Shindo and Tetsuo Oikawa. Energy dispersive x-ray spectroscopy. In *Analytical electron microscopy for materials science*, pages 81–102. Springer, 2002.
- [233] Paul HC Eilers and Hans FM Boelens. Baseline correction with asymmetric least squares smoothing. *Leiden University Medical Centre Report*, 1(1):5, 2005.

- [234] Alejandro P Ayala, HW Siesler, R Boese, GG Hoffmann, GI Polla, and DR Vega. Solid state characterization of olanzapine polymorphs using vibrational spectroscopy. *International journal of pharmaceuticals*, 326(1-2):69–79, 2006.
- [235] Sean Askin, Jeremy K Cockcroft, Louise S Price, Andrea D Goncalves, Min Zhao, Derek A Tocher, Gareth R Williams, Simon Gaisford, and Duncan QM Craig. Olanzapine form iv: discovery of a new polymorphic form enabled by computed crystal energy landscapes. *Crystal Growth Design*, 19(5):2751–2757, 2019.
- [236] Rajni M Bhardwaj, Louise S Price, Sarah L Price, Susan M Reutzel-Edens, Gary J Miller, Iain DH Oswald, Blair F Johnston, and Alastair J Florence. Exploring the experimental and computed crystal energy landscape of olanzapine. *Crystal growth design*, 13(4):1602–1617, 2013.
- [237] Ranjit Thakuria and Ashwini Nangia. Polymorphic form iv of olanzapine. *Acta Crystallographica Section C: Crystal Structure Communications*, 67(11):0461–0463, 2011.
- [238] Susan M Reutzel-Edens, Julie K Bush, Paula A Magee, Greg A Stephenson, and Stephen R Byrn. Anhydrides and hydrates of olanzapine: crystallization, solid-state characterization, and structural relationships. *Crystal growth design*, 3(6):897–907, 2003.
- [239] Ana Borba, Merwe Albrecht, Andrea Gomez-Zavaglia, Martin A Suhm, and Rui Fausto. Low temperature infrared spectroscopy study of pyrazinamide: from the isolated monomer to the stable low temperature crystalline phase. *The Journal of Physical Chemistry A*, 114(1):151–161, 2010.

BIBLIOGRAPHY

- [240] Ricardo AE Castro, Teresa MR Maria, Antonio OL Evora, Joana C Feiteira, M Ramos Silva, A Matos Beja, Joao Canotilho, and M Ermelinda S Eusebio. A new insight into pyrazinamide polymorphic forms and their thermodynamic relationships. *Crystal growth design*, 10(1):274–282, 2010.
- [241] Suryanarayan Cherukuvada, Ranjit Thakuria, and Ashwini Nangia. Pyrazinamide polymorphs: relative stability and vibrational spectroscopy. *Crystal growth & design*, 10(9):3931–3941, 2010.
- [242] Ashim Kumar Bain. *Crystal optics: properties and applications*. John Wiley & Sons, 2019.
- [243] G Radtke, D Taverna, N Menguy, S Pandolfi, A Courac, Y Le Godec, OL Krivanek, and TC Lovejoy. Polarization selectivity in vibrational electron-energy-loss spectroscopy. *Physical Review Letters*, 123(25):256001, 2019.
- [244] Jian Li, Junghoon Jahng, Jie Pang, William Morrison, Jin Li, Eun Seong Lee, Jing-Juan Xu, Hong-Yuan Chen, and Xing-Hua Xia. Tip-enhanced infrared imaging with sub-10 nm resolution and hypersensitivity. *The Journal of Physical Chemistry Letters*, 11(5):1697–1701, 2020.
- [245] Anthony J Stone and M Alderton. Distributed multipole analysis: methods and applications. *Molecular Physics*, 56(5):1047–1064, 1985.
- [246] Volker Heine and D Weaire. Solid state physics vol 24 ed h ehrenreich. *F Seitz and D Turnbull (New York: Academic) pp*, pages 249–463, 1970.
- [247] Stefan Blugel. A 2 scattering theory: Born series. 2012.
- [248] Harald Friedrich. *Scattering theory*, volume 872. Springer, 2013.

- [249] Roger G Newton. *Scattering theory of waves and particles*. Springer Science & Business Media, 2013.