THE IMPACT OF CRYSTAL STRUCTURE ON
ELECTRON-PHONON COUPLING AND
PHONON-MEDIATED PROPERTIES

by
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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Applied Physics (Physics).

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ABSTRACT

The impact of crystal structure on electron-phonon coupling (EPC) was analyzed by computing (i) the electron-phonon mediated superconductivity and (ii) electron-phonon induced eigenenergy renormalizations. Our primary goal is to compare these EPC effects in a wide range of materials with various crystal symmetries and compositions in order to reveal the connection between EPC and crystal structure. First-principles calculations were done employing the density functional theory (DFT) and the density functional perturbation theory (DFPT) within the linear-response approach, for obtaining electron-phonon matrix elements, which were then used in post-processing codes to calculate superconductivity and electronic structure renormalization.

The Migdal-Eliashberg formalism and the McMillan equations were used to determine the electron-phonon coupling strength ($\lambda$) and the critical temperature ($T_c$) for sodium (Na) under high pressures. A thorough investigation was performed of superconductivity in Na from ambient pressure to 260 GPa, where the metal-to-insulator transition occurs, and at 15.5 terapascals (TPa), after Na reenters a metallic phase. We evaluated phonon dispersions and the superconducting parameters for body-centered cubic (bcc), fcc, $cI16$, $tI19$, and $cI24$ Na. Our results for the bcc and fcc phases are consistent with prior theory, and the previously unknown critical temperatures and electron-phonon coupling strengths were calculated for the $cI16$, $tI19$, and $cI24$ phases. The peak value of $\lambda$, between 0 and 30 TPa, was calculated to be 0.5 for $cI16$-Na. However, as superconductivity is associated with $\lambda \geq 1$, we conclude that Na is not likely to present scientifically interesting superconductivity, even at ultra-high pressures, despite favorable comparisons to structurally similar superconducting alkali metals.

The second EPC-induced phenomenon we examined is the electronic structure renormalization. Calculations and careful convergence tests were carried out for two silicon (Si)
allotropes, three carbon (C) allotropes, and four boron nitride (BN) polymorphs. Determination of the energy shifts from the DFPT electron-phonon matrix elements was done within the Allen-Heine-Cardona (AHC) theory in the adiabatic approximation as well as with non-adiabatic corrections. Our results demonstrate that the magnitude of the renormalizations at $T = 0$ K, or zero-point renormalization (ZPR), of the electronic band structure is comparable to the many-body GW corrections to Kohn-Sham eigenenergies for some materials, and, thus, need to be considered in electronic structure calculations. Examination of the phonon dispersion for each structure along with the non-adiabatic ZPR magnitudes revealed that bulk materials with optical phonons at higher maximum frequencies, have larger ZPR magnitudes, and that two dimensional structures exhibit significantly different behavior than those of the bulk materials.

This study investigates two well-known phonon-mediated properties: superconductivity and eigenenergy renormalization. These results are not only useful in these two fields. As the core part of these investigations is the computation of the electron-phonon coupling elements, they are also pertinent to the study optical and transport properties affected or mediated by lattice vibrations.
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LIST OF SYMBOLS

\( \varepsilon_{nk} \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . single-particle eigenenergies

\( \omega_{q\nu} \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . phonon frequency

\( N_p \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . number of unit cells in the BvK supercell

\( g_{mn\nu}(\mathbf{k}, \mathbf{q}) \) . . . . . . . . . . . . . . . . . . . . . first order EPC matrix element

\( g^{DW}_{mn\nu\nu'}(\mathbf{k}, \mathbf{q}, \mathbf{q}') \) . . . . . . . . . . . . . . . . second order EPC matrix element

\( T_c \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . critical temperature

\( N(\varepsilon_F) \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . electronic DOS at the Fermi level

\( \Delta \varepsilon_{nk} \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . EPC induced eigenenergy shift

\( \Delta E_g^{ZP} \) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . the total ZPR of the band gap
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<td>EPC</td>
<td>electron-phonon coupling</td>
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<tr>
<td>DFPT</td>
<td>density functional perturbation theory</td>
</tr>
<tr>
<td>BvK</td>
<td>Born-von Kármán</td>
</tr>
<tr>
<td>SCF</td>
<td>self-consistent field</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>LDA</td>
<td>local density approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>ZPR</td>
<td>zero-point renormalization</td>
</tr>
<tr>
<td>RMTA</td>
<td>rigid-muffin-tin approximation</td>
</tr>
<tr>
<td>PDOS</td>
<td>projected density of states</td>
</tr>
<tr>
<td>QP</td>
<td>quasiparticle</td>
</tr>
<tr>
<td>z-BN</td>
<td>zincblende boron nitride</td>
</tr>
<tr>
<td>w-BN</td>
<td>wurtzite boron nitride</td>
</tr>
<tr>
<td>h-BN</td>
<td>layered-hexagonal boron nitride</td>
</tr>
<tr>
<td>2D-BN</td>
<td>two dimensional boron nitride</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
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For Jean
CHAPTER 1
INTRODUCTION

Electron-phonon coupling (EPC) has been the topic of unflagging interest since the inception of the quantum theory of solids. As early as 1929, Bloch referred to the “interaction of the electrons and the elastic waves of the lattice” in his discussion of formal solutions to Schrödinger’s equation [1]. These so called “elastic waves” were renamed in 1932 when Frenkel introduced the term “phonons” [2] along with a disclaimer which cautioned, “[I]t is not in the least intended to convey hereby the impression that such phonons have a real existence. On the contrary, the possibility of their introduction rather serves to discredit the belief in the real existence of photons.” Like the term “photon”, used to describe the particle-like properties of electromagnetic radiation in a vacuum, the name “phonon” is a direct analogy to that of the “electron”, and has since been used to refer the fictitious quantum of energy in the elastic waves, or lattice vibrations, of crystals [3].

Why then is there such pervasive study of these particles with no “real existence”? The answer is that the effects of coupling between electrons and phonons, as well as numerous phonon mediated properties, have abundant consequences for the electronic structures of solids and to the study of condensed matter. For example, EPC is the primary mechanism behind superconductivity and the thermal dependence of the electrical resistivity in metals; it leads to the optical absorption by the indirect gap in semiconductors such as silicon, the temperature-dependence of the band gap, the distortion of electronic band structures, and hot carrier thermalization, and it is one of the dominant factors determining the carrier mobility in semiconductors [4].

Since first-principles electron-phonon coupling calculations are highly demanding, early theoretical studies in this area employed semiempirical models [4]. The last two decades have seen rapid progress in ab initio EPC calculation methods heavily relying on the density func-
tional perturbation theory (DFPT) based on the works of Baroni, Giannozzi, and Testa [5] and Gonze, Allan, and Teter [6] published in the late 1980’s to early 1990’s. DFPT facilitates the examination of the system response to first and second order atomic displacements in the lattice. From this, calculations can be done to determine the vibrational frequencies and dynamical eigenmodes necessary to analyze EPC and its numerous associated phenomena. Another approach is the use of many-body perturbation theory through the GW method [8], or $G_0W_0$[7]. These calculations are done by examining the first order perturbation with respect to the screened Coulomb interaction and have been shown to result in more accurate electron-electron interactions and EPC calculations [9].

These first-principles EPC calculation methods have made it feasible to explore phonon-mediated properties in a variety of materials from insulators to metals and variations in-between. Significant theoretical studies have been done on EPC induced superconductivity by exploring the properties of a wide range of materials including MgB$_2$ [10, 11, 12], several forms of doped graphene [13, 14, 15], and various pressurized alkali metals [16, 17, 18, 19, 20, 21, 22, 23]. These studies have explored the effects of both material composition and pressure on the electron-phonon coupling strength and the superconducting critical temperature. EPC effects have also been analyzed theoretically for the optical spectra of semiconductors as well as the overall temperature dependence of electronic band structures [24, 25, 26, 27]. This area of research has led to advances in the understanding of EPC and its impact on electronic structure as well as development of computational methods such as Wannier interpolation [28, 29, 30], non-adiabatic corrections [31, 32], and anharmonic calculations [32]. Other areas of EPC research include carrier dynamics and transport [33], kinks in angle-resolved photo-emission spectra [34] linked to phonon induced electron self-energies, and electron mass enhancements in metals [35, 36, 37].

The current body of work on EPC provides a broad sampling of phenomena, materials, parameters, and methods. However, at the time of this work, we are unaware of any study that directly relates crystal symmetry and structure to EPC behavior. As such, the objective
of our research is to compare and analyze the impact of crystal structure on EPC and phonon-mediated properties for bulk structures and two dimensional materials. Our study focuses on the superconducting behavior of different structural phases of pressurized sodium and the EPC induced renormalization of electronic band structures for several isoelectronic structures with differing dimensions and compositions. In this way, we examine and compare EPC properties for over a dozen crystal structures in order to identify trends that can be used to better understand how phonon-mediated properties are related to crystal symmetry and dimensionality.

The following section (1.1) gives a brief historical overview of ab initio EPC calculations, followed by a discussion of current state-of-the-art methods in section 1.2. Section 1.3 reviews recent advances in theory and methods on the EPC calculation, and section 1.4 gives a brief review of relevant experimental methods for measuring electron-phonon coupling. Section 1.5 is dedicated to a discussion of the objectives and motivation of this thesis.

1.1 Historical overview of electron-phonon coupling calculations

Following the notations used by Giustino [4], the Hamiltonian for a coupled, harmonic, electron-phonon system can be expressed as

\[
\hat{H} = \sum_{nk} \varepsilon_{nk} \hat{c}_n^{\dagger} \hat{c}_n + \sum_{q\nu} \hbar \omega_{q\nu} \left( \hat{a}_{q\nu}^{\dagger} \hat{a}_{q\nu} + \frac{1}{2} \right) + \frac{N_p^{-1/2}}{2} \sum_{k,q} g_{mn\nu}(k,q) \hat{c}_{m,k+q}^{\dagger} \hat{c}_{n,k} \left( \hat{a}_{q\nu}^{\dagger} \hat{a}_{q\nu} + \hat{a}_{-q\nu}^{\dagger} \hat{a}_{-q\nu} \right) + \left[ N_p^{-1/2} \sum_{k,q,q'} g_{mn\nu}(k,q,q') \hat{c}_{m,k+q+q'}^{\dagger} \hat{c}_{n,k} \times \left( \hat{a}_{q\nu}^{\dagger} + \hat{a}_{-q\nu}^{\dagger} \right) \left( \hat{a}_{q'\nu'}^{\dagger} + \hat{a}_{-q'\nu'}^{\dagger} \right) \right].
\]  

(1.1)

Here, the first term describes the Hamiltonian of the electron subsystem, and the second term specifies the phonon subsystem. The single-particle eigenenergies are denoted by \( \varepsilon_{nk} \), where \( k \) is the crystal momentum and \( n \) the band index. The lattice vibration frequency is denoted by \( \omega_{q\nu} \) for phonon branch \( \nu \) with momentum \( q \). The operators \( \hat{c}^{\dagger} \) and \( \hat{c} \) are the fermionic creation and destruction operators while \( \hat{a}^{\dagger} \) and \( \hat{a} \) are the corresponding bosonic
 creation and destruction operators, respectively.

The third and forth terms in equation 1.1 correspond to the first- and second-order expansions of the electron-phonon coupling, respectively [38]. Here $N_p$ is the number of unit cells in the Born-von Kármán (BvK) supercell, such that $N_p = N_1 \times N_2 \times N_3$ [4]. The term $g_{mn\nu}(k, q)$ is the first-order EPC matrix element, while $g_{mn\nu
u'}^{DW}(k, q, q')$ is the second-order EPC matrix element, corresponding to the Debye-Waller (DW) self-energy. The DW term in equation 1.1 was often omitted in early EPC calculations due to the dramatic increase in complexity compared with the first-order term. It is, however, essential to the electron self-energy calculation (Figure 2.1) as well as band gap renormalization [24, 25, 26]. Figure 1.1 shows the Feynman diagrams for two examples of first and second order electron-phonon interactions.

The progress of \textit{ab initio} EPC studies can be tracked through the development of methods to calculate the parameters necessary for evaluating the Hamiltonian expressed in equation 1.1. The intricacy and difficulty of this task lies in formulating accurate and feasible procedures by which to determine $\varepsilon_{nk}$, $\omega_{q\nu}$, $g_{mn\nu}(k, q)$ and $g_{mn\nu
u'}^{DW}(k, q, q')$. Additionally, the systems that can be accurately described by equation 1.1 are assumed to be characterized by
well defined quasiparticle excitations and accurately described by the harmonic and adiabatic approximations. With many challenging aspects of the problem still unresolved, research and development in this area are ongoing.

Metals were the subjects of the first EPC studies of solids, which were part of an undertaking to form a quantum theory of electrical resistivity [39]. These early methods were dominated by the free-electron-gas model for quasiparticle eigenenergies and the Debye model for lattice vibrations. As the systems under consideration were primarily alkali and noble metals, these assumptions yielded reasonable results though they did not deal with the complexities of realistic electron-phonon matrix elements [4]. It was not until 1929 that Felix Bloch derived a form of the electron-phonon matrix element for monovalent metals [1]. Though his expression ignored umklapp processes, Bloch’s matrix element was a stepping stone in the general understanding of EPC.

Subsequently, revisions were made to Bloch’s model in the works of Nordheim [40] and Bardeen [41]. Nordheim employed the assumption that the potential felt by the electrons is approximately the sum of the individual ionic potentials, so that the average potential is replaced by the Fourier component of the ionic Coulomb potential. This is known today as the “rigid-ion” approximation due to the assumption that when a nucleus is shifted, its corresponding potential shifts, rigidly, with it. However, in this approximation the Coulomb potential diverges at large phonon wavelengths leading to impractically strong electron-phonon coupling [4]. A rudimentary form of electronic screening was used to overcome this defect by by cutting off the ionic potential at the Wigner-Seitz unit cell [42]. This was not, however, enough to improve the predictive power of the “rigid-ion” model where it was limited by its neglect of the electronic response to ionic displacement in the solid. Bardeen’s work in 1937 attempted modeling the electronic screening by incorporating the Thomas-Fermi screening wave vector into the potential [41]. Giustino [4] describes Bardeen’s work as a “precursor of modern ab initio approaches” due to its use of a self-consistent field (SCF) method similar to that of contemporary DFT calculations. He also pointed out that the
main difference between Bardeen’s method and DFPT is the neglect of the exchange and correlation effects in the former’s formulation of electronic screening.

The study of EPC later expanded to include works on semiconductors and ionic crystals from which emerged key milestones in the development of current calculation methods. In the case of semiconductors, the EPC is more complex than it is in metals due to the fact that carriers in these systems are typically restricted to energy levels around the band gap, thus the major contribution to the electron-phonon interactions comes from large wavelength phonons for which the “rigid ion” model is insufficient. This complication lead to Bardeen and Shockley’s [43, 44] work on the “deformation potential” method which uses acoustic waves with long wavelengths to describe the atomic displacements. This procedure relies on empirical deformation potentials and, therefore, lacks the predictive features of fully \textit{ab initio} calculations [4]; however, the new understanding of carrier behavior in semiconductors lead to progress in the general understanding of EPC.

Ionic solids presented yet more challenges in accurately characterizing EPC due to the long-ranged electric fields formed by atomic displacement in these materials. In the late 1930’s Fröhlich and Mott [45, 46] explored a theoretical approach to the insulation breakdown in ionic crystals considering electric field strength as well as the mean free path of electrons in these solids. Due to the low density of free carriers in insulating materials they were able to reduce the model to one electron interacting with the polarization field of the ion[4]. This is also known as polar electron-phonon coupling, which characterizes the electronic screening as resulting from the dielectric polarization of insulators rather than from a sea of electrons as in Bardeen’s [41] contemporary work. The development of the Fröhlich model [47] was instrumental in the understanding of polar EPC at long wavelengths as well as the interaction between atomic displacement and the resulting electric fields.

The combined methods of Nordheim [40], Bardeen and Shockley [41, 43, 44], and Fröhlich [47], while useful and groundbreaking, are relevant only to a limited number of materials that can be described by these approximations with known empirical parameters. It was not until
the development of the pseudopotential method [48, 49, 50, 51, 52] between the late 1950’s and mid 1960’s that EPC studies could be performed for elements spanning the periodic table. Sham [53] first applied the pseudopotential method to EPC formalism, showing that the first-order electron-phonon matrix element can be accurately evaluated within the “rigid ion” approximation by substituting pseudopotentials and pseudo wavefunctions in place of the localized potentials and wave functions, respectively. This has been employed to formulate the electron-phonon matrix elements in numerous materials for the purpose of exploring the resistivity of metals [54, 55, 56, 57], superconducting critical temperatures [58, 59] semiconductor mobility [60], and temperature dependence of electronic band structures [25, 26] among other things. Like its predecessors, the pseudopotential method relied partially on empirical data, but it can be credited with taking EPC calculations to a quantitative status [4].

The first fully \textit{ab initio} EPC studies with predictive calculations were done using DFT, and despite the fact that early DFT [61, 62] and the pseudopotential method were in use in the sixties, it was not until nearly two decades later that DFT methods were capable of calculating electron-phonon matrix elements [35]. The first DFT calculation of electron-phonon coupling, done in 1985 by Dacorogna \textit{et al.} [35], relied on the “frozen phonon” approach, in which atoms are displaced in a supercell according to a specific phonon mode. The disadvantage of this method is that long-wavelength phonons may require very large supercells and consequently demanding DFT computations. This issue has been overcome through DFPT [5, 6, 63], which uses the linear response perturbative approach. The development of DFPT was critical to the theoretical study of EPC, as it allows the full phonon spectrum calculations to be done using a single unit cell. This step in the progress of \textit{ab initio} EPC calculations led to theoretical predictions for electrical resistivity, thermal conductivity, electron mass enhancement, and superconductivity in numerous materials by the late 1990s [36, 64, 65].
While predictive EPC calculations are possible with DFPT, there are two drawbacks requiring further development. The first is the harmonic and adiabatic approximations [4], which are not suitable for all materials, particularly metals and narrow gap semiconductors. Second is the sensitivity of DFT-based methods, to the Kohn-Sham potential and consequently the choice of exchange-correlation (XC) functional as well as the type and quality of the pseudopotential, which can drastically affect EPC calculations. A rigorous and complete general theory can be built for EPC from the works of Baym, Hedin, and Lundqvist [66, 67]. This formulation is based on quantum field theory [68] and tied in with the development of the GW approximation [8]. In addition, it is valid for metals, semiconductors, and insulators. Giustino [4] provides a thorough summary of this theory in what he calls the Hedin-Baym equations. We will not go into further detail on the full field-theory approach here as a direct numerical solution is not currently attainable. Instead, we will focus on current framework of computational EPC methods.

1.2 Modern electron-phonon coupling calculations

A combination of DFT [69, 70] and DFPT [71] is the current de facto method for most electron-phonon coupling calculations. Modifications and improvements to the core theory have had a good deal of success in recent years, including use of the GW method, non-adiabatic formulations, and anharmonicity studies which are discussed in section 1.3. In this section we describe the most common computational method and their associated approximations used for contemporary EPC studies.

Equation 1.1 contains the necessary components for describing the electron-phonon interactions of a system. We can rewrite this equation as the sum of four distinct Hamiltonians, such that

\[ \hat{H} = \hat{H}_e + \hat{H}_p + \hat{H}_{ep} + \hat{H}_{ep}^{(2)}. \]  

(1.2)

The first Hamiltonian, \( \hat{H}_e \), corresponds to the the first term of equation 1.1. The evaluation of this term is most often done using a Kohn-Sham (KS) Hamiltonian [61, 62] for which
the eigenfunctions and eigenvalues are characterized by \( \hat{H}^{KS}_{nk}(r) = \varepsilon_{nk}\psi_{nk}(r) \). In order to evaluate the wave functions, \( \psi_{nk} \), and electronic eigenenergies, \( \varepsilon_{nk} \), the KS equations are solved self-consistently until convergence is reached. The first term in equation 1.1 is written by treating the KS Hamiltonian as a one-body operator and can be expressed in the second quantized formalism as

\[
\hat{H}_e = \sum_{nk,n'k'} \langle \psi_{nk} | \hat{H}^{KS} | \psi_{n'k'} \rangle \hat{c}_{nk}^{\dagger} \hat{c}_{n'k'} = \sum_{nk} \varepsilon_{nk} \hat{c}_{nk}^{\dagger} \hat{c}_{nk}.
\]

(1.3)

Putting the Hamiltonian in this form is convenient for dealing with electron-phonon interactions as it is consistent with the formalism commonly used for the phonon subsystem and the electron-phonon coupling. It does, however, imply that the electronic system can be characterized by sharp quasiparticle excitations[4].

The second Hamiltonian in equation 1.2 represents the phonon subsystem, and the first step in its evaluation is to apply the harmonic approximation [42]. This is a ubiquitous practice in the study of lattice vibrations, which neglects third and fourth order electron-phonon coupling terms in the system Hamiltonian (Eq. 1.1). This approximation facilitates practical calculations of electron-phonon interactions. Then the interatomic force constants matrix can be built from the second derivatives of the total energy of the ionic perturbations, which is the basis for calculating the Hermitian “dynamical matrix”. The real eigenvalues of the dynamical matrix are the squared vibrational frequencies of the harmonic oscillators, \( \omega^2_{q\nu} \). The phonon subsystem Hamiltonian can then be determined from the interatomic force constants and the ionic perturbation energies and can also be written as:

\[
\hat{H}_p = \sum_{q\nu} \hbar \omega_{q\nu} \left( \hat{a}_{q\nu}^{\dagger} \hat{a}_{q\nu} + \frac{1}{2} \right)
\]

(1.4)

As mentioned above, this method relies on two approximations. The first is the harmonic approximation. The second is the adiabatic, or Born-Oppenheimer approximation [72], which is employed by treating the phonons as quasistatic perturbations. Physically, this allows the electrons to settle back to their ground states with each vibration cycle so that the interatomic force constants may be calculated for the electrons in the ground state.
Theoretically, the adiabatic approximation amounts to making the many-body electronic screening frequency independent of lattice vibrations [4]. This assumption does not hold for many materials, however, including metals, semimetals [73, 74], and polar materials [31]. Methods of evaluating lattice vibrations through DFT beyond the adiabatic approximation [75, 76, 31] will be discussed in section 1.3.

The third Hamiltonian in equation 1.2 corresponds to the electron-phonon coupling to the first order. It is built around the expanded KS potential in terms of the first-order nuclear (or ionic) displacements. It is common practice to define the KS potential in terms of the scattering potential, $\Delta_{q\nu} v^{KS}$ (where $\Delta_{q\nu}$ is the partial derivative with respect to the nuclear displacement due to the vibrational frequency of phonon branch $\nu$), which operates on the KS wavefunctions (in Bloch form), $N_p^{-1/2} u_{nk}(\mathbf{r}) e^{i k \mathbf{r}}$, to form the electron-phonon matrix elements, $g_{mn\nu}(\mathbf{k}, \mathbf{q}) = \langle u_{mk+q} \Delta_{q\nu} v^{KS} u_{nk} \rangle$ [4]. The full first-order electron-phonon coupling Hamiltonian can be written in terms of the the matrix elements as

$$\hat{H}_{ep} = N_p^{-1/2} \sum_{\mathbf{k}, \mathbf{q}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{c}^\dagger_{m\mathbf{k}+\mathbf{q}} \hat{c}_{n\mathbf{k}} \left( \hat{a}_{q\nu} + \hat{a}^\dagger_{-q\nu} \right).$$ (1.5)

The last piece on the righthand side of equation 1.2 is the second-order EPC Hamiltonian. The procedure for defining this system is the same as for the first-order EPC Hamiltonian save for the inclusion of second derivatives of the KS potential, such that the second-order matrix elements have the form,

$$g^{DW}_{mn\nu\nu'}(\mathbf{k}, \mathbf{q}, \mathbf{q}') = \langle u_{mk+q+q'} \Delta_{q\nu} \Delta_{q'\nu'} v^{KS} u_{nk} \rangle,$$ (1.6)

and the Hamiltonian is

$$\hat{H}_{ep}^{(2)} = N_p \sum_{\mathbf{k}, \mathbf{q}, \mathbf{q}'} g^{DW}_{mn\nu\nu'}(\mathbf{k}, \mathbf{q}, \mathbf{q}') \hat{c}^\dagger_{m\mathbf{k}+\mathbf{q}+\mathbf{q}'} \hat{c}_{n\mathbf{k}} \times \left( \hat{a}_{q\nu} + \hat{a}^\dagger_{-q\nu} \right) \left( \hat{a}_{q'\nu'} + \hat{a}^\dagger_{-q'\nu'} \right).$$ (1.7)

Despite the simplicity with which the above can be stated, the evaluation of the second-order electron-phonon coupling is notoriously difficult and is often excluded from EPC calculations. Allen and Heine, [24] however, showed that the evaluation of the second order displacements was necessary to describe the temperature dependence of the electronic band structures.
In the DFPT of Baroni et al. [71] the KS potential is differentiated to obtain the lattice-periodic scattering potential in terms of the variation in the ionic potential, the Hartree potential, and the exchange-correlation potential. This is done through a self-consistent calculation method using available exchange-correlation functionals, i.e. the local density approximation (LDA), the generalized gradient approximation (GGA) [77], etc. Once this is done the first-order electron-phonon matrix elements can be evaluated form the first derivatives of the KS wavefunctions with respect to the first order atomic displacements (see Eq. 1.5).

It is common in literature and convenient, at this point, to use the Sternheimer formulation to express the first-order derivatives of the KS equations [78]. This has the advantage of only needing to evaluate the occupied KS states, which will be useful in evaluating the phonon self energies associated with the the electron-phonon matrix elements. The Sternheimer equations are solved by an iterative procedure similar to that in standard DFT, and the details are described in Chapter 2, section 2.1.

With the first-order matrix elements accounted for, the only piece left is to calculate the second order matrix elements. This, however, is considerably more complicated as it involves the second-order Sternheimer equations for the second derivatives of the KS equations [4, 79]. The standard method for avoiding the difficulties associated with these manipulations is to approximate the second order matrix elements, \( g_{\mu \nu \sigma}^{DW}(k, q, q') \), as the product of the first-order matrix elements \( g_{\mu \nu \sigma}(k, q) \). This was first done by Allen and Heine [24] and Allen and Cardona [25] in their calculations of the electron-phonon induced temperature dependence on electronic structures.

The procedure described above is the standard method for analyzing EPC, as there is currently no way to achieve a numerical solution to the field-theoretical approach described by the Hedin-Baym equations discussed at the end of section 1.1. However, considering the speed with which new techniques, both theoretical and computational, are being developed a field-theoretical approach may soon be the new standard of operation. Current advances
in EPC analysis have already taken considerable steps toward a more general approach that relies on fewer approximations. A sampling of these works is given in the following section.

1.3 Advances and current research in electron-phonon coupling theory

The last decade of research in EPC has seen remarkable progress in the reach and accuracy of theoretical calculations. While a numerical field-theoretical solution is not yet possible, there have been multiple studies that expand standards on DFPT methods in such areas as non-adiabatic formulations, anharmonic effects, GW corrections, and advanced interpolation methods. Furthermore, the applications of ab initio EPC calculation methods have been extended to numerous areas of electronic structure and condensed matter including studies of carrier lifetimes [80, 34], optical properties of semiconductors, photoelectron spectroscopy [34], the DFT implementation for the Migdal-Eliashberg [81, 82] theory of superconductors [83, 84], and more. In this section we will briefly review some of the recent methods and research by which the theory of electron-phonon interactions has been advanced.

One major area of focus within the study of EPC is the improvement and ultimate circumvention of approximations that limit the generality of calculation methods. Applications of the approximations made in the DFPT theory detailed in section 1.2 are sometimes inadequate to describe the electron-phonon interactions within certain materials, such as the adiabatic approximation which fails in the cases of metals and narrow-gap semiconductors. In order to improve the theory and accuracy of results studies have been done on non-adiabatic corrections to DFPT methods. The inclusion of these corrections has a variety of consequences such as shifts of adiabatic frequencies, spectral broadening, coupling between vibrational modes, and the appearance of multiple poles for single phonon branches due to frequency dependent perturbations [4]. The background and formalism of non-adiabatic renormalization is discussed in greater detail in chapter 2.

The second main approximation made in the majority of EPC calculations is the harmonic approximation. While this modification is valid in many cases, anharmonicity has recently be shown to have effects on numerous aspects of EPC including phonon dispersions [85, 86],
superconducting critical temperatures [87, 88], and temperature dependence in electronic band structures [32, 89]. The study of these effects requires the third and fourth order derivatives of the total potential energy, which can be done with DFPT [90, 91, 92, 93, 94] or through the use of a “self-consistent” phonon method [95, 96]. For the purposes of this project, anharmonic effects were not considered, but the reader is advised of their possible consequence.

Another promising advance in EPC calculations is the use of the GW approximation [7, 97, 98] to correct the KS energies of the density functional theory. Several studies have demonstrated the effects of these corrections on the electron-phonon matrix elements. In 2008, Lazzeri et al. [99] performed GW calculations for the EPC in graphene and found that the matrix elements showed an overall increase in magnitude compared to the DFT results. Similar reports of matrix element enhancements have been made by several studies [100, 101, 102]. The increase in the electron-phonon matrix elements naturally ties into the electron-phonon induced renormalization of electronic band gaps. The work of Antonius et al. [9] demonstrated large GW corrections to the zero-point renormalization in diamond. Similar investigations made by Monserrat [103] found large GW corrections in silicon, but small renormalizations for LiF, MgO, and TiO$_2$. Calculations of the superconducting properties of materials have also been done using the GW approximation. Several materials were found to have a large increase in the electron-phonon coupling strength, $\lambda$, and a drastic improvement in the calculation of the critical temperature with respect to experimental data [104, 105, 106].

There has also been a strategy proposed to incorporate the GW approximation into EPC calculations by evaluating variations in the Green’s function with a frozen phonon method and combining it with the Coulomb interaction of the ground state [107]. Overall, GW approximations have greatly benefited electron-phonon calculations and their inclusion in future studies is likely to become more common.

The issue of efficiency and cost when performing EPC calculations is another area of increasing importance. The Sternheimer formulation [78] of the KS equations is one method
Another method is Wannier interpolation, which uses maximally localized Wannier functions [28] in place of KS wavefunctions. A number of studies have used this method to increase the efficiency of electron-phonon matrix element calculations by reducing the computational cost [30, 108]. Cheaper and faster calculations of matrix elements become more important for complex materials, such as nano structures with many atoms in their unit cells. They are also useful when large numbers of matrix elements must be calculated to reach convergence of EPC properties.

Due to the progress of first principles methods over the last decade, EPC calculations have become a valuable tool in studying the properties of solids. For this project we will focus on two prevalent applications: the calculation of EPC induced shifts of electronic band structures and the analysis of superconducting properties of metals. In the case of the former, evaluation of temperature dependent semiconductor band gaps [24, 25, 26] and phonon assisted optical absorption [109] is based on calculations of electron-phonon matrix elements as the temperature dependence of the band gap stems from the overall electron-phonon induced renormalization of the electronic eigenenergies. The formalism and theory behind the renormalization calculations was first put forth by Allen and Heine [24] in 1976. Since then the “rigid ion”, adiabatic, non-adiabatic, “frozen phonon”, and GW formulations have been used to determine the temperature dependent eigenenergy shifts for numerous materials. This topic is covered in depth in Chapter 4.

In the case of phonon-mediated superconductors, EPC methods are used to perform predictive calculations. With DFT it possible to determine the electron-phonon coupling strength and superconducting critical temperatures of metals through the implementation of anisotropic Migdal-Eliashberg theory [81, 82] and the McMillan-Allen-Dynes formula [110, 111] in place of Bardeen-Cooper-Schrieffer (BCS) theory [112]. The application of DFT to evaluate the superconducting properties of a material was applied as recently as 2005 [113] for MgB$_2$. Since then superconducting critical temperatures and electron-phonon
coupling strengths have been predicted for many more materials and calculation methods have extended to include plasmon-assisted superconductivity [114] and magnetic materials [115, 116]. Research in this area is vast, and, though we will not go into further detail here, the formalism of DFT superconductivity calculations is discussed more in Chapter 2.

1.4 Experimental techniques in electron-phonon coupling

While the methods used in this project are based in *ab initio* computational calculations, we compare our results to experimental work whenever possible (see Chapters 3 and 4). There are a variety of established experimental techniques for investigating EPC and its effects in solids including optical spectroscopy and resistivity measurements to detect superconducting transitions. Here we briefly review these methods and their impact.

Several of the more direct methods of EPC measurement involve optical spectroscopy, including Raman spectroscopy [117, 118], photoluminescence excitation (PLE) spectroscopy [117], and Angle-resolved photoemission spectroscopy (ARPES) [119, 120, 121]. Using these methods, the phonon energies can be determined through electron-phonon scattering, and the phonon dispersion can be built. Through a combination of extracted experimental data and theoretical equations, useful EPC mediated characteristics can be calculated such as the electron phonon coupling constant [117], the spectral function, and the Fan and Debye Waller self energies [121].

In their review of the effects of isotopes on optical spectra of semiconductors, Cardona and Thewalt[117] detail measurements using Raman and PLE spectroscopy for numerous semiconductors, including diamond and silicon. They describe the phonon linewidths, the derivatives of the electronic energy gaps with respect to the isotope masses, and the subsequent temperature dependent band gap described by the Varshni effect [122], which is now know to be a consequence of EPC [118]. The zero point renormalization(ZPR) can then be found by extrapolating the band gap renormalization to \( T = 0 \). Cardona and Thewalt’s experimentally extracted ZPR results for diamond and Si are given in Table 4.4 along with our *ab initio* calculations.
Another technique used to measure pertinent data is spectroscopic ellipsometry [123], from which the complex dielectric function can be obtained. In their work on the temperature dependent band gap of diamond, Logothetidis et al. used spectroscopic ellipsometry with synchrotron radiation to calculate the dielectric function. Using first and second derivative line-shape analysis, they extracted the electronic band gap renormalization as a function of temperature. Their results for the gap renormalization at a low temperature of 7 Kelvin (K) are in good agreement with the previously described method of Cardona and Thewalt [117].

While Raman and PLE spectroscopy are useful to determine the phonon energies, the phonon momentum and electron energy and momentum are left unresolved; however, the energy and parallel electron momentum can be determined from the ARPES spectrum [119, 121, 120]. ARPES is particularly suited to studying EPC in two dimensional and quasi-two dimensional materials as it takes very accurate measure of surface electron-phonon scattering. As such, it is a convenient technique for studying the EPC in graphene [124, 121, 125]. In addition, ARPES has been used to evaluate the electronic structure and EPC behavior in superconductors [119, 120].

Experimental measurements can also be done for phonon mediated phenomena such as superconductivity. These methods generally do not require a direct measurement of the electron-phonon scattering. Rather the electrical resistance is measured as a function of temperature to determine the superconducting critical temperature of particular materials [126, 127, 128, 129, 130]. As we will examine the superconductivity of alkali metals under pressure in Chapter 3, here we describe the general experimental procedure to determine the superconducting transitions of such materials.

While the exact setups and techniques may vary in pressurized superconductivity measurements, most begin by applying pressure to a small sample using a diamond anvil. The resistivity measurements are then made, generally using a direct current technique, as the temperature of the sample is increased. The pressure and temperature of the sample are often regulated with helium gas. In 1970, Wittig [128] reported results showing superconductivity
in high-pressure cesium and yttrium using the method described above. Later, lithium was also observed to have a superconducting transition in a high-pressure phase with a critical temperature between 16 K and 20 K [129, 126]. A number of other materials have been found to exhibit pressure induced superconductivity including several elemental materials. This is further discussed in Chapter 3.

Whether through optical spectroscopy or resistivity measurement, the experimental methods for observing EPC in materials is notoriously difficult. Many measurements require that the temperature of the sample be very low and well regulated. In the case of the pressurized superconductors, large pressures must be applied to materials, which can cause defects in the sample giving less accurate observations. While it is beyond the scope of this project to discuss the experimental techniques further, there have been substantial efforts to developed new methods that produce more accurate measurements of EPC properties.

1.5 Summary of our research objectives

In the previous sections we have detailed the historical development (section 1.1) and current practice (section 1.2) for \textit{ab initio} EPC calculations used in the study of electron-phonon interactions. We have also reviewed key advances in the methodology and research areas associated with EPC (section 1.3 and 1.4).

Our current research is focused on the impact of crystal structure and dimension on electron-phonon coupling properties. In the proceeding chapters, our goal is to answer the following questions:

(i) Does sodium, like lithium, become a superconductor in any of its high pressure phases \((cI16, tI19, \text{ or } cI24)\)?

(ii) Is Wannier interpolation a superior technique for converging the electron-phonon matrix elements as compared to the homogeneous phonon wavevector sampling method of the ABINIT[131] DFPT implementation?
(iii) How is the EPC induced eigenenergy renormalization related to crystal symmetry and composition for various carbon and silicon allotropes and boron nitride polymorphs?

(iv) Is the EPC induced eigenenergy renormalization affected by the lower-dimensionality of 2D structures?

The project can be separated into two parts. In the first part, we analyze the phonon-mediated superconducting properties in several pressurized crystal structures of sodium. Here we have performed the first calculations of the superconducting critical temperature and electron-phonon coupling strength for several high pressure phases of sodium: $cI_{16}$, $tI_{19}$, and $cI_{24}$. We have also compared our results for these structural phases with previous studies of alkali metals with similar crystal symmetries and electronic properties. In the second part of this thesis, we evaluate the electron-phonon induced, temperature dependent, electronic-band-structure renormalization for a range of crystal structures. The renormalization results are compared for three-dimensional (3D) and two-dimensional (2D) isoelectronic structures of carbon, silicon, and boron nitride using adiabatic and non-adiabatic calculation methods. We have calculated previously unknown EPC induced eigenenergy renormalizations for several materials including hexagonal boron nitride, wurtzite boron nitride, two-dimensional boron nitride, graphene, graphite, and silicene. In addition, we have discovered a relationship between stiff structures and large renormalization magnitudes.

The specifics of the calculation methods are described in Chapter 2, but in general, DFT and DFPT linear response calculations were used to evaluate electron-phonon matrix elements and various post-processing implementations were used to analyze properties of the electron-phonon interactions. For the majority of calculations, the ABINIT package [131] was used to perform the DFPT calculations and post-processing analysis required for the above research. The Wannier interpolation technique [30, 108] employed in Chapter 4, section 4.3.1 is used in order to compare convergence techniques for ZPR calculations of C and Si to those done with ABINIT. It uses the QUANTUM ESPRESSO package[132] as well
as a modified post-processing code. This is the first work to compare a Wannier interpolation based ZPR convergence technique to a homogeneous phonon wavevector sampling technique (as used by ABINIT).

In Chapter 3 the superconducting properties of alkali metals at ambient and elevated pressures are reviewed, and calculations are made for the stable structural phases of Na from ambient pressure to 260 GPa. This study looks at the structural phase transitions in Na as a function of pressure. The phonon dispersions, McMillan superconducting critical temperatures, and electron-phonon coupling strengths are calculated for each distinct phase; bcc, fcc, \textit{c}I16, and \textit{t}I19. We extend this to include a recently predicted \cite{133} ultra-high pressure phase of Na. Found to be a stable metallic phase at 15.5 TPa, the \textit{c}I24-Na structure is highly symmetrical and displays orbital hybridization that is not seen in any metallic Na structure at a lower pressure. Previous calculations have been performed to determine the superconducting parameters of Na in its bcc and fcc phases \cite{20, 18}, but this is the first time that superconductivity calculations have been performed for the Na phases \textit{c}I16, \textit{t}I19, and \textit{c}I24.

Chapter 4 contains the results for calculations of the temperature dependent electronic eigenenergies in various forms of silicon, carbon, and boron nitride. We compare the eigenenergy shifts and zero-point renormalizations (ZPRs) for two silicon (Si) allotropes three carbon (C) allotropes and four boron nitride (BN) polymorphs; silicon (Si), silicene, diamond, graphite, graphene, zincblende BN (z-BN), hexagonal BN (h-BN), mono-layered hexagonal BN (2D-BN), and wurtzite BN (w-BN). Adiabatic and non-adiabatic formalisms are used, and the standard DFPT method is compared to a Wannier interpolation method for Si and diamond. The electron-phonon dispersions, ZPRs, and temperature dependent electronic energy shifts are compared for Si, C, and BN isoelectronic structures (i.e. structures having the same number of valence electrons). Previous ZPR calculations for C, Si, and z-BN are in good agreement with our own \cite{32, 181, 182, 31}, which gives us confidence that our calculation method is valid. This is the first time that the EPC induced eigenenergy renormalizations
have been calculated for h-BN, w-BN, 2D-BN, silicene, graphene, and graphite, as well as the first time that eigenenergy renormalizations have been compared for isoelectronic structures and for 3D and 2D materials.

Our hope is that the pursuit of the topics above will expand upon the existing knowledge of phonon-mediated properties and reveal new questions for further study.
CHAPTER 2
THEORY AND METHODOLOGY

This chapter covers the general theory and methodology for the EPC calculations performed in current research. First, we will give an overview of the linear-response method and DFPT, which are the current mainstream approach for calculating the EPC matrix elements. All the phonon-mediated properties, such as superconductivity and electronic band-structure renormalization, can be evaluated from the EPC matrix elements; thus it is critical to obtain the accurate EPC matrix elements efficiently from first principles. We will then briefly describe the Migdal-Eliashberg theory for computing superconductivity, and review the adiabatic Allen-Hein-Cardona (AHC) theory and the non-adiabatic corrections to AHC. The last section (section 2.4) is dedicated to a description of the technical computational details used in our calculations.

2.1 Lattice vibrations

The theory of lattice vibrations has been well established in solid-state physics (see Chapter 1). In addition to electron-phonon interactions, a number of measurable properties depend on the dynamical behavior of the lattice including neutron-diffraction spectra, Raman scattering, specific heats, heat conduction, and thermal expansion [71]. As better \textit{ab initio} techniques have been developed, our knowledge of lattice vibrations and EPC only becomes broader. Here we review the formalism of the density functional perturbation theory, the most commonly employed computational method for lattice vibrations. DFPT implements the linear-response theory within the harmonic and adiabatic approximations.

Using the notation of Giustino [4], we begin by considering the unit cell of a solid containing $M$ atoms or ions at Cartesian coordinates $\tau_{\kappa\alpha}$, where $\kappa$ is the nucleus index and $\alpha$ is the index of the nuclear position in the unit cell. The solid can be expanded using BvK boundary conditions to build a super cell of $N_p$ unit cells with lattice vectors $\mathbf{R}_p$, such that $p$
is the primitive cell index with a range from 1 to \( N_p \), and the reciprocal-space wave vectors, \( q \), lie in the uniform grid in each unit cell. DFT can be used to calculate the total potential energy, \( U \), of the electronic ground state as a function of the unperturbed nuclear coordinates \( \tau_{\kappa\alpha p} \). By making the harmonic approximation, the \( U \) can be expanded to second order in the nuclear displacements, \( \Delta \tau_{\kappa\alpha p} \), which indicate the distance an atomic nucleus is shifted from its equilibrium position. Then the potential energy is given by,

\[
U(q) = U_0 + \frac{1}{2} \sum_{\kappa\alpha p,\kappa'\alpha' p'} \frac{\partial^2 U(q)}{\partial \tau_{\kappa\alpha p} \partial \tau_{\kappa'\alpha' p'}} \Delta \tau_{\kappa\alpha p} \Delta \tau_{\kappa'\alpha' p'}. \tag{2.1}
\]

Here, \( U_0 \) is the total potential energy of the system at equilibrium, and the second derivative of \( U \) with respect to the nuclear coordinates can be defined as the matrix of interatomic force constants,

\[
C_{\kappa\alpha p,\kappa'\alpha' p'}(q) = \frac{\partial^2 U(q)}{\partial \tau_{\kappa\alpha p} \partial \tau_{\kappa'\alpha' p'}}. \tag{2.2}
\]

This matrix is determined from the linear response of the electron-density to nuclear displacements within the crystal [71], and physical properties associated with the matrix elements are referred to as linear-response coefficients [79]. Additionally, the dynamical matrix is directly related to the Fourier transform of equation (2.2) and contains eigenvalues with information on the vibrational frequency of each harmonic oscillator.

Within the DFPT, the computation of the interatomic force constants begins by evaluating \( \partial_{\kappa\alpha q} V^{KS} \), from the Kohn-Sham potential defined by the sum of the nuclear, Hartree, and exchange-correlation (XC) potentials:

\[
V^{KS} = V^{en} + V^H + V^{xc}. \tag{2.3}
\]

This combination of the bare potential plus the XC potential is the effective screened potential. Then

\[
\partial_{\kappa\alpha q} V^{KS} = \sum_p e^{iq \cdot (r - R_p)} \frac{\partial V^{KS}}{\partial \tau_{\kappa\alpha}} \bigg|_{r = R_p}. \tag{2.4}
\]
gives the lattice-periodic scattering potential. Applying the differential operator in equation (2.4) to equation (2.3), we can write the scattering potential as

\[ \partial_{\kappa\alpha, q} v^{KS} = \partial_{\kappa\alpha, q} v^{en} + \partial_{\kappa\alpha, q} v^{H} + \partial_{\kappa\alpha, q} v^{xc}. \]  

(2.5)

Each of these components is evaluated separately, which is covered in detail by Giustino [4] and Baroni et al. [71], but it is significant to note that the variation in the Hartree and exchange-correlation contributions to the potential depend on the variation in electron density, \( \partial n_{\kappa\alpha, q}(r) \), due to the nuclear displacement in the solid. Evaluating \( \partial n_{\kappa\alpha, q}(r) \) is done by determining the first order perturbation in the KS wave functions, where \( \psi_{n,k}(r) = N_p^{-1/2} u_{nk}(r) e^{i k \cdot r} \) are the unperturbed wave functions in the Bloch form. Then the variation of the wave function has the general form \( \partial u_{n,k,q} e^{i q \cdot r} \), where \( q \) indicates that \( \partial u_{n,k,q} \) is a lattice-periodic function.

Recalling that the KS hamiltonian is \( \hat{H}^{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + V^{KS}(r; \{ \tau_{\kappa\alpha} \}) \) and the resulting form of the Schrödinger equation is

\[ \left( -\frac{\hbar^2}{2m_e} \nabla^2 + V^{KS}(r; \{ \tau_{\kappa\alpha} \}) \right) \psi_{n,k}(r) = \varepsilon_{n,k} \psi_{n,k}(r), \tag{2.6} \]

the first-order variation of the KS equations can be expressed in a Sternheimer equation [78]:

\[ (\hat{H}^{KS}_{k+q} - \varepsilon_{v,k}) \partial u_{v,k,q} = -\partial_{\kappa\alpha, q} v^{KS} u_{v,k}. \tag{2.7} \]

Here \( \hat{H}^{KS}_{k+q} = e^{-i (k+q) \cdot r} \hat{H}^{KS} e^{i (k+q) \cdot r} \) and the wave functions have been converted to Bloch form. Also, the change of index from \( n \) to \( v \) is to specify the occupied states. However, solving equation (2.7) becomes problematic for small eigenvalues which result in singularities in the system. This is circumvented by following the observation that only the unoccupied KS states in \( \partial u_{v,k,q} \) contribute to the variation in the electron density [134, 4, 71]. Thus, a projector of over the occupied states, \( \hat{P}^{occ}_{k+q} = \sum_v |u_{v,k+q}\rangle \langle u_{v,k+q}| \), can be used to filter the necessary component of the variation in the wave function, giving \( \partial u_{v,k,q} = (1 - \hat{P}^{occ}_{k+q}) \partial u_{v,k,q} \). Plugging this into equation (2.7) returns the “trimmed” Sternheimer expression

\[ (\hat{H}^{KS}_{k+q} - \varepsilon_{v,k}) \partial \tilde{u}_{v,k,q} = -(1 - \hat{P}^{occ}_{k+q}) \partial_{\kappa\alpha, q} v^{KS} u_{v,k}. \tag{2.8} \]

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Solving this equation makes it possible to construct the variation in electron density corresponding to the wave vector \( \mathbf{q} \), such that

\[
\partial n_{\kappa, q}(\mathbf{r}) = 2N_p^{-1} \sum_{\nu k} \partial \tilde{u}_{\nu k, q}.
\]  

(2.9)

Here it is assumed that the system is spin-degenerate and that the time reversal symmetry is applied [4].

In DFPT calculations, equation (2.8) is solved iteratively for each occupied state, \( \nu \), by setting an initial perturbation of \( \partial_{\kappa, q}^\nu v_{KS} = \partial_{\kappa, q}^\nu v_{en} \). For each iteration a new electron density response is calculated to determine the induced density in equation (2.9), which is used to determine the Hartree and exchange-correlation contributions to equation (2.4). The sum of these contributions along with the initial variation in the nuclear potential are combined to form the total screened perturbation, and the iteration cycle is continued until consecutive values of \( \partial n_{\kappa, q}(\mathbf{r}) \) have a difference smaller than a set tolerance [4].

As part of this procedure, the electron phonon matrix elements,

\[
g_{\mu \nu}(\mathbf{k}, \mathbf{q}) = \langle u_{m k+q} | \Delta_{\nu \nu}^K S | u_{n k} \rangle,
\]

(2.10)

are obtained. They are directly dependent on the scattering potential, \( \Delta_{\nu \nu}^K S \), which is related to the lattice-periodic scattering potential, \( \partial_{\kappa, q}^\nu v_{KS} \), via

\[
\Delta_{\nu \nu}^K S = l_{q \nu} \sum_{\kappa\alpha} (M_0/M_\kappa)^{1/2} e_{\kappa, \nu}(\mathbf{q}) \partial_{\kappa, q}^\nu v_{KS},
\]

(2.11)

where \( l_{q \nu} \) is the zero-point displacement amplitude, \( M_\kappa \) is the nuclear mass, \( M_0 \) is an arbitrary reference mass related to the zero-point displacement, and \( e_{\kappa, \nu}(\mathbf{q}) \) are the eigenvectors of the dynamical matrix, where

\[
\sum_{\kappa\alpha} e_{\kappa, \nu}^*(\mathbf{q}) e_{\kappa, \nu'}(\mathbf{q}) = \delta_{\nu \nu'}.
\]

(2.12)

Consequently, all software implementations supporting DFPT have the ability to calculate the electron-phonon matrix elements along with the interatomic force constant matrix (equation 2.2) [71, 4]. The electron-phonon matrix elements are, in turn, used in numerous calculations used to analyze electron-phonon induced effects, such as the superconducting...
properties calculated through Migdal-Eliashberg theory \[82, 81, 4\] (section 2.2) and the approximation of the second-order, Debye-Waller matrix elements (equation 1.6) needed to determine temperature dependent electronic band-structure renormalization (section 2.3.1) \[24, 25\].

2.2 Migdal-Eliashberg theory for electron-phonon induced superconductivity

This section reviews Migdal-Eliashberg theory \[82, 81\], as it applies to phonon-mediated superconductivity, and its implementation in the ABINIT [131] DFT package. The method involves several assumptions, namely that the superconductor is isotropic and has a single superconducting gap \[37, 4\]. It requires initial calculations of the electron-phonon matrix elements and interatomic force constants performed by DFPT (section 2.1).

The following formalism is the basis for the results presented in Chapter 3 of the pressure-induced superconductivity of various stable structural phases of Na. The ABINIT [131] DFPT and post-processing codes were used, which are similar to those implemented by Liu and Quong [37] and Savrasov \textit{et al.} [36]. To begin, the linewidth of the phonon mode, \( q \), due to electron-phonon coupling is obtained by averaging over the Fermi surface to give

\[
\gamma_{q\nu} = 2\pi \omega_{q\nu} \sum_{mn\nu} \int \frac{d\mathbf{k} d\mathbf{q}}{\Omega_{BZ}} |g_{mn\nu(k, q)}|^2 \\
\times \delta(\varepsilon_{nk} - \varepsilon_F)\delta(\varepsilon_{mk+q} - \varepsilon_F),
\]

(2.13)

where \( \Omega_{BZ} \) denotes the volume of the Brillouin zone, \( \omega \) is phonon frequency, \( \varepsilon_{nk} \) represents the Kohn-Sham eigenvalues, \( \varepsilon_F \) is the Fermi energy level, and \( g_{mn\nu(k, q)} \) is the electron-phonon matrix element from equation 2.10, which represents scattering of an electron from one Bloch state \((nk)\), to another Bloch state \((mk + q)\), with phonon of frequency \( \omega_{q\nu} \). These matrix elements are obtained through the linear-response DFPT calculations discussed in section 2.1.

From the line width, \( \gamma_{q\nu} \), several parameters for the Migdal-Elisashberg theory can be determined, including the EPC constant \((\lambda)\) and the electron-phonon spectral function \((\alpha^2F)\).
The electron-phonon coupling constant for phonon $q$ is defined by

$$
\lambda_{q\nu} = \frac{\gamma_{q\nu}}{\pi \hbar N(\varepsilon_F) \omega_{q\nu}^2},
$$

where $N(\varepsilon_F)$ is the electron density of states (DOS) at the Fermi level. The electron-phonon spectral function $\alpha^2 F(\omega)$ is defined in terms of the phonon linewidth as

$$
\alpha^2 F(\omega) = \frac{1}{2\pi \hbar N(\varepsilon_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\hbar \omega_{q\nu}} \delta(\omega - \omega_{q\nu}).
$$

Then the electron-phonon coupling constant, $\lambda$, can be expressed as the first reciprocal moment of the electron-phonon spectral function $\alpha^2 F(\omega)$

$$
\lambda = 2 \int_{0}^{\infty} \frac{\alpha^2 F(\omega)}{\omega} d\omega.
$$

Similarly, the logarithmic average of the phonon frequencies can be extracted from the spectral function such that

$$
\omega_{\log} = \exp \left[ \frac{2}{\lambda} \int_{0}^{\infty} \frac{\alpha^2 F(\omega)}{\omega} d\omega \right].
$$

From here the McMillan equation [110] as modified by Allen and Dynes [111] can be used to approximate $T_c$,

$$
T_c = \frac{\omega_{\log}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],
$$

where $\mu^*$ is the effective Coulomb potential, which is treated as an adjustable parameter in the range $\mu^* \sim 0.1 - 0.2$. In the weak coupling regime, an empirical value of $\mu^* \sim 0.1$ is often adopted. In this work we employ $\mu^* = 0.13$ as used by Profeta et al.[21] as well as Christensen and Novikov [17]. This approximation of the superconducting transition temperature is valid for conventional, single gap superconductors [111]. The materials, for which we will be using the method described above, are satisfactorily described within these approximations [18, 19, 20, 21].
2.3 Temperature dependence of electronic eigenenergies

In addition to our analysis of superconductivity in pressure-accessible phases of sodium (Chapter 3), we also examine the structural impact on the EPC induced temperature dependence of the electronic eigenenergies as discussed in section 1.5 and Chapter 4. This section is devoted to an overview of the theory for both the adiabatic and non-adiabatic formulations used to calculate the temperature dependence in band gaps and band structures.

2.3.1 Allen-Heine-Cardona theory

Allen and Heine [24] laid out the theoretical framework for temperature dependence of electronic band structures based on second order perturbation theory in the adiabatic and harmonic approximations. An effective study of these treatments requires the use of the Fan-Migdal (FM) and Debye-Waller (DW) electron self-energies where the shift in a particular energy level is defined by

$$\Delta \varepsilon_{nk} = \Delta^{\text{FM}} \varepsilon_{nk} + \Delta^{\text{DW}} \varepsilon_{nk},$$

(2.19)

where $\varepsilon_{nk}$ is the eigenenergy of the state with band $n$ and wave vector $k$. The FM self-energy, $\Delta^{\text{FM}} \varepsilon$, is the dynamic correction to the electronic excitation energies. It derives its name from the 1951 work done by Fan [135] and the work done by Migdal in 1958 [81], but it is most often referred to as either the Fan term [24, 25, 118] or the Migdal term [136, 112]. For continuity, the names are combined in recent literature [4]. The Fan-Migdal term describes the dynamic polarization of the lattice, and it is obtained by multiplying the first-order perturbation terms to recover the energy shift due to the second-order atomic displacement. The second term in equation 2.19 is commonly called the Debye-Waller electron self-energy, $\Delta^{\text{DW}} \varepsilon$, due to its similarities to the factor of the same name associated with temperature dependent x-ray diffraction spectra. This is a static term that describes the difference between the total potential for an interacting system and the potential for the same system with its nuclei clamped at equilibrium [4]. In other words, it is the result of the second-order perturbation due to lattice vibrations in the potential.
The theory developed by Allen and Heine [24] relies on two approximations: first is the implementation of the Rayleigh-Schrödinger approximation and, second, the assumption that the phonon energies associated with the FM self-energy are negligible [4]. Then, using translational invariance of the thermal shift, Allen and Heine expressed both the FM and DW corrections in terms of the first order perturbations of the self consistent potential $\partial_{\kappa \alpha, q \nu} K^S$ (Eq. 2.4) via the electron-phonon matrix elements in equation 2.10, such that

$$
\Delta_{\text{FM}} \varepsilon_{nk} = \sum_{m \neq n, \nu} \int_{\Omega_{BZ}} dq \frac{(2n_{q\nu} + 1) |g_{mn}(k,q)|^2}{\varepsilon_{nk} - \varepsilon_{mk+q} + i\eta},
$$

$$
\Delta_{\text{DW}} \varepsilon_{nk} = -\sum_{m \neq n, \nu} \int_{\Omega_{BZ}} dq \frac{(2n_{q\nu} + 1)|g_{mn}^{\text{DW}}(k,q)|^2}{(\varepsilon_{nk} - \varepsilon_{mk} + i\eta)}.
$$

Here $n_{q\nu}$ is the Bose-Einstein occupation factor for the phonon frequency associated with phonon $q$ and branch $\nu$ (Eq. 2.27) and $\Omega_{BZ}$ denotes the volume of the Brillouin zone. The small imaginary term, $i\eta$, in both the FM and DW terms is added as a computational method to smooth the self-energy functions and speed convergence of the energy shifts. In a majority of studies, $i\eta$ is set to 100 meV to account for the finite lifetimes of the electronic states defined by the imaginary part of the self-energy [31, 9, 32, 108]. In equation 2.21, the DW electron-phonon matrix element, $g_{mn,\nu}^{\text{DW}}(k,q)$, is an effective matrix element approximated from the products of standard electron-phonon matrix elements (Eq. 2.10) [108, 4]:

$$
[g_{mn,\nu}^{\text{DW}}(k,q)]^2 = \frac{1}{2\omega_{q\nu}} \sum_{\kappa, \alpha} t_{\kappa\alpha, \kappa'\alpha'}^{\nu}(q) h_{mn,\kappa\alpha}(k) h_{mn,\kappa'\alpha'}^{*}(k),
$$

where

$$
t_{\kappa\alpha, \kappa'\alpha'}^{\nu}(q) = \frac{e_{\kappa\alpha\nu}(q) e_{\kappa'\alpha'\nu}^{*}(q)}{M_\kappa} + \frac{e_{\kappa'\alpha'\nu}(q) e_{\kappa\alpha\nu}^{*}(q)}{M_{\kappa'}},
$$

$$
h_{mn,\kappa\alpha}(k) = \sum_\nu (M_\kappa \omega_{0\nu})^{1/2} e_{\kappa\alpha\nu}(0) g_{mn\nu}(k,0).
$$

In the above expressions, $e_{\kappa\alpha\nu}(q)$ are phonon eigenvectors of the dynamical matrix with atomic species $\kappa$, Cartesian direction $\alpha$, and phonon branch $\nu$. 

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Combining the FM and DW self-energy terms, as dictated by equation 2.19, the temperature dependent eigenenergy shift is

$$\Delta \varepsilon_{nk} = \sum_{m \neq n, \nu} \int \frac{dq}{\Omega_{\text{BZ}}} \left[ \sum_{m} \frac{|g_{mn\nu}(k, q)|^2}{\varepsilon_{nk} - \varepsilon_{mk} + i\eta} \right. - \frac{|g_{DW}^{\text{FM}}(k, q)|^2}{(\varepsilon_{nk} - \varepsilon_{mk} + i\eta)} \left. \right] (2n_{qv} + 1), \quad (2.25)$$

and the renormalized eigenenergy is

$$E_{nk} = \varepsilon_{nk} + \Delta \varepsilon_{nk}. \quad (2.26)$$

The temperature dependence in equation 2.25 resides entirely in the Bose-Einstein factor, where

$$n_{qv} = \frac{1}{e^{\omega_{qv}/k_B T} - 1}. \quad (2.27)$$

In order to determine the eigenenergy shifts at zero temperature, we set $T = 0$, and the Bose-Einstein factor vanishes. The remaining energy shift, $\Delta \varepsilon_{ZP}^{nk} = \Delta \varepsilon_{nk}(T = 0)$, is the “zero-point renormalization” or ZPR.

Equation 2.25 is the adiabatic formulation of eigenenergy renormalization based on the initial work of Allen and Heine [24]. Later this theory was developed into a computational method by Allen and Cardona [25, 26]. Thus, the literature generally refers to the complete formalism as the Allen-Heine-Cardona (AHC) theory. The theory is limited by its use of Rayleigh-Schrödinger perturbation theory and static treatment of the electronic screening. This is insufficient for certain materials including metals, semi-metals, and polar materials, thus, in the next section (2.3.2), we discuss the non-adiabatic correction to the AHC theory.

### 2.3.2 Non-adiabatic corrections to Allen-Heine-Cardona theory

The following section reviews the necessity for and formalism of the non-adiabatic correction to the EPC effects on the electron self-energies. As was mentioned in section 1.2, the Born-Oppenheimer [72], or adiabatic approximation, treats phonons as static perturbations such that the interatomic force constants of equation 2.2 are calculated for electrons in the ground state, resulting in a phonon-frequency independent electronic screening. This
approximation is effective for insulators and large gap semiconductors in which the band gap is much larger than the phonon energy; however, for narrow-gap semiconductors, semimetals, metals, and polar materials variations in adiabatic and non-adiabatic phonon energies become significant at the center of the BZ. This is due to the phonon behavior in the region around $q = 0$, where the non-adiabatic phonon energy correction is comparable to the adiabatic phonon energy [137, 138, 4]. In this case, the static perturbation approximation fails and a dynamic correction, which does not neglect the phonon frequencies ($\omega_{q\nu}$) in the FM self-energy, is used.

The effects of non-adiabatic vibrational frequencies were first investigated in the works of Lazzeri and Mauri [73] and Pisana et al. [74]. They performed calculations in the adiabatic approximation on a particular phonon branch of graphene then added a non-adiabatic frequency renormalization derived from the phonon self energy. Around the same time, studies were done on metallic single-walled carbon nanotubes (CNT) that confirmed the importance of non-adiabatic effects for such materials around $q = 0$ [139, 140]. A broader study of non-adiabatic renormalizations was done for a variety of graphite intercalation compounds by Saitta et al. [137] where they found that the non-adiabatic results were in much better agreement with experiments than the adiabatic calculations. Two years later Calandra et al. [138] published complete phonon dispersions calculated with non-adiabatic corrections, which confirmed that non-adiabatic effects are most significant for small $q$.

In addition to certain metals and semi-metals, EPC in polar materials is not adequately described by the adiabatic approximation. The difficulty arises from the existence of the polar singularity in the electron-phonon matrix elements, which results in a divergence of the FM term as $|q| \to 0$ [4]. Antonius et al. [32] have explored the effects of a dynamic correction to energy band renormalizations for several materials including diamond and zincblende BN. Using a similar method, Poncé et al. [31] have done a thorough study on the convergence issues arising from the computational adiabatic and non-adiabatic methods of calculating the ZPR in polar and non-polar materials. The same formalism used for their study is
Figure 2.1: Diagrams of the (a) Fan-Migdal and (b) Debye-Waller electron self-energies. (a) For the FM term, the straight line represents the electron Green’s function, the wavy arc is the phonon propagator, the two gray circles are the standard electron-phonon coupling matrix elements, \( g_{mn\nu}(k, q) \), and the white circle is the vertex related to the inverse Green’s function and the total potential. (b) The Debye-Waller term is comprised of similar elements, where the wavy circle represents the phonon propagator and the small lined circle is the magnitude of the DW matrix element, \( g_{mn\nu\nu'}^{DW}(k, q, q') \). The horizontal axis represents time progression.

implemented in ABINIT package [131], and is the method we have used to calculate non-adiabatic corrections to the electronic band-structure renormalization.

A full treatment of the non-adiabatic electron self-energy requires the Green’s function formalism of the Hedin-Baym equations summarized by Giustino [4]. However, it is not currently possible to perform self-consistent calculations using this method, so for practical \textit{ab initio} calculations, DFT or the GW method is used to obtain an approximate non-adiabatic correction. Figure 2.1 shows the Feynman diagrams of the FM and DW self-energies in terms of the electronic Green’s functions, phonon propagators, and electron-phonon matrix elements. The time dependence of each terms is shown on the horizontal axis, form which it is clear that the FM term is dynamic and the DW term is static. From this representation, several approximations are made to achieve a practical \textit{ab initio} method.

In order to address the FM term in Figure 2.1(a), the vertex, represented by the white circle, is approximated by a product of delta functions. The electron Green’s function is replaced with the KS Green’s functions and the full phonon propagator is replaced the adiabatic phonon propagator “dressed” with a non-adiabatic correction. The electron-phonon matrix elements are evaluated with the random phase approximation (RPA) and the DFT exchange-correlation electronic screening. Lastly, the frequency dependence of the EPC is
neglected. Similarly, the DW self-energy is modified by approximating the phonon propagator with the “dressed” adiabatic phonon propagator and replacing the total potential with the KS potential, $V^{KS}$ [4, 31]. These approximations manifest as the following self-energy expressions:

$$\Delta \varepsilon_{nn'k}(\omega) = \frac{1}{\hbar} \sum_{m\nu} \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} g_{mn\nu}^*(\mathbf{k}, \mathbf{q}) g_{m'n'\nu}(\mathbf{k}, \mathbf{q})$$

$$\times \left[ \frac{1 - f_{mk+q} + n_{q\nu}}{\omega - \varepsilon_{mk+q}/\hbar - \omega_{q\nu} + i\eta} + \frac{f_{mk+q} + n_{q\nu}}{\omega - \varepsilon_{mk+q}/\hbar + \omega_{q\nu} + i\eta} \right]$$

$$\Delta \varepsilon_{nm'k}^{\text{DW}} = \sum_{\nu} \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} g_{nm'\nu}^{\text{DW}}(\mathbf{k}, \mathbf{q}, -\mathbf{q})(2n_{q\nu} + 1)$$

Here $n_q$ is, again, the Bose-Einstein factor of equation 2.27 and

$$f_{nk} = \frac{1}{e^{(\varepsilon_{nk} - \varepsilon_F)/k_B T} + 1}$$

is the Fermi-Dirac factor derived from the Fermi-Dirac distribution. The combination of equations 2.28 and 2.29. Gives the total eigenenergy correction

$$E_{nk} = \varepsilon_{nk} + \frac{1}{\hbar} \sum_{\nu} \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} \sum_m g_{mn\nu}^*(\mathbf{k}, \mathbf{q}) g_{m'n'\nu}(\mathbf{k}, \mathbf{q})$$

$$\times \left[ \frac{1 - f_{mk+q} + n_{q\nu}}{\omega - \varepsilon_{mk+q}/\hbar - \omega_{q\nu} + i\eta} + \frac{f_{mk+q} + n_{q\nu}}{\omega - \varepsilon_{mk+q}/\hbar + \omega_{q\nu} + i\eta} \right]$$

$$+ \sum_{\nu} \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} g_{nm'\nu}^{\text{DW}}(\mathbf{k}, \mathbf{q}, -\mathbf{q})(2n_{q\nu} + 1),$$

known and the “non-adiabatic extension” of the AHC theory in equations 2.25 and 2.26 [4, 31]. The expression is temperature and frequency dependent. The ZPR is regained by setting $T = 0$, as was done at the end of section 2.3.1.

### 2.4 Computational methodology

Bellow are the details of the computational programs and parameters used in our calculations. First, we discuss our methods for determining the superconducting critical temperatures and electron-phonon coupling strengths of Na. Then, we describe the procedures used
to determine the zero-point renormalizations and temperature dependent eigenenergy shifts in the Carbon, Boron Nitride, and Silicon structures.

2.4.1 Sodium EPC calculation parameters and computation methods

In Chapter 3 we perform EPC calculations for five, stable, crystal structure phases of sodium (bcc, fcc, cI16, tI19, and cI24). Specifically, we have analyzed and compared the phonon dispersions, superconducting critical temperatures, and electron-phonon coupling parameters for each distinct structure of elemental Na.

First-principles calculations were performed within the framework of DFT using the pseudopotential-planewave approach implemented in the ABINIT package [131]. The OPIUM program [141] was employed to generate a norm-conserving pseudopotential for Na in order to have control over the core radius and adjust the parameters for pressurized phases. We used a valence electron configuration of $2s^22p^63d^{0.5}$ and a radius cutoff of 1.5 Bohr for the $s$, $p$, and $d$ orbitals in order to describe the orbital configuration on Na between pressures of 0 and 260 GPa. We used the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (GGA-PBE [77]) for the exchange-correlation functional. A planewave energy cutoff of 50 Hartree (Ha) and dense $k$-point meshes of $24 \times 24 \times 24$ were used for the fcc and bcc phases to guarantee total energy convergence of $10^{-6}$ eV, while a $12 \times 12 \times 12$ and a $8 \times 8 \times 8$ $k$-mesh were used for the cI16 and tI19 phases respectively. Our linear-response calculations of the lattice vibrations employed DFPT, [142, 143, 71] using $q$-point meshes of $8 \times 8 \times 8$ for the bcc and fcc structures while a $4 \times 4 \times 4$ mesh was used for the cI16 and tI19 phases.

For the cI24 structure slightly different parameters were used due to the extremely high pressures (15.5 TPa) needed to achieve this crystal phase [133]. OPIUM [141] was used to, once again, create a norm-conserving pseudopotential with the same valence electron configuration as described above; however, the pseudopotential needed to be harder than the one used for the lower pressure structures, so a radius cutoff of 1.002 Bohr for the $s$, $p$, and $d$ orbitals was set and a planewave energy cutoff of 62 Ha used. A $k$-point mesh of
16 × 16 × 16 was used to sample the Brillouin Zone (BZ) for the $cI24$ structure, and the phonon dispersion and EPC parameters were calculated with a $q$-point mesh of $4 \times 4 \times 4$. This structural phase also required careful relaxation of the interatomic forces to a threshold of $10^{-7}$ Ha/Bohr in order to obtain the correct phonon dispersion.

2.4.2 Temperature dependent eigenenergy renormalization calculation parameters and methods

Chapter 4 contains the results of our analysis of the EPC induced temperature dependence of electronic band structures for three Carbon (C) allotropes (diamond, graphite, and graphene), four Boron Nitride (BN) polymorphs (zincblende, layered-hexagonal, 2D-hexagonal, and wurtzite), and two Silicon (Si) allotropes (diamond Si, and buckled 2D silicene). Both adiabatic AHC theory and non-adiabatic methods were used and compared for each structure and material.

First-principles calculations were performed using the ABINIT [131] DFT pseudopotential-planewave approach and the dynamic DFPT method with Sternheimer equations[78]. The GGA-PBE [77] was adopted for the exchange-correlation functional. We have used Troullier-Martins [144] pseudopotentials, generated using the Fritz-Haber code [145], and written in the FHI format. Energy cutoffs of 30 Ha for diamond, graphene and 2D-BN, 40 Ha for graphite and hexagonal BN (h-BN), and 35 Ha for zincblende BN (z-BN) and wurtzite BN (w-BN) were necessary for convergence. Optimized lattice parameters and electronic structures were calculated for each material using $8 \times 8 \times 8$ $k$-mesh for the bulk materials and a $12 \times 12 \times 1$ $k$-mesh for 2D-BN, graphene, and silicene. For the phonon dispersions, linear response calculations were done using a $12 \times 12 \times 12$ $k$-mesh for the bulk materials and a $20 \times 20 \times 1$ $k$-mesh for the 2D structures. The coarse $q$-point grids used in the phonon dispersion calculations were $12 \times 12 \times 12$ and $6 \times 6 \times 6$ for the diamond bulk structures and hexagonal bulk structures, respectively. Likewise, $q$-point grids of $20 \times 20 \times 1$ were used for the 2D structures in order to accommodate the difficult convergence of the acoustic phonon branches. Fine $q$-point grids of $24 \times 24 \times 24$ and $40 \times 40 \times 1$ were used for the 3D and 2D
materials, respectively.

For graphene and, particularly, graphite, it was necessary to include van der Waals corrections to the exchange-correlation energy. According to Mounet and Marzari [146], DFT alone does not accurately predict the interlayer interactions dependent on van der Waals dispersion forces. These forces are known to be present in graphite, therefore, we have applied the vdw-DFT-D3(BJ) correction, with Becke-Johnson dampening, developed by Grimme [147, 148]. This correction gives a calculated interlayer distance for graphite that is significantly closer to experimental measurements as well as more accurate phonon dispersions in both graphite and graphene [149, 146]. Calculations of the lattice constants for graphite, as well as the other structures considered in this study, are given in Table 4.1.

Using AHC formalism, as well as non-adiabatic corrections implemented in ABINIT and its corresponding post-processing programs [31], the convergence of the ZPR, \( \Delta \varepsilon_{nk}^{ZP} \), was tested for each structure. Linear response calculation were performed using k-point grids of 8 × 8 × 8 for all bulk materials and 12 × 12 × 1 for all 2D structures. Sternheimer equations [78] were employed to limit the necessary number of bands needed to converge equations 2.25 and 2.31 to 18 bands for the bulk and 2D structures. We tested convergence for homogeneous q-point grids of up to 34 × 34 × 34 for diamond and zincblende BN; up to 24 × 24 × 24 for wurtzite BN, h-BN, and graphite; and up to 60 × 60 × 1 for the monolayer structures, graphene, silicene, and 2D-BN. An imaginary smearing parameter, \( i\eta = 100\text{meV} \) was implemented for each structure to speed convergence in equations 2.25 and 2.31.

In addition to the calculations using ABINIT’s [131] implementation of AHC, we performed convergence tests for Si and diamond using the procedure of Giustino et al.’s [108] 2010 work on the temperature dependent band gap renormalization in diamond. They use Allen-Heine theory [24] calculations based on the EPW (electron-phonon coupling using the maximally localized Wannier functions [150]), QUANTUM ESPRESSO [132], and WANNIER90 [29] codes [30, 151, 150]. They were able to demonstrate the expected Varshni effect [122] and band gap temperature dependence for diamond in the range of 80-800 K.
We used the same approach with slightly modified parameters to compare the convergence speeds and accuracy of this method with the ABINIT [131] framework. In this case, the convergence of the \( \mathbf{k} \)-point wavefunctions was tested with grids as large as \( 12 \times 12 \times 12 \) for Si and \( 16 \times 16 \times 16 \) for diamond. Fine \( \mathbf{q} \)-point grids as large as \( 120 \times 120 \times 120 \) were tested for both materials. The AHC calculations, via equation 2.25, were done using a summation over 300 bands for both Si and diamond. The same imaginary smearing value of \( i\eta = 100 \) meV was used. In Chapter 4, we refer to the calculation method of Giustino et al. [108] as the QE+EPW method; however, we stress that this code is not an official distribution of the EPW [151] code. It is and independently modified code based on EPW [151] and altered to include Allen-Heine theory [24].
IS SODIUM A SUPERCONDUCTOR UNDER HIGH PRESSURE?

Modified from a paper published in *The Journal of Chemical Physics*¹

Roxanne Tutchton²,³, Xiaojia Chen⁴, and Zhigang Wu²,⁵

Superconductivity has been predicted or measured for most alkali metals under high pressure, but the computed critical temperature ($T_c$) of sodium (Na) is vanishingly low. However, previous studies have only done superconductivity calculations of Na in its ambient, body-centered cubic (bcc), phase and its second pressurized transition phase, face-centered cubic (fcc), for pressures up to \( \sim 90 \) GPa [18, 20]. In this chapter we report a thorough, first-principles investigation of superconductivity in Na under pressures up to 260 GPa, where the metal-to-insulator transition occurs, and at 15.5 terapascals (TPa), where Na transitions back to a metallic phase. Linear-response calculations and density functional perturbation theory were employed to evaluate phonon dispersions and the electron-phonon coupling for bcc, fcc, $cI_{16}$, $tI_{19}$, and $cI_{24}$ Na. Of these, the $cI_{16}$, $tI_{19}$, and $cI_{24}$ phases have not been the subjects of superconductivity calculations prior to this study.

We found that the maximum electron-phonon coupling strength, \( \lambda \), is 0.5 for the $cI_{16}$ phase, corresponding to a critical temperature of $T_c \approx 1.2$ K. When pressure decreases or increases from 130 GPa, $T_c$ drops quickly. This is mainly due to the lack of $p$-$d$ hybridization in Na as pressure is increased from 0 to 260 GPa as indicated by the steady, nearly-free-electron-like, decrease in the density of states at the Fermi surface. Since current methods

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¹Text from sections 3.1 through 3.2 has been reproduced from [Roxanne Tutchton, Xiaojia Chen, and Zhigang Wu. Is sodium a superconductor under high pressure? *The Journal of Chemical Physics*, 146(1):014705, 2017.], with the permission of AIP Publishing.

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based on the Migdal-Eliashberg and McMillan formalisms tend to overestimate the $T_c$ (especially the peak values) of alkali metals, we conclude that under high pressure—before the metal-to-insulator transition at 260 GPa—superconductivity in Na is very weak, if it is measurable at all. Calculations were also done for $cI24$-Na, a stable ultra-high pressure metallic phase of Na occurring 15.5 TPa. Unlike the metal Na phases below 260 GPa, $cI24$-Na exhibits $p$-$d$ hybridization as well as higher critical temperatures between 16 and 30 TPa. However, despite a relatively high critical temperature of $T_c=12$ K, the electron-phonon coupling strength never exceeds 0.45 in this pressure range. This is do to a significant increase in average frequency accompanied by a decrease in the density of states at the fermi energy indicating that even at ultra-high pressures, metallic Na is not a good candidate for conventional superconductivity.

### 3.1 Superconductivity in alkali metals

At ambient pressure alkali metals have simple electronic band structures well described by a nearly-free-electron model. As the pressure applied on these systems increases, alkali metals evolve through a series of structural phase transitions from the highly symmetric body-centered cubic (bcc) metallic phase to insulating phases with low symmetries [152, 153, 154, 155, 156, 157]. High pressure has been observed, in many cases, to enhance superconductivity. For materials described by the nearly free-electron model, increasing pressure causes valence-core overlap and electronic orbital hybridization, which changes the behavior of the density of states at the Fermi surface such that it fluctuates with increasing pressure rather than simply decreasing. When the DOS at the Fermi level increases the electron-phonon coupling tends to become stronger and the and superconducting critical temperatures rise. Both experiments [158, 129, 126, 130, 127, 159] and first-principles calculations [16, 17, 18, 19, 20, 21, 22, 23] have found that lithium (Li), potassium (K), rubidium (Rb), and cesium (Cs) exhibit strengthened electron-phonon coupling in their high-pressure structures leading to observable, pressure-induced superconductivity.
Cs was the first alkali metal found, through experimental measurements, to have a superconducting phase near 12 GPa with a critical temperature, $T_c$, of 1.3 K [158]. Li was the first alkali metal predicted to be superconducting at ambient pressure with a $T_c \lesssim 1$ K [160]. However, experimental measurements revealed no evidence of superconductivity at temperatures above 4 mK [161]. Jarlborg [16] then considered the bcc and the hexagonal closed pack (hcp) structures of Li, and his calculations showed that at pressure $P \approx 22$ GPa, $T_c = 2.4$ K. Christensen and Novikov [17] studied the face-centered cubic (fcc) Li and cI16 Li using the rigid-muffin-tin approximation (RMTA [162]), concluding that for cI16 Li, $T_c$ could be as high as $60 - 80$ K. Their calculations gained immediate attention from experimentalists [129, 126, 130], and the measured maximum $T_c$ was found to be between $14 - 17$ K for $P \approx 30 - 35$ GPa. Later calculations [18, 19, 20, 21, 22, 23] employing more rigorous first-principles methods obtained $T_c$ values in closer agreement with experimental data.

Subsequent theoretical works investigated other alkali metals. Shi et al. [20] found that in fcc K, Rb and Cs, $T_c$ values were in the range of $5 - 14$ K, $6 - 8$ K, and $2 - 6$ K, respectively. Although no experimental evidence [158, 127, 159] for superconductivity has been found in the fcc phases of these three alkali metals their first-principles predictions for K are in good agreement with Sanna et al. [19] and Profeta et al. [21]. Therefore, further experimental efforts are required to clarify this discrepancy.

In contrast to Li, K, Rb, and Cs, previous first-principles studies [20, 18] have asserted that $T_c \lesssim 1$ K for fcc-Na. This is consistent with experimental measurements, which found no superconductivity in Na at temperatures above 4 K [127, 159]. However, previous theoretical and experimental investigations of Na have only explored its superconductivity up to the fcc structure. Na could become significantly more superconducting under yet higher pressures.

As pressure increases, Na is subjected to a series of structural phase transitions: from bcc to fcc at 65 GPa, [163] to the cI16 structure at 103 GPa [164], and to the tI19 (oP8) structure at about 125 – 132 GPa [165, 166] before entering an optically transparent hP4 structure at

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[6] The measured superconductivity in Cs is associated with the Cs-IV (tetragonal) and Cs-V (Cmca) phases [158].
Based on trends seen in other alkali metals, the critical temperature of Na could become significantly higher for the metallic \( cI_{16} \) and/or \( tI_{19} \) phases.

With the advances in structural prediction and first-principals calculations, it is also possible to study structures at ultra-high pressures where materials reenter metallic states that may have superconducting properties. A recent publication by Li et al. [133] reported the surprising reentrance of Na into a metallic icosahedron phase (body-centered cubic \( cI_{24} \)) at 15.5 TPa. Like the \( cI_{16} \) and \( tI_{19} \) phases, \( cI_{24}-Na \) may exhibit stronger electron-phonon coupling properties and superconductivity, which we explore in section 3.3. Though no experimental studies have been performed at pressures this high, diamond has been observed at 5 TPa through dynamic ramped compression [167]. Progress with this measurement method may eventually allow studies of Na and other alkali metals in ultra-high pressure metallic phases.

In this work, we studied electron-phonon coupling in five metallic phases of Na (bcc, fcc, \( cI_{16} \), \( tI_{19} \), and \( cI_{24} \)) employing the linear-response approach and first-principles calculations based on density functional perturbation theory (DFPT) [142, 143, 71]. The electronic structure, phonon spectrum, and the Eliashberg spectral function \( \alpha^2F \) were determined at pressures ranging from 0 GPa to 260 GPa and from 16 TPa to 30 TPa, in order to evaluate \( T_c \) as a function of \( P \) up to the initial metal-to-insulator transition point and at the high pressure re-metalization threshold. Chapter 2 contains the details for the theoretical formalism (section 2.2) and computational procedure (section 2.4.1) used to obtain the following results, which include phase transitions, electronic and phonon band structures, electron-phonon coupling parameters, and superconducting critical temperatures. We will first discuss our results for the low pressure structures (bcc, fcc, \( cI_{16} \), and \( tI_{19} \)) that occur before the insulator transition. Then we will recount our findings for the ultra-high pressure structure, \( cI_{24}-Na \).
3.2 Results and discussion

We first verified structural phase transitions under pressures as high as 260 GPa, where the metal-to-insulator transition occurs. Then we computed the electronic structures and lattice vibrations under increasing pressures for the four metallic phases of Na. We evaluated the electronic DOS at the the Fermi level $N(\varepsilon_F)$, the logarithmic averaged phonon frequencies $\omega_{\log}$ (Eq. 2.17), and the electron-phonon coupling constant, $\lambda$ (Eq. 2.16), based on results obtained through DFT and DFPT calculations. Finally, the critical temperatures $T_c$ were determined using the McMillan equation (Eq. 2.18) with the calculated $\lambda$ and $\omega_{\log}$ at each pressure.
3.2.1 Phase transitions

We incrementally increased the pressure on different relaxed phases of Na to study transitions between the four metallic phases (bcc, fcc, cI16 and tI19) from ambient pressure to 260 GPa. Stable phases were found by calculating the enthalpy, where the lowest enthalpy \( H = E + PV \) corresponds to the most stable structure under a certain pressure at 0 K. Figure 3.1 shows that the bcc to fcc transition occurs at 71 GPa, fcc to cI16 at 130 GPa, and cI16 to tI19 at 152 GPa, which is in excellent agreement with previous calculations [17, 152, 153, 155] and consistent with experimental measurements [164, 165, 166, 155, 157].

![Figure 3.2: Crystal structures of Na in the (a) cI16 and (b) tI19 phases. (a) The cI16 structure has cubic symmetry and contains 16 atoms per unit cell. (b) The tI19 structure is described as an incommensurate guest-host structure with 116 atoms per unit cell. This figure has been reproduced from [168], with the permission of AIP Publishing.](image)

Here we focus on investigating superconductivity in Na by considering these four metallic phases between bcc-Na and tI19-Na. Ma et al. [155] theoretically calculated a metal-to-insulator (tI19 to hP4) transition occurring at 260 GPa. They attribute this transition to and insulating phase to the emergence of strong localization of valence electrons at the interstitial sites of hP4-Na facilitated by \( p - d \) hybridization. Thus, we computed the electron-phonon coupling in metallic Na from 0 to 260 GPa. The cI16 structure [Figure 3.2(a)] is cubic, with 16 atoms in its unit cell, whereas the tI19 phase [Figure 3.2(b)] is an incommensurate
structure, consisting of host and guest atoms, which can be approximated by incorporating
a $1 \times 1 \times 5$ supercell of the guest lattice into a $1 \times 1 \times 3$ supercell of the host lattice to create
a conventional cell with 116 atoms [155, 166, 157].

3.2.2 Electronic and phonon band structures

![Figure 3.3: Electronic band structures and density of states (DOS) in units of number of
states/eV/bohr$^3$ for the (a) bcc phase at ambient pressure, (b) the fcc phase at 100 GPa,
(c) the $cI16$ phase at 140 GPa, and (d) the $tI19$ phase at 220 GPa. This figure has been
reproduced from [168], with the permission of AIP Publishing.](image)

We computed the electronic band structures and densities of state for the four metallic
phases of Na at various increasing pressures, as summarized by Figure 3.3. The band struc-
tures do not change remarkably at different pressures within each phase. When pressure
increases and Na goes through the bcc, fcc, $cI16$, and $tI19$ phases, the electron DOS at the
the Fermi level, $N(\varepsilon_F)$, decreases[Figure 3.6(a)]. We also find that the fcc and $cI16$ Na are
semimetals, in contrast to “real” metallic bcc and $tI19$ phases.

We note that the Fermi surfaces of all four metallic phases remain spherical, as shown
in Figure 3.4, unlike other alkali metals (Li, K, Rb, and Cs) whose Fermi surfaces of the
Figure 3.4: Fermi surfaces of Na in the (a) bcc, (b) fcc, (c) $cI_{16}$ and (d) $tI_{19}$ phases generated with XCrySDen (http://www.xcrysden.org/). All four structures exhibit spherical Fermi surfaces indicating free electron behavior. This figure has been reproduced from [168], with the permission of AIP Publishing.

The fcc phase already show copper-like necks and develop extended nesting [19, 169, 170]. This indicates that in bcc, fcc, $cI_{16}$, and $tI_{19}$ Na the nearly-free-electron model is still valid, and there are no signs of a $p \rightarrow d$ transition near the Fermi surface under pressures up to 260 GPa. This is consistent with electronic band structures plotted in Figure 3.3, which resemble free electron bands within the empty lattice approximation. In the $cI_{16}$ phase, the $s$-$p$ hybridization leads to an indirect gap [166, 171], as seen in Figure 3.3(c).

Figure 3.5 summarizes the calculated phonon band structures and DOS for bcc, fcc, $cI_{16}$, and $tI_{19}$ Na. Panel(a) of Figure 3.5 shows that, as pressure increases from 0 GPa to 60 GPa, phonon bandwidth rises nearly 4-fold leading to the pressure-induced stiffening of Na. But the phonon bandwidth of Na in the fcc, $cI_{16}$, or $tI_{19}$ structure does not change significantly.
Figure 3.5: Phonon band structures, density of states (DOS), and the spectral function ($\alpha^2 F$), for the four metallic phases. The phonon density of states is given in units of number of states/cm$^{-1}$/atom. Panel (a) plots the phonon band structure, DOS ($F(\omega)$) and $\alpha^2 F$ for the BCC phase at 0, 20, 40, and 60 GPa; (b) for the FCC phase at 100 GPa; (c) for the cI16 phase at 140 GPa, and (d) for the tI19 phase at 220 GPa. This figure has been reproduced from [168], with the permission of AIP Publishing.

with respect to pressure; in fact, it only increases from about 510 cm$^{-1}$ at 100 GPa in the fcc phase to 620 cm$^{-1}$ at 220 GPa in the tI19 phase.

In contrast to Li, the bcc-to-fcc phase transition in Na is not due to phonon softening but, rather, the Kohn anomalies in the phonon spectrum, which result in dynamic instability [172, 157]. These can be seen in Figure 3.5(a) along $\Gamma - H - N$. On the other hand, acoustic phonon softening along $\Gamma K$ induces the fcc-to-cI16 transition in Na, which is similar to the fcc-to-cI16 transition in Li [170]. The cI16-Na and tI19-Na structures have 9 and 29 atoms in their primitive cells respectively, therefore both of their phonon spectra are dominated by numerous optical phonon branches. The transition from cI16-Na to the open and incommensurate structure of tI19-Na is explained by the Peierls distortions [173] and the localization of interstitial electrons [174], whereas the strong $s$-$p$ electron hybridization
in Li leads to Fermi surface nesting and different phase transitions from the \textit{cI16} structure. Likewise, in the heavier alkali metals (K, Rb, and Cs), hybridization between the semi-core \textit{p} states and valence \textit{d} states contributes to the emergence of Fermi surface nesting as pressure increases \cite{175, 20}.

### 3.2.3 Superconductivity

As mentioned in the section 2.2, we adopted Migdal-Eliashberg theory to compute the electron-phonon coupling constant, $\lambda$, by integrating the electron-phonon spectral function, $\alpha^2F(\omega)$, according to equation 2.16. The spectral functions evaluated using equation 2.15...
for the bcc, fcc, cI16, and tF19 phases are plotted in Figure 3.5 in comparison with phonon DOS distribution, $F(\omega)$. In general, $\alpha^2 F(\omega)$ and $F(\omega)$ have very similar distributions except that the low-frequency peak positions in $\alpha^2 F(\omega)$ vary with pressure in a slightly different way than those in $F(\omega)$ because of the larger weights of the low-frequency terms in summation of equation 2.15.

The most important physical quantity entering the McMillan equation (Eq. 2.18) is the electron-phonon coupling constant, $\lambda$, which is plotted in Figure 3.6(b) as a function of pressure. A good superconductor normally has a $\lambda \gtrsim 1$; however, $\lambda$ peaks at only $\sim 0.5$ for $P = 130$ GPa in cI16-Na. Figure 3.6(a) shows that the electronic DOS at the Fermi level tends to decrease as pressure increases due to the lack of $sp$-$d$ hybridization under pressures up to 260 GPa. As previously discussed, $sp$-$d$ hybridization would disrupt the nearly-free-electron like behavior of Na, and $N(\varepsilon_f)$ would cease to drop as pressure increased. Figure 3.6(c) summarizes the calculated logarithmic averaged phonon frequency, $\omega_{\log}$, which is determined from the reciprocal moment of the electron-phonon spectral function $\alpha^2 F(\omega)$ [11].

We plotted the critical temperature, $T_c$, of Na for pressures in the range of $0 - 260$ GPa, as shown in Figure 3.6(d). For the bcc and fcc structures, our results are in decent agreement with Christensen and Novikov, [18] while $T_c$ of fcc-Na obtained by Shi et al. is about 1/2 to 1/3 of our value, as they used the RMTA to compute $\lambda$ instead of evaluating the electron-phonon interactions directly. $T_c$ of cI16-Na is slightly higher than that of fcc-Na near the transition pressure due to a slightly enhanced $\lambda$, while $T_c$ of tI19-Na quickly approaches zero (0.053 K at 180 GPa) because of a significantly reduced $\lambda$.

Since current methods tend to overestimate superconductivity of alkali metals, especially for the peak values of $T_c$, our present investigation suggests that Na is unlikely to be a superconductor with a measurable critical temperature between 0 and 260 GPa. This is at odds with other alkali metals including Li, K, Rb, and Cs. Among them Li has the highest $T_c$ between 14 – 17 K in the cI16 phase, [129, 126, 130] which is mainly attributed to strong
s-p hybridization [17, 18, 21, 22, 23]. In K, Rb, and Cs the compression-induced s-p and 
p-d hybridizations contribute to superconductivity [18, 20, 19, 21]. However, even at 260
GPa, the p-d hybridization in Na is nearly non-existent, as indicated by the spherical Fermi
surfaces(Figure 3.4). Although the s-p hybridization is enhanced by pressure, especially at
the cI16 phase, the average phonon frequency of Na is much higher than that of Li [20]
leading to a much smaller $\lambda$ in cI16-Na than the $\lambda$ of cI16-Li.

Furthermore, the lack of d-electron hybridization in Na leads to a decreasing $N(\varepsilon_F)$ due
to its continued free-electron-like characteristics at elevated pressures. According to the
McMillan’s original theory [110, 111],

$$\lambda = \frac{N(\varepsilon_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle},$$

(3.1)

where $M$ is the atomic mass, $\langle I^2 \rangle$ is the square of the electron-ion matrix element at the
fermi level, and $\langle \omega^2 \rangle$ is the averaged square of phonon frequency. Therefore, a reduction of
$N(\varepsilon_F)$ often lowers the value of $\lambda$. This expression is no longer used to calculate $\lambda$ directly as
the Eliashberg formalism [82, 81] provides a more accurate method; however, it is useful in
demonstrating the relationships between the electron-phonon coupling strength parameter,
$N(\varepsilon_F)$, and the phonon frequency.

Theoretical calculations place the metal-to-insulator transition in at 260 GPa (\sim 200 GPa
in experiment) where the metallic tI19-Na becomes insulating hP4-Na. There is evidence
of the $p \rightarrow d$ electron transfer in the hP4 structure, but it also has a sizable band gap,
larger than 1 eV [155, 176]. This leads us to conclude that Na is unlikely to be a measurable
superconductor between 0 GPa and 260 GPa.

3.3 Metallic sodium at ultra-high pressures

Recently it was discovered that sodium re-enters into a metallic state under an extremely
high pressure of 15.5 TPa [133], and thus we extend our research of superconductivity in Na
to this pressure range. As mentioned before, a transition from a metallic tI19 structure to
a large-gap insulator occurs at 260 GPa due to strong localization of valence electrons at
the interstices of $hP4$-Na [155]. Then at 1.75 TPa the $hP4$-Na structure undergoes another transition to the orthorhombic $oP8$ structure,\(^7\) which remains stable until the high-pressure metallization threshold is reached at 15.5 TPa. Here the transition from insulator back to metal occurs when the interstitial sites of the insulating $oP8$ phase, containing localized valence electrons, are compressed forcing the electrons into conducting channels. Figure 3.7 shows the corresponding stable metallic structure of Na, $cI24$ (space group $Im-3$), which is a bcc structure populated by Na\(_{12}\) icosahedra.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3_7.png}
\caption{The $cI24$ structure of Na at 16 TPa. The lattice constant is $a=3.12\, \text{Å}$ with atoms at $24g$ positions ($0, 0.302, 0.183$). The Na-Na distance in each icosahedron is $\sim 1.138\, \text{Å}$, and the distance between icosahedra is $\sim 1.168\, \text{Å}$. These parameters are in very good agreement with those from Li et al. [133].}
\end{figure}

At 16 TPa, the lattice constant of $cI24$-Na is 3.12 Å and the minimum distance between atoms within the icosahedra is about 1.138 Å, while the minimum distance between icosahedra is 1.168 Å, indicating strong core overlap given that the radius of ionic Na\(^+\) is 1.02 Å. Therefore, we employed the same pseudopotential parameters for Na as those used by Li et al. [133], when carrying out DFT calculations for the $cI24$-Na at 16 TPa. Using an inter-

\(^7\)This transition is driven by softening of the transverse acoustic phonon mode in $hP4$-Na [133].
atomic force threshold of $10^{-7}$ Ha/Bohr, our relaxed structures are in excellent agreement with their previous results.

Figure 3.8 plots the electronic band structures for $cI24$-Na at four pressures between 16 and 30 TPa. There is barely any significant variations among these 4 band-structures as pressure increases, and there is a slight decrease in the total DOS. In contrast to Na under pressure less than 260 GPa, the projected density of states (PDOS) indicated that the $s$-wave contribution is significantly smaller than the contributions from the $p$- and $d$-wave. In fact, above 16 TPa, the $d$-wave character dominates electronic DOS, which can be clearly seen from the Fermi surfaces plotted in Figure 3.9, where each shape represents the contribution to the Fermi surface from a particular energy band. The topologies at each pressure indicate a $p$-$d$ transition of electronic states. In Figure 3.9(a) the two visible surfaces are relatively self contained with minimal distortion, but Figure 3.9(b) shows a marked increase in nesting at 20 TPa. The next two pressures are accompanied by less drastic distortions of the surfaces as the band contributions become more distinct and the green/purple surface expands past the limits of the BZ.

In addition to the electronic structures, we also calculated the phonon dispersion curves, phonon DOS, and spectral functions $[\alpha^2 F(\omega)]$ for $cI24$-Na at 16, 20, 25, and 30 TPa, as shown in Figure 3.10(a), (b), (c), and (d), respectively. Aside from the fact that the maximum optical-band frequency increases from $\sim 4500$ cm$^{-1}$ to $\sim 6000$ cm$^{-1}$ as pressure rises from 16 to 30 TPa, the corresponding figures in the four panels in Figure 3.10 show little variation. The entire frequency range for $cI24$-Na also increases drastically compared with those of the low pressure metallic phases (Figure 3.5), which have a maximum optical frequency of about 600 cm$^{-1}$ for $tI19$-Na.

Figure 3.11 shows $N(\varepsilon_f)$, $\lambda$, $\omega_{\log}$, and $T_c$ as functions of pressure. Comparing Figure 3.11 with Figure 3.6, we note that $N(\varepsilon_f)$ in the range of 16-30 TPa is roughly an order of magnitude smaller than the values calculated around the ambient pressure; in contrast, the values for $\omega_{\log}$ are nearly an order of magnitude larger. Based on the McMillan theory of
Figure 3.8: The electronic band structure, total densities of states (in units of states/eV/bohr$^3$), and projected DOS for $cI24$-Na at (a) 16 TPa, (b) 20 TPa, (c) 25 TPa, and (d) 30 TPa. The dashed line at $\varepsilon_F$ marks the Fermi energy with respect to the bands. The projected DOS shows the $s$ (black), $p$ (red), and $d$ (blue) densities of state. Pressure was increased by shrinking the lattice constant, and each structure was optimized using an interatomic force threshold of $10^{-7}$ Ha/Bohr. Our band structure at 16 TPa is in excellent agreement with that calculated by Li et al. [133].

From equation 3.1, the decrease in $N(\varepsilon_f)$ accompanied by the increase in $\omega_{\log}$ results in weak electron-phonon coupling. We find that $\lambda = 0.46$ at 16 TPa is the calculated maximum EPC strength for $cI24$-Na, which is slightly smaller than the peak value of 0.5 for $cI16$-Na at 130 GPa.

Comparing Figure 3.11(d) with Figure 3.6(d), we find that $T_c$ for $cI24$-Na is much higher than it is for Na under pressures lower than 260 GPa. The peak critical temperature in the pressure range from 16-30 TPa occurs at 16 TPa with a value of $T_c = 12.2$ K, which is increased by an order of magnitude from $T_c = 1.2$ K for $cI16$-Na at 130 GPa. This higher critical temperature is due solely to the dramatic increase in the average phonon frequency,
Figure 3.9: The Fermi surface plots for $cI24$-Na at (a) 16 TPa, (b) 20 TPa, (c) 25 TPa, and (d) 30 TPa generated with XCrySDen (http://www.xcrysden.org/). Here the green/purple surface and the blue surface represent contributions to the total Fermi surface from particular energy bands near the Fermi energy ($\varepsilon_F$). The plots indicate $p$-$d$ orbital hybridization, with the most dramatic nesting at (b) 20 TPa.

$\omega_{\log}$, since the electron-phonon coupling strength at 16 TPa is still very weak at $\lambda = 0.46$.

The lack of increase in $\lambda$ is directly related to the decrease in the electronic DOS at the Fermi level [$N(\varepsilon_f)$], despite the evident $p$-$d$ hybridization as shown in Figure 3.9. We examine this more by plotting the ratio of the angular-momentum-decomposed $s$, $p$, and $d$ PDOS contributions, $N_i(\varepsilon_f)$, to the total DOS in Figure 3.12, which demonstrates that the $d$-electrons provide the largest contribution to the DOS. But the ratio $N_d(\varepsilon_f)/N(\varepsilon_f)$ decreases over the pressure range save only a small increase at 20 TPa, while $N_s(\varepsilon_f)/N(\varepsilon_f)$ and $N_p(\varepsilon_f)/N(\varepsilon_f)$ exhibit a slight overall decrease from 16 to 30 TPa. It is noteworthy that the behavior of $cI24$-Na, in this case, is opposite to the behavior of Na at lower pressures: in the bcc and fcc phases $N_s(\varepsilon_f)/N(\varepsilon_f)$ is the largest DOS ratio and $N_d(\varepsilon_f)/N(\varepsilon_f)$ the smallest.
Figure 3.10: Phonon dispersion curves, density of states, and the spectral function ($\alpha^2 F$) for $cI24$-Na at (a) 16 TPa, (b) 20 TPa, (c) 25 TPa, and (d) 30 TPa. The phonon DOS is given in units of number of states/cm$^{-1}$/atom and $\alpha^2 F(\omega)$ is in atomic units (a.u.).

Based on the behavior of the PDOS, the high-pressure $cI24$ phase of Na appears to have more in common with heavy alkali metals. Shi and Papaconstantopoulos [20] have shown that the $N_t(\varepsilon_f)/N(\varepsilon_f)$ ratios in the fcc phases of K, Rb, and Cs all have the same trend as those in Figure 3.12: the $s$-PDOS having the smallest contribution while the $d$-PDOS having the largest. There are, however, two significant differences: (1) $N_d(\varepsilon_f)/N(\varepsilon_f)$ increases steadily for K, Rb, and Cs and (2) the total DOS at the Fermi level also increases over the fcc phase, accompanied by reduced average phonon frequency, when pressure rises.

In the case of $cI24$-Na, the DOS only increases between 16 and 20 TPa before decreasing even more. In addition, $\omega_{\log}$ is extremely high and steadily increases over the designated pressure range, indicating structural stiffening rather than softening.
3.4 Summary

In this study we discovered that, despite similarities to other superconducting alkali metals, Na is not likely to become a superconductor in any of its high-pressure phases between 0 and 30 TPa. This was determined by calculating the superconductivity parameters $\lambda$ and $T_c$ along with phonon frequencies and the densities of state at the fermi surface. Our superconductivity calculations for the bcc and fcc phases of Na are consistent with previous theory [18, 20], and we have performed new calculations for $cI16$-Na, $tI19$-Na, and $cI24$-Na.
Figure 3.12: Ratios of the $s$, $p$, and $d$ electron DOS contributions at the Fermi level $[N(\varepsilon_f)]$, as functions of pressure in the range 16-30 TPa. The black circles are the data points for $N_s(\varepsilon_f)/N(\varepsilon_f)$, the red squares are $N_p(\varepsilon_f)/N(\varepsilon_f)$, and the blue diamonds are $N_d(\varepsilon_f)/N(\varepsilon_f)$.

In light of the discovery of superconductivity in Cs and, especially, Li at high pressures, the alkali metals have received considerable attention from both a superconductivity and structural phase transition studies. Despite the fact that Na shares many similarities with the other alkali metals, we have found that it exhibits weak superconductivity under pressures as high as 260 GPa, where the metal-to-insulator transition occurs. Theoretically, the peak critical temperature of Na from 0 to 260 GPa, is $\sim 1$ K in the $cI16$ phase, where as the maximum $T_c$ of other alkali metals under high pressure is $T_c \gtrsim 6 - 20$ K.

This departure from the majority behavior of alkali metals is due to the fact that Na is the second lightest and simplest alkali metal next to Li. Under high pressure, enhanced $s$-$p$ hybridization and the structural softening (lower average phonon frequency) in Li leads to its high $T_c$, but Na’s bcc structure stiffens when pressure is applied. On the other hand, pressure induces the $p$-$d$ hybridization for the alkali metals heavier than Na. This has been demonstrated and well documented by previous theoretical works; however, only the bcc and
fcc phases of Na were considered before. This study has revealed that there is almost no 
$s$-$p$ or $p$-$d$ hybridization in Na before the metal-to-insulator transition due to the persistent 
free-electron-like behavior evident from the spherical Fermi surfaces in the bcc, fcc, $cI16$ and 
$tI19$ phases and from the decreasing $N(\varepsilon_F)$.

Gatti et al. [156] argued that Na behaved counterintuitively under pressure because 
it favors less symmetric structures at high pressures than other alkali metals due to the 
existence of $p$-states in the core, which are eventually forced out to hybridize with the $d$-
orbitals leading to higher total energy changes and less symmetric structures than those of 
Li [153, 157]. Indeed, for metallic $cI24$-Na, at pressures above 15.5 TPa, we have discovered 
evidence of $p$-$d$ hybridization. Despite this, the structure of Na shows no softening, and the 
increasing average phonon frequencies combined with the small density of states at the Fermi 
energy results in weak electron-phonon coupling. This suggests that, even though there is 
a rise in the critical temperature of $cI24$-Na to around 12 K at a pressure of 16 TPa, the 
structure is unlikely to be a scientifically interesting superconductor.
In this chapter, we explore the impact of crystal structure and dimension on the EPC induced renormalization of electronic band structures through first-principles calculations based on the density functional perturbation theory. Our results demonstrate that the magnitude of the zero-point renormalization (ZPR), defined by the EPC induced eigenenergy shifts at $T = 0$ K, of the electronic band structure is dependent on both crystal structure and material composition. Analysis of the EPC induced renormalization was done for two silicon (Si) allotropes, three carbon (C) allotropes, and four boron nitride (BN) polymorphs. This is the first time that the EPC induced eigenenergy renormalizations of isoelectronic structures have been directly compared. It is also the first comparison of eigenenergy renormalizations in 3D and 2D structures. Phonon dispersions of each material were computed, and our analysis indicates that bulk materials with optical phonons at higher maximum frequencies, such as graphite and hexagonal BN, have larger ZPR magnitudes, which was not previously known. Two-dimensional materials do not follow this trend. Depending on the structure and material, renormalizations can be comparable to the GW many-body corrections to Kohn-Sham eigenenergies and, thus, needs to be considered in electronic structure calculations. The temperature dependence of the renormalizations is also considered, and in all materials, the eigenenergy renormalization at the band gap and around the Fermi level increases with increasing temperature, as expected.

4.1 A review of electron-phonon renormalization calculations

The effects of electron-phonon coupling on the electronic structure of materials has been a complex and vital area of study since its discovery over sixty years ago. In current first-principles electronic structure calculations, the electron-electron interaction responsible for
the quasiparticle (QP) excitation can be quantitatively described by the $GW$ approximation [7, 97, 98], and the $GW$ band gaps ($E_g$) agree with experimental data for many semiconductors to within a few tenths of an eV. However, the electron-phonon interaction involved in the QP excitation has been largely ignored. This is because the QP eigenenergy shifts ($\Delta \varepsilon_{nk}$) due to lattice vibrations in common semiconductors are generally less than 100 meV, which is well within the margin of error for the current $GW$ approximation methods.

The $GW$ approximations are usually performed in addition to density functional theory (DFT [69, 70]) calculations within the local density approximation (LDA) or the generalized gradient approximation (GGA) in order to provide many-body corrections to the KS eigenenergies and band gaps. In certain materials $\Delta \varepsilon_{nk}$ and the resulting band gap renormalization, $\Delta E_g$, are comparable to the corresponding many-body corrections, such that the electron-phonon renormalization is significant to electronic-structure calculations. For example, the lattice vibrations at 0 K, or zero-point renormalization (ZPR), of the direct band gap of diamond is $\sim 0.4$ eV, [31] which, compared to the $GW$ correction of 2.04 eV, is non-negligible. Furthermore, EPC could depend on the crystal structures of allotropes and polymorphs: for instance, nanoscale materials [177] or structures under high pressures may have enhanced EPC (as with well-known, high pressure induced superconductivity) despite the fact that the $\Delta E_g$ in these materials is negligible for their bulk counterparts under ambient conditions.

Early calculations performed by Allen and Cardona [25, 26] using rigid-ion pseudopotentials approximations and empirical phonon models (Weber’s bond-charge model), demonstrated that both Fan Migdal (Eq. 2.20) and Debye Waller (Eq. 2.21) self energy contributions are significant in determining the band gap renormalization in Si and germanium (Ge). Rigorous first-principles calculations [30, 27, 108, 178, 179, 180, 181, 182, 31] of $\Delta \varepsilon_{nk}$ based on density functional perturbation theory (DFPT [71, 183]) emerged in the late 2000s. Giustino et al. [30, 108] implemented Allen-Heine theory [24] calculations based on the EPW[150]), QUANTUM ESPRESSO[132], and WANNIER90[29] codes [30, 151], while
Poncé et al. [181, 182, 31] used the Allen-Heine-Cardona (AHC) formalism in the ABINIT package, [131], which uses the Sternheimer[78] method that allows the summation in equations 2.20 and 2.21 to be limited to occupied bands. This drastically decreases the burden of computational convergence. Another implementation [27, 179, 180] was incorporated into the Yambo code [184]. Like Giustino’s[108] method (which we will call the QE+EWP method for convenience), the Yambo implementation uses QUANTUM ESPRESSO [132] as its base DFT package. Poncé et al. [181] have compared the ZPR’s of eigenenergies in diamond obtained from ABINIT and QE+Yambo and found that the discrepancy between the two codes was less than 4 meV.

Other first-principles approaches to evaluate $\Delta \varepsilon_{nk}$ include the frozen phonon (FP) method, which has been used to examine the accuracy of the harmonic adiabatic approximation [32, 182] as well as to evaluate the significance of many-body effects on EPC [9]. As mentioned previously, in section 1.1, the FP approach suffers from the necessity of untenably large supercells for long-wavelength phonon modes; however, the intuitive aspect of the method makes it attractive for calculations using smaller $q$-point grids. The perturbative $G_0W_0$ approximation is another method used to improve the accuracy of $\Delta \varepsilon_{nk}$ calculations. It has been used in concert with the FP approach to compare the renormalization results from perturbative DFT [9] as well as incorporate GW corrections into the EPC calculations for nano structures, such as fullerene $C_{60}$ [102]. In their comparison of FP, DFT, and GW calculations of the ZPR of diamond, Antonius et. al. [9], found that the perturbative $G_0W_0$ corrections resulted in a roughly 200 meV increase in the magnitude of $\Delta E_g$ at the $\Gamma$-point, indicating that GW corrections are a significant factor in accurate ZPR calculations. As the goal of this study is to compare and analyze EPC induced renormalizations for a large number of structures, we have not included GW corrections do to time and computational constraints.

Non-adiabatic corrections are also a key factor in $\Delta \varepsilon_{nk}$ and $\Delta E_g$ calculations as discussed in section 2.3.2. Comparisons of adiabatic and non-adiabatic effects on $\Delta E_g$ calculations
have been performed by Antonius et. al. [32] and Poncé et al. [31]. These studies focus on semiconductors and the semiconducting band gap. The results suggest that certain materials, such as polar materials, metals, and semimetals, are not well described by the adiabatic approximation and, thus, require a non-adiabatic correction. Poncé et al. [31], in particular, have performed extensive convergence studies on the adiabatic and non-adiabatic methods for various semiconductors and insulators. They also used fitting techniques to predict the convergence of the ZPR as the broadening parameter, \( i\eta \), approaches zero, which yielded larger renormalizations for polar materials than were perviously calculated by Antonius et. al. [32].

Here we study the effects of crystal structure and dimensionality on EPC from first-principles. Using isoelectronic (structures having the same number of valence electrons) C and Si allotropes and BN polymorphs as prototypical examples, we show that the zero-point renormalization of the electronic eigenenergies around the Fermi energy can be reduced or enhanced when the crystal structure or dimension is modified. A total of nine structures were examined: diamond Si, quasi-2D buckled silicene, diamond, graphite, graphene, zincblende BN (z-BN), wurtzite BN (w-BN), layered hexagonal BN (h-BN), and 2D hexagonal BN (2D-BN). We have included the semimetals in our work to maintain the continuity of our comparison of isoelectronic structures. For graphene and silicene, the typical focus is the Dirac point, however, we will primarily be concerned with the behavior of the gap at \( \Gamma \) in our comparisons of 2D and 3D structures. In addition to the ZPR, we examined the temperature dependence of \( \Delta\epsilon_{nk} \) and \( \Delta E_g \) and the relationship between the ZPR and phonon dispersion. Our results suggest that it becomes necessary to examine the phonon spectrum and renormalization of electronic band structures when new bulk crystal structures or new nanostructures are proposed with computational materials design.

In the next section (sec. 4.2) we will briefly summarize the electronic structure calculation results from our initial DFT calculations. Then we compare two programs for calculating \( \Delta E_g \) in Si and diamond (sec. 4.3.1). We find that the ABINIT [131] implementation not
only predicts $\Delta E_g$ more accurately than does the QE+EPW method\cite{108}, but also converges more quickly for diamond, thus we used the ABINIT package to carry out the remaining calculations of $\Delta \varepsilon_{nk}$ and $\Delta E_g$ in each structure. Section 4.3.2 contains the results of the convergence tests for the ZPR of each structure. In section 4.4, adiabatic and non-adiabatic ZPR calculations are compared and analyzed with respect to the phonon spectra results. The results of the temperature dependent renormalization calculations in both the adiabatic and non-adiabatic formulation are analyzed in section 4.5.

### 4.2 Electronic structures

Relaxed lattice constants and electronic band structures were calculated for the structures described above. The methodology and computational parameters are discussed in section 2.4.2. In Table 4.1 the lattice constants are listed with comparisons to previous theoretical results and experimental data, and our calculations are in good agreement. The interlayer distances for the 2D structures were optimized and found to be 2.0 nm for silicene, 1.8 nm for graphene, and 1.7 nm for 2D-BN, and the buckled separation, $\Delta_0$, for silicene was predicted to be 0.443 Å. As mentioned in section 2.4.2, van der Waals corrections to the exchange-correlation energy (vdw-DFT-D3(BJ) \cite{147, 148}) were considered for graphite and graphene. The calculated out of plane lattice constants with this correction are very close to the experimental values \cite{149, 185}; without the van der Waals correction, $c/a = 3.45$ for graphite, which is consistent with previous DFT calculations\cite{146}. Our EPC computations were done using the theoretical equilibrium structures calculated in Table 4.1. Changes in $\Delta \varepsilon_{nk}$ due to small variations in lattice constants compared with measured parameters are expected to be negligible (less than a few percent).

For this study we have considered isoelectronic structures with different elemental compositions. For example, Si, diamond, and z-BN all have diamond crystal structures; silicene, graphene, and 2D-BN all have planar hexagonal structures; and graphite and h-BN both have layered hexagonal structures.
Table 4.1: Lattice constants (in Å), calculated using GGA-PBE[77] pseudopotentials. Current values are compared to previous theoretical results and experimental data. In the case of silicene, $\Delta_0$ is the relaxed buckled separation. The interlayer distances for the 2D structures are 20Å, 18Å, and 17Å for silicene, graphene, and 2D-BN respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Present Calculation</th>
<th>Previous theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>5.465</td>
<td>5.475[186]</td>
<td>5.430[186]</td>
</tr>
<tr>
<td>Silicene</td>
<td>3.870</td>
<td>3.830[187]</td>
<td>3.850[188]</td>
</tr>
<tr>
<td></td>
<td>$\Delta_0=0.443$</td>
<td>$\Delta_0=0.440[187]$</td>
<td>$\Delta_0=0.47[189, 190]$</td>
</tr>
<tr>
<td>Graphite</td>
<td>$a = 2.458$</td>
<td>$a = 2.460[149]$</td>
<td>$a = 2.462[185]$</td>
</tr>
<tr>
<td></td>
<td>$c/a = 2.725$</td>
<td>$c/a = 2.740[149]$</td>
<td>$c/a = 2.725[185]$</td>
</tr>
<tr>
<td>Graphene</td>
<td>$a = 2.458$</td>
<td>$a = 2.460[146]$</td>
<td>$a = 2.462[185]$</td>
</tr>
<tr>
<td>zincblende BN</td>
<td>3.620</td>
<td>3.621[191]</td>
<td>3.615[192]</td>
</tr>
<tr>
<td>Wurtzite BN</td>
<td>$a = 2.572$</td>
<td>$a = 2.542[193]$</td>
<td>$a = 2.550[194]$</td>
</tr>
<tr>
<td></td>
<td>$c/a = 1.652$</td>
<td>$c/a = 1.630[193]$</td>
<td>$c/a = 1.630[194]$</td>
</tr>
<tr>
<td>Hexagonal BN</td>
<td>$a = 2.508$</td>
<td>$a = 2.511[193]$</td>
<td>$a = 2.504[194]$</td>
</tr>
<tr>
<td></td>
<td>$c/a = 2.674$</td>
<td>$c/a = 2.660[193]$</td>
<td>$c/a = 2.660[194]$</td>
</tr>
<tr>
<td>2D-BN</td>
<td>$a = 2.508$</td>
<td>$a = 2.511[193]$</td>
<td>$a = 2.504[194]$</td>
</tr>
</tbody>
</table>

Despite their similar symmetries, these materials have notable differences in their electronic characteristics. Si, diamond, z-BN, w-BN, h-BN, and 2D-BN are standard (in the case of Si) or wide-gap semiconductors. On the other hand, graphite, graphene, and silicene are semi-metals, so we anticipate that the EPC characteristics in these materials may differ notably. We have included calculations of silicene, graphene, and graphite for continuity in our isoelectronic comparisons as well as to compare 3D and 2D structures of similar crystal symmetries. Given that these materials are not semiconductors, we will focus our calculations on the gap in the bandstructure at the $\Gamma$-point. While we have also considered the Dirac points at $K$ in both silicene and graphene, they are not significant to our comparisons in later sections. Table 4.2 summarizes the direct and indirect band gaps for the semiconducting materials. Our results are in good agreement with those of previous DFT calculations, which are known to underestimate the band gap as compared to experiment data.
Table 4.2: The electronic band gaps, in units of electron volts, of each of the semiconducting materials: Si, diamond, z-BN, w-BN, h-BN, and 2D-BN.

<table>
<thead>
<tr>
<th>Material</th>
<th>Direct Gap (eV)</th>
<th>Indirect Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gap</td>
<td>Present</td>
</tr>
<tr>
<td>Si</td>
<td>Γ − Γ</td>
<td>2.568</td>
</tr>
<tr>
<td>Diamond</td>
<td>Γ − Γ</td>
<td>5.583</td>
</tr>
<tr>
<td>w-BN</td>
<td>Γ − Γ</td>
<td>8.150</td>
</tr>
<tr>
<td>h-BN</td>
<td>Γ − Γ</td>
<td>6.560</td>
</tr>
<tr>
<td>2D-BN</td>
<td>Γ − Γ</td>
<td>6.340</td>
</tr>
<tr>
<td></td>
<td>K-K</td>
<td>4.640</td>
</tr>
</tbody>
</table>
The band structures and densities of state for each material are given in Figure 4.1, Figure 4.2, and Figure 4.3. Si and silicene are shown in Figure 4.1. In addition to being the most widely used semiconducting material, Si is also one of the few materials for which there have been experimental measurements done of the ZPR at the indirect band gap, making it a useful structure for comparison in this and similar studies [117]. Silicene is reminiscent of graphene with its similar Dirac point at $K$ as well as its hexagonal symmetry, and it is thought to share many of graphene’s electronic properties [189, 190]. However, silicene differs from graphene, as well as 2D-BN, in that it is not flat. Due to $sp^2-sp^3$ hybridization, free standing silicene has a buckled honeycomb structure, making it a quasi-2D structure [190]. Furthermore, free standing silicene is not likely to be able to exist naturally. It is typically deposited on a metallic substrate, which changes its lattice parameters slightly for experimental studies [189].

![Figure 4.1: The electronic band structures and densities of state for Si (a) and silicene (b). The DOS is given in units of states/eV/bohr$^3$. Zero energy is set at the valence band maximum and $\varepsilon_F$ indicates the Fermi energy.](image)

The electronic dispersions of the carbon allotropes are shown in Figure 4.2. Of these structures, only diamond is a semiconductor with a wide indirect band gap calculated to be 4.233 eV (Table 4.2). Graphite and graphene are considered semimetals as they have a zero band gap, but do not share the electronic properties of true metals. Graphite, for instance, has strong in-plane bonds but weak, van der Waals dominated, interactions between each
layer [146]. In its single layer allotrope, graphite is known as graphene, which is the most famous and broadly studied of the 2D structures. Its zero band gap associated with the relativistic Dirac fermions at the $K$ point in the BZ, make it unfeasible for optoelectronic applications in its unaltered form [200]. Graphene is, however, prevalent in a wide range of EPC based studies including superconductivity [13, 14, 15], non-adiabatic vibrational frequencies [73, 74], and GW corrections to electron-phonon matrix elements [99].

![Graphene Band Structure](image)

Figure 4.2: The electronic band structures and densities of state for diamond (a), graphite (b), and graphene (c). The DOS is given in units of states/eV/bohr$^3$. Zero energy is set at the valence band maximum and $\varepsilon_F$ indicates the Fermi energy.

Figure 4.3 shows our calculations of the electronic band structures and DOS for the four BN polymorphs. Boron nitride can exist in various crystal configurations, but its default form is the layered hexagonal structure, h-BN, which consists of layers of flat sheets governed by $sp^2$ bonds between boron and nitrogen atoms. Large out-of-plane distances separate each
layer resulting in a lower density structure. Conversely, zincblende BN, also known as cubic BN, is second only to diamond in hardness. It is constructed from $sp^3$ bonds, which make is denser and harder than h-BN. In addition, z-BN is chemically inert, has a high thermal conductivity and a low dielectric constant, as well as a wide band gap [201]. Like z-BN, w-BN has $sp^3$ bonds and a higher density structure than h-BN. 2D-BN is the single layer polymorph of h-BN and has the same honeycomb structure seen in graphene, though, unlike graphene, 2D-BN is a wide gap semiconductor [193]. BN crystals do not occur naturally, however, h-BN has been synthesized and transformed, through pressure, into its denser polymorphs (z-BN and w-BN) [202, 203], as well as isolated to extract single layers, forming 2D-BN [199].

![Figure 4.3](image.png)

Figure 4.3: The electronic band structures and densities of state for z-BN (a), w-BN (b), h-BN (c), and 2D-BN (d). The DOS is given in units of states/eV/bohr$^3$. Zero energy is set at the valence band maximum and $\varepsilon_F$ indicates the Fermi energy.
4.3 Convergence of the zero point renormalization

We performed calculations to test the convergence of the eigenenergy renormalizations for each of the structures discussed above. This section describes the results of our tests to converge the total zero point renormalizations of the energy bands nearest the Fermi level or at the band gap. We define this quantity as

\[ \Delta E_{\text{ZP}} = \Delta \varepsilon_{\text{ZP}}^{\text{VB}} + \Delta \varepsilon_{\text{ZP}}^{\text{CB}}, \]

(4.1)

where \( \Delta \varepsilon_{\text{ZP}}^{\text{VB}} \) is the ZPR of the valence band (VB), and \( \Delta \varepsilon_{\text{ZP}}^{\text{CB}} \) is the ZPR of the conduction band (CB). For the considered semiconductors with non-zero \( E_g \), we calculated the total ZPR at the band gap, \( \Delta E_{\text{ZP}}^{g} \). For the semimetals with \( E_g = 0 \), we calculated the total ZPR around the Fermi energy, \( \Delta \varepsilon_{\text{ZP}}^{\text{VB}} + \Delta \varepsilon_{\text{ZP}}^{\text{CB}} \), which we will call \( \Delta E_{\text{ZP}}^{g} \) for convenience despite the fact that there is not a true band gap in the case of the semimetals. Details of the computational methods and parameters are given in section 2.4.2.

Our initial investigations into calculation methods for ZPR and temperature-dependent eigenenergy renormalization include a comparison of two methods: the QE based Allen-Heine theory method used by Giustino et al. [108], which we call QE+EPW for convenience, and the ABINIT [131] implementation of AHC-theory as used by Poncé et al. [181, 182, 31]. Our QE+EPW calculations were in good agreement with Giustino et al.’s [108] results. However, we found that while the QE+EPW method can well reproduce the temperature-dependent trend for \( \Delta E_{g} \) in Si and diamond, it yields \( \Delta E_{g}^{ZP} \) magnitudes that are \( \sim 0.2 \) eV larger than other DFT-based results. After we performed these QE+EPW calculations, a thorough comparison of calculation methods was done [181], which discovered a misuse of symmetries of the DW term in an early version of the QE+Yambo protocol, and a similar version of QE was used in our QE+EPW calculations. We strongly suspect the same issue was present in our method as the resulting \( \Delta E_{g}^{ZP} \) values from the QE+EPW code and the early version of QE+Yambo were both \( \sim 0.6 \) eV for diamond.
Because the QE+EPW method is not accurate enough, we employ the ABINIT method in the subsequent calculations. Convergence tests were performed for each structure using an imaginary smearing of $i\eta = 100$ meV in the denominators of equations 2.25 and 2.31 to speed convergence and mitigate computational demand. The details of our comparison of the QE+EPW and ABINIT method as well as our ABINIT convergence tests are included below.

### 4.3.1 Comparison of ABINIT and QE methods

Here we compare the convergence of $\Delta E_{g}^{ZP}$ of Si and diamond for the ABINIT [131] method and the QE+EPW method [108] in the adiabatic approximation. By calculating $\Delta E_{g}^{ZP}$ at the $\Gamma$-point with increasingly large $q$-point grids, we are able to determine the rate of convergence for each method with respect to the number of $q$-points, $N_q$. Figure 4.4 shows the convergence tests for Si and diamond using ABINIT and QE+EPW calculations. These two materials were chosen for our initial tests due to their frequent use in previous literature on EPC induced eigenenergy renormalization. The wealth of data for these materials makes it possible to compare our results to other DFT based calculations as well as experimental measurements.

The QE+EPW method has the advantage of efficient parallelization; however, the convergence with respect to the $q$-mesh appears to be slower than ABINIT’s, particularly for diamond, thus it can be extremely demanding, computationally, with respect to the necessary number of $q$-wavevectors. We also find that QE+EPW overestimates the magnitude of $\Delta E_{g}^{ZP}$. In their 2010 work, Giustino et al.[108] calculated the total ZPR of the direct gap of diamond to be 615 meV using a $q$-mesh of $10 \times 10 \times 10$, or $N_q=47$. Increasing $N_q$ to 897 we found $\Delta E_{g}^{ZP} = -529$ meV (this value is not yet converged, but the $q$-mesh could not be increased due to computational limits), which is still significantly larger in magnitude than the experimental value [117] of $-450$ meV and the previous DFPT result [181] of $-409$ meV (Table 4.4).
Figure 4.4: The ZPR convergence tests for (a) Si and (b) diamond, using the ABINIT and QE+EPW methods. The black squares represent the ZPR values calculated using ABINIT post-processing methods, and the red circles are the ZPR values obtained from the unofficial QE+EPW code [108]. Renormalization values are given as a function of the number of q-points in increasingly large homogeneous q-point grids. The experimental data and previous theoretical results for $\Delta E_{g}^{ZP}$ are listed in Table 4.4.

On the other hand, the ABINIT implementation, in general, predicts $\Delta E_{g}^{ZP}$ in closer agreement with previous theory. This is evident from Figure 4.4, where $\Delta E_{g}^{ZP}$ for diamond is $\sim -408$ meV. For Si, we calculate $\Delta E_{g}^{ZP} \sim -42$ meV and $\Delta E_{g}^{ZP} \sim -63$ meV using ABINIT and QE+EPW, respectively. We do not know of any experimental data for the ZPR of the direct gap of Si to compare with, but the previous, adiabatic, DFPT result is $\sim -47$ meV [181]. ABINIT predicts the ZPR for the fundamental gap of Si to be $-63$ meV, which is in excellent agreement with experimental value of $-62$ meV [117] (Table 4.4). Therefore, in the remaining investigation of C and Si allotropes and BN polymorphs, we employed the ABINIT package to perform the DFPT calculations of lattice vibrations and to carry out the post-processing calculations of EPC induced renormalizations.

4.3.2 ABINIT ZPR convergence tests for 3D and 2D structures

Figure 4.5 summarizes our ZPR convergence tests for each Si and C allotrope and BN polymorph using the ABINIT [131] implementation. We have calculated the total ZPR of the semiconductor band gap for Si, diamond, z-BN, w-BN, h-BN, and 2D-BN. In the cases of graphite, graphene, and silicene, where $E_g = 0$, we calculate the total ZPR around the
Fermi energy. All ZPR calculations for the convergence tests were done at the Γ-point using the non-adiabatic corrections to AHC theory.

Figure 4.5: The ZPR convergence tests for (a) the 3D structures (Si, diamond, graphite, z-BN, w-BN, and h-BN) and (b) 2D structures (silicene, graphene, and 2D-BN). Renormalization values of are given as a function of the number of q-points in increasingly large homogeneous q-point grids of up to 34 × 34 × 34 for the diamond-like structure, 24 × 24 × 24 for w-BN and h-BN, and 60 × 60 × 1 for the 2D structures.

Figure 4.5 suggests that 3D structures require at least 500 irreducible q-wavevectors to reach satisfactory convergence. The 2D structures, on the other hand, start to converge with around 300 q-wavevectors. For each material, we have calculated $\Delta E_{ZP}^E$ values converged to within 3-5 meV, and the final results are listed in Table 4.3 along with the VB and CB eigenenergy shift components. These convergence results are consistent with those of similar materials [181]. Both adiabatic and non-adiabatic calculations were done for each structure, but because the adiabatic approximation is not valid for the polar BN materials [31], the data in Figure 4.5 were obtained using the non-adiabatic formulation, as it is valid for all of the materials considered.

The convergence of EPC eigenenergy renormalizations is notoriously difficult. Due to our use of the smoothing parameter $i\eta = 100$meV, the convergence calculations shown in Figure 4.5 are relatively quick, but they still require extremely dense homogeneous q-point grids. However, the computation of each energy band shift relies on the outcomes of consecutive first-principles calculations: the structural relaxation, linear response calcula-
tions, computation of the phonon eigenmodes and frequencies, the EPC and electron-phonon matrix-elements, and finally the calculation of the FM and DW self-energies. There are numerous possible methods to perform each of these steps as well as small numerical errors from associated approximations that become amplified in later calculations. The calculation protocol, pseudopotentials, and approximations all factor into the variations in results for the total ZPR of a given structure.

In 2014, Ponc´e et al. [181] conducted a study to compare several methods, pseudopotentials, and convergence techniques used to calculate the direct gap ZPR of diamond. They showed that the resulting ZPR is sensitive to each aspect of the calculation. Different formalisms or methods, such as FP and DFPT, can yield different ZPR values across the band structure. Likewise, the use of different pseudopotentials and exchange-correlation functional approximations produced variations as large as 50 meV in the total ZPR, as can the size of the \( q \)-point sampling. For our calculations, we use homogeneous \( q \)-meshes, which, combined with the imaginary broadening parameter, \( i\eta \), result in quicker convergence and smaller variations in ZPR values than random \( q \)-wavevector sampling [181]. Large random \( q \)-meshes can also be used, to aid in extrapolation. This is often done using Wannier functions to reduce the computational burden [30]. In 2015, Ponc´e et al. [31] performed ZPR convergence tests in the adiabatic and non-adiabatic formulations of AHC theory using interpolation methods to test the convergence behavior as the \( q \)-mesh goes to infinity and the \( i\eta \) goes to zero. Due to this difference in technique, their results for certain materials (z-BN in particular) are vastly different from other DFT results (Table 4.4).

Our converged values for \( \Delta E_{g}^{ZP} \) are within the acceptable range of variation (50 meV), based on differences in pseudopotential and \( q \)-mesh size. The results for the calculations are recorded in Table 4.3 and Table 4.4.

4.4 Electron-phonon eigenenergy renormalizations

Having tested the convergence of \( \Delta E_{g}^{ZP} \) for each of the considered structures, we will discuss the effects of the zero-point renormalization on the electronic band structures. In
Table 4.3: The calculated zero-point renormalization (in meV) of the CB, VB, and $\Delta E_{g}^{ZP}$ at the Γ-point.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\Delta \varepsilon_{VB}$</th>
<th>$\Delta \varepsilon_{CB}$</th>
<th>$\Delta E_{g}^{ZP}$</th>
<th>$\Delta \varepsilon_{VB}$</th>
<th>$\Delta \varepsilon_{CB}$</th>
<th>$\Delta E_{g}^{ZP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>34.92</td>
<td>-8.019</td>
<td>-42.94</td>
<td>33.57</td>
<td>-8.603</td>
<td>-42.18</td>
</tr>
<tr>
<td>Silicene</td>
<td>52.28</td>
<td>-16.59</td>
<td>-68.87</td>
<td>51.30</td>
<td>-16.57</td>
<td>-67.87</td>
</tr>
<tr>
<td>Diamond</td>
<td>144.9</td>
<td>-263.3</td>
<td>-408.3</td>
<td>133.2</td>
<td>-274.1</td>
<td>-407.3</td>
</tr>
<tr>
<td>Graphite</td>
<td>693.7</td>
<td>56.05</td>
<td>-637.7</td>
<td>682.1</td>
<td>58.25</td>
<td>-623.9</td>
</tr>
<tr>
<td>Graphene</td>
<td>259.6</td>
<td>0.1830</td>
<td>-259.4</td>
<td>215.1</td>
<td>4.399</td>
<td>-210.7</td>
</tr>
<tr>
<td>z-BN</td>
<td>146.7</td>
<td>-174.8</td>
<td>-321.5</td>
<td>132.7</td>
<td>-182.3</td>
<td>-314.9</td>
</tr>
<tr>
<td>w-BN</td>
<td>120.0</td>
<td>-137.5</td>
<td>-257.5</td>
<td>113.9</td>
<td>-133.3</td>
<td>-247.2</td>
</tr>
<tr>
<td>h-BN</td>
<td>285.3</td>
<td>-160.2</td>
<td>-445.5</td>
<td>253.4</td>
<td>-154.7</td>
<td>-408.1</td>
</tr>
<tr>
<td>2D-BN</td>
<td>306.5</td>
<td>-203.7</td>
<td>-510.2</td>
<td>304.2</td>
<td>-164.9</td>
<td>-469.1</td>
</tr>
</tbody>
</table>

addition we will compare the two Si allotropes, three C allotropes, and four BN polymorphs to demonstrate the effects of bulk crystal structure and dimensionality on EPC induced renormalizations calculated in the adiabatic and non-adiabatic formulations of AHC theory. Our final values for $\Delta E_{g}^{ZP}$ at the direct and indirect semiconductor gaps as well as the Dirac-points of graphene and silicene are enumerated in Table 4.4. Corrected electronic band structures were calculated along with phonon dispersions in order to show that the relative magnitude of the phonon frequencies is related to the size of the ZPR at the electronic band gap.

4.4.1 Zero-point corrections of the electronic energy bands using the adiabatic and non-adiabatic calculations

We begin our discussion with Si, the most common and widely used semiconductor, which has a diamond cubic crystal structure. Our adiabatic calculations show the $\Delta \varepsilon_{nk}$ for the conduction band (CB) edge and valence band (VB) edge at the Γ-point are −8.0 meV and 34.9 meV, respectively, leading to a direct $\Delta E_{g}$ of −42.9 meV. We also note that $\Delta \varepsilon_{CB}$ is negative, while $\Delta \varepsilon_{VB}$ is positive, so that both $\Delta \varepsilon_{CB}$ and $\Delta \varepsilon_{VB}$ reduce the band gap. The non-adiabatic calculation gives $\Delta \varepsilon_{CB} = -8.6$ and $\Delta \varepsilon_{VB} = 33.6$ for a total renormalization of −42.2 meV, as summarized in Table 4.3. The difference between the adiabatic and non-
adiabatic renormalization values is only 0.8 meV, or less than a thousandth of an eV. This suggests that the adiabatic approximation is appropriate for Si.

Table 4.4 shows the calculated $\Delta E_{ZP}^{g}$ of Si for both its direct and indirect band gaps in the adiabatic and non-adiabatic formalisms. As mentioned before, the current adiabatic result of $\Delta E_{ZP}^{g} = -63.6$ meV for the fundamental (indirect) band gap agrees well with experimental data [117] and previous predictions [31]. The value of the non-adiabatic renormalization at the fundamental gap is slightly smaller at $-54.6$ meV, but this is within the normal variation limits for this type of calculation. While there is no experimental data for the direct gap renormalization of Si, the calculated adiabatic value, $\Delta E_{ZP}^{g} = -42.9$ meV, is consistent with the value of $-47.1$ meV obtained by Ponc`e et al. [31]. The non-adiabatic value of $\Delta E_{ZP}^{g} = -42.2$ meV is even closer to Ponc`e et al.’s of 42.1 meV.

The Si electronic band structure with non-adiabatic zero-point eigenenergy corrections is plotted in Figure 4.6. The red lines indicate $\Delta \varepsilon_{ZP}^{CB}$ for the conduction bands and the blue lines are the valence band renormalizations. The energy band shifts in Si are so minimal, they can hardly be seen without a close up view of the band gap. As such the band gap renormalization of Si at $T = 0$ is generally considered negligible as it is less than a tenth of an eV.

For silicene, we have calculated the renormalization of the bands around the Fermi energy, $\Delta E_{ZP}^{g}$. At the $\Gamma$-point we found $\Delta \varepsilon_{CB} = -16.6$ meV and $\Delta \varepsilon_{VB} = 52.3$ meV in the adiabatic formulations and $\Delta \varepsilon_{CB} = -16.6$ meV and $\Delta \varepsilon_{VB} = 51.3$ meV in the non-adiabatic formulation. Again the difference in the total renormalization between the two formulations is minuscule at 1 meV (Table 4.3), which indicates that the adiabatic approximation is sufficient to describe electron phonon renormalizations in silicene. Table 4.4 summerizes the renormalization results at the Dirac-point. Here the cancellation of shifts in the CB and VB gives $\Delta E_{ZP}^{g} = 0$. This is apparent in Figure 4.6, where a very slight shift in the VB can be seen at $\Gamma$ and there is no visible shift at $K$. 

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Table 4.4: The calculated total ZPR (in meV) for energy bands around the Fermi energy of all nine materials studied in comparison with previous theoretical results and experimental data. The direct and indirect band gaps are given where appropriate as are the Dirac-points of silicene and graphene.

| Materials | Adiabatic | | Non-adiabatic | | |
| --- | --- | | --- | --- | --- |
| | Present | Other DFT | Present | Other DFT | exp. |
| Si | Γ - Γ | -42.94 | -47.1 [31] | -42.18 | -42.1 [31] | - |
|  | Γ - 0.848X | -63.59 | -64.3 [31] | -54.55 | -56.2 [31] | -62 [117] |
| Silicene | Γ - Γ | -68.87 | | -67.87 | | - |
|  | K - K | 0.000 | | 0.000 | | - |
| Diamond | Γ - Γ | -408.3 | -409[181] | -407.3 | 415.8 [31] | -450 [123] |
|  | Γ - 0.727X | -331.9 | -379.3 [31] | -329.3 | -329.8 [31] | -364 [117] |
| Graphite | Γ - Γ | -637.7 | -439 [31] | -623.9 | | - |
|  | K - K | 0.027 | -436 [32] | -0.019 | | - |
| Graphene | Γ - Γ | -259.4 | | -210.7 | | - |
|  | K - K | 0.021 | | 0.020 | | - |
|  | Γ - X | -246.3 | | -221.9 | -502 [31] | - |
| w-BN | Γ - Γ | -257.5 | | -247.2 | | - |
|  | Γ - K | -256.5 | | -239.4 | | - |
| h-BN | Γ - Γ | -422.5 | | -408.1 | | - |
|  | K - K | -232.6 | | -217.6 | | - |
| 2D-BN | Γ - Γ | -510.2 | | -469.1 | | - |
|  | K - K | -472.2 | | -445.9 | | - |
Next we discuss ZPR in the C allotropes. As recorded in Table 4.3 and Table 4.4, the direct gap of diamond at the Γ-point has a $\Delta E_{g}^{ZP}$ of $-408.3$ meV in adiabatic approximation and $-407.3$ meV with the non-adiabatic correction. The fundamental gap between Γ and 0.848X along the Γ–X direction is $\Delta E_{g}^{ZP} = -331.9$ meV and $-329.3$ meV in the adiabatic and non-adiabatic formulations respectively. These values are in excellent agreement with previous theory [181, 31, 32, 9] and experimental data [117]. Figure 4.7 plots the renormalized band structures of the C allotropes at $T = 0$, which shows an overall shrinking of the direct and indirect band gaps and the CB and VB shift closer together in diamond.

When the crystal structure changes from diamond to hexagonal graphite, $\Delta E_{g}^{ZP}(\Gamma - \Gamma)$ increases to $-637.7$ meV in the adiabatic approximation and $-623.9$ meV with the non-adiabatic correction. As summarized in Table 4.3, the magnitude of the shift in the VB is almost twelve times larger than the shift in the CB at the Γ-point, and both $\Delta \varepsilon_{CB}$ and $\Delta \varepsilon_{VB}$ are positive, which is not seen in other semiconductors calculated or silicene. The renormalized band structure in Figure 4.7 shows a particularly large upward shift in the VB and a nearly undetectable upward shift in the CB. Interestingly, the conduction bands are dramatically altered by the EPC renormalizations as compared to the valence bands. This is not the case with graphene, which has the same in-plane structure but very little distortion of its electronic band structure due to electron-phonon renormalization.

Surprisingly, for a single layer of graphite (i.e., graphene [204]) the magnitude of $\Delta E_{g}^{ZP}$ at the Γ-point is reduced by a factor of about 2.5, to $-259.4$ meV, in the adiabatic approximation and a factor of around 3, to $-210.7$, in the non-adiabatic formulation. We suspect this significant decrease in the magnitude of the renormalization at Γ is due to the interactions between the layers of graphite that are not present in graphene. However, like graphite, $\Delta \varepsilon_{CB}$ and $\Delta \varepsilon_{VB}$ in graphene are positive at the Γ-point and the main contribution to the total renormalization is from the VB, which suggests these may be a characteristic of the hexagonal C allotropes. Furthermore, in both graphite and graphene, $\Delta E_{g}^{ZP}(K - K)$ is $0.02$ meV using both the adiabatic and non-adiabatic methods. This value for the renormalization
is a numerical artifact further demonstrating the difficulty in the convergence of ZPR calculations, which is particularly delicate for the phonon frequencies in the 2D structures. While spin-orbit coupling has been shown to open a small gap in graphene [205], any opening of a band gap by EPC is prevented by symmetry of the structure around the Fermi energy [74]. Again, in this work we focus on the gap at $\Gamma$ of graphene and silicene to directly compare 3D and 2D materials; however, this methodology could be used to calculated renormalizations for modified graphene or allotropes of graphene with an opened gap at $K$.

It should also be noted that there is a substantial difference of 18.8% between the adiabatic and non-adiabatic calculations of $\Delta E^{ZP}_g$ for graphene. The variation for the same calculations is only 2.2% in graphite and 0.25% in diamond. Based on this, the adiabatic approximation fails for graphene, which has been previously confirmed by Pisana et al. [74]. We also suspect that the adiabatic approximation is insufficient for ZPR convergence in graphite as well, due to its semimetallic properties.

In the four polymorphs of BN, the variation of $\Delta E^{ZP}_g$ is much more gradual than it is for the C allotropes. zincblende BN, also known as cubic boron nitride, is isoelectronic to diamond and has superior chemical stability [194]. Our adiabatic and non-adiabatic calculations yielded $\Delta E^{ZP}_g(\Gamma - \Gamma) = -321.5$ meV and $-314.9$ meV, respectively. These results are in decent agreement (i.e. within 50 meV) with the prediction by Antonius et al. [32]. The difference between the adiabatic and non-adiabatic results is about 2% at the $\Gamma$-point and 11% for the ZPR at the indirect gap, $\Delta E^{ZP}_g(\Gamma - X)$. Poncè et al. [31] argued that a non-adiabatic treatment is necessary for polar materials, which have a non-zero Born effective charge. They showed that $\Delta E^{ZP}_g$ at $\Gamma$ diverges in the adiabatic approximation as the $q$-mesh increases. This combined with the variation in the values yielded by the adiabatic and non-adiabatic treatments suggests that the non-adiabatic method is better suited in the case of z-BN. Figure 4.8 shows the renormalized band structures of each BN material. The renormalized band gap of z-BN is extremely similar to diamond in that the largest contribution to $\Delta E^{ZP}_g(\Gamma - \Gamma)$ is from the CB.
Wurtzite BN is isoelectronic to Lonsdaleite (a.k.a hexagonal-diamond) [206], which is not included in this study due to its relative obscurity. Like z-BN, w-BN is a stable structure and is nearly as hard as diamond [194]. Its ZPR values are the smallest among the BN structures at $\Delta E_{g}^{ZP}(\Gamma - \Gamma) = -257.5$ in the adiabatic approximation and $\Delta E_{g}^{ZP}(\Gamma - \Gamma) = -247.2$ with the non-adiabatic correction, which have a variation of about 4%. The non-adiabatic ZPR at the indirect gap of w-BN is, likewise, about 7% smaller than its adiabatic counterpart. The corrected band structure shows consistent, mild renormalization with contributions of comparable magnitude from the VB and CB [Figure 4.8(c&d)].

Hexagonal BN is isoelectronic to graphite and is stable at ambient conditions [194]. Unlike semi-metallic graphite, however, h-BN is a wide-gap semiconductor. The adiabatic and non-adiabatic ZPR results for this structure are $\Delta E_{g}^{ZP}(\Gamma - \Gamma) = -445.5$ meV and $-408.1$ meV, respectively. These two results differ by 8%, while ZPR’s for the gap at $K$ differ by 6% using adiabatic and non-adiabatic approximations, respectively. In both cases, the more accurate non-adiabatic approximation reduces the magnitude of ZPR against the adiabatic approximation. The renormalized band structure [Figure 4.8(e&f)] is similar to that of graphite [Figure 4.7(c&d)], particularly in that the majority of the contribution to $\Delta E_{g}(\Gamma - \Gamma)$ is from the VB.

A structural analog to graphene, 2D-BN is a monolayer material with a hexagonal lattice and a large band gap whose $\Delta E_{g}^{ZP}$ at the $\Gamma$-point was calculated to be $-510.2$ meV in the adiabatic approximation and $-469.1$ meV with a non-adiabatic treatment. This is the largest predicted ZPR among the BN materials, and the difference in the $\Gamma$-point renormalization between the adiabatic and the non-adiabatic results is 8%. The ZPR for the band gap at $K$ is also sizable at $K$: $\Delta E_{g}^{ZP}(K - K) = -445.9$ meV in the non-adiabatic formulation. The renormalized band structure shown in Figure 4.8(g&h) displays extensive alterations to the conduction energy bands with large shifts to both the CB and VB at $\Gamma$.

In each of nine structures for which ZPR calculations have been performed, the non-adiabatic treatment always yielded smaller renormalizations at the band gap than the adia-
batic treatment. For Si, silicene, and diamond the variations in $\Delta E_g^{ZP}$ were minuscule and the $\Gamma$-point. For graphite, z-BN, and w-BN, the adiabatic and non-adiabatic calculations varied by roughly 7-10 meV, which is slightly larger than the variation in our convergence tests done using the non-adiabatic treatment (Figure 4.5). In h-BN and 2D-BN, the difference in the two calculation methods is $\sim$ 40 meV with non-adiabatic ZPR’s reduced by about 8% as compared to the adiabatic values. Graphene has the largest disparity, of nearly 50 meV, between its adiabatic and non-adiabatic renormalization calculations.

These results suggest that Si and diamond behave similarly. They are both non-polar semiconductors for which the zero-point electron-phonon renormalizations are consistently calculated in either the adiabatic or non-adiabatic treatments of AHC theory. Likewise, z-BN and w-BN have similar behaviors. Both are dense, wide-gap semiconductors with hardness comparable to diamond, and both are polar materials. The variations in their adiabatic and non-adiabatic ZPR at $\Gamma$ are significant though not dramatic given that the differences only slightly exceed the variation seen in their convergence tests. For these materials, the non-adiabatic correction is important; however, the adiabatic approximation gives reasonable ZPR values that are within the expected variation due to the use of different pseudopotential \[181].\footnote{This is true for calculations using a substantial broadening parameter, such as $i\eta = 100$, to speed convergence (see Antonius \textit{et. al.} [32]). As was mentioned in section 4.3.2 the convergence tests done by Poncé \textit{et al.} [31] indicate divergence in $\Delta E_g^{ZP}$ for increasing $N_q$, which suggests that the non-adiabatic corrections to the ZPR are necessary for any material with a non-zero Born effective charge.}

Following this trend, h-BN and 2D-BN have aspects consistent with expectations. Given that 2D-BN is essentially a single layer of h-BN, it is intuitive that the two structures would share similar EPC characteristics, especially since they are both semiconductors. This is confirmed, to a degree, by their $\Gamma$-point energy band shifts, which are close in magnitude (though 2D-BN has a much larger renormalization at the $K$-point than does h-BN). In addition, their adiabatic and non-adiabatic calculations vary by about 8% for both structures indicating that non-adiabatic corrections are necessary.

The exceptions are silicene, graphite, and graphene, which are also the semimetals. In the case of silicene, the unexpected element is the small difference between the adiabatic
and non adiabatic calculations. As it is a semimetal, we expected the ZPR convergence in the adiabatic approximation to fail for silicene. However, we have only performed ZPR convergence tests for the non-adiabatic treatment in this study. It may be necessary to examine the convergence of the adiabatic ZPR in silicene to gain a better understanding of its reaction to the adiabatic approximation as it applies to AHC theory. Graphite’s outlying characteristic its relationship to graphene. Unlike their isoelectronic counterparts, h-BN and 2D-BN, graphite and graphene do not have similar ZPR magnitudes at Γ. The renormalization in graphite is considerably larger than it is in graphene. On the other hand, graphene and graphite have in common that both the $\Delta \varepsilon_{\text{CB}}$ and $\Delta \varepsilon_{\text{VB}}$ are positive resulting in a general upward shift of the energy bands, and the largest component of $\Delta E_{g}^{ZP}(\Gamma - \Gamma)$ is from the VB. We also note that the adiabatic and non-adiabatic ZPR calculations for graphite are not drastically different as they are in graphene. While the non-adiabatic corrections are needed for an accurate treatment of both materials, the failure of the adiabatic approximation in graphene is apparent from the ZPR values alone.

Of the materials considered for this study, experimental data is currently only available for diamond and Si. As these structures have electron-phonon renormalizations that can be well described by the adiabatic approximation, it is difficult to asses, with the ZPR alone, whether or not the EPC properties of other materials are accurately calculated by the adiabatic or non adiabatic treatments. Additional tests and calculations are typically needed for a thorough understanding of the approximation’s validity. However, our renormalization calculations do indicate that the non-adiabatic corrections are more general as they do not contradict the results of the adiabatic approximation where it is known to be valid. From the ZPR calculations, we can also determine the relative significance of the EPC on the electronic structure. In 2D-BN, for example, the total ZPR of its indirect band gap is $\sim 0.45$ eV, which is non-negligible for a material with $E_{g} = 4.64$eV. Save for Si and silicene, all of the other structures considered above exhibit significant EPC renormalizations to their electronic energy structures.
Figure 4.6: The DFT electronic band structures and non-adiabatic electron phonon renormalization for silicon (a&b) and silicene (c&d). The solid black line is the plain DFT band structure, the dashed blue lines are the renormalized valence bands, and the dashed red lines are the renormalized conduction bands. The renormalization was calculated at T=0.
Figure 4.7: The DFT electronic band structures and non-adiabatic electron phonon renormalization for diamond (a&b), graphite (c&d), and graphene (e&f). The solid black line is the plain DFT band structure, the dashed blue lines are the renormalized valence bands, and the dashed red lines are the renormalized conduction bands. The renormalization was calculated at T=0. Panels (a), (c), and (e) give the wide view of the band structure, and panels (b), (d), and (f) give a close up view of the band gap.
Figure 4.8: The DFT electronic band structures and non-adiabatic electron phonon renormalization for z-BN (a&b), w-BN (c&d), h-BN (e&f), and 2D-BN (g&h). The solid black line is the plain DFT band structure, the dashed blue lines are the renormalized valence bands, and the dashed red lines are the renormalized conduction bands. The renormalization was calculated at T=0. Panels (a), (c), (e), and (g) give the wide view of the band structure, and panels (b), (d), (f), and (h) give a close up view of the band gap.

4.4.2 Phonon dispersions

To demonstrate the link between the electron-phonon renormalization and the phonon characteristic of various crystal structures, we have plotted phonon dispersions and phonon densities of state (DOS) for the Si allotropes in Figure 4.9, the C allotropes in Figure 4.10, and the BN polymorphs in Figure 4.11. We find that the general trend that higher maximum
optical phonon frequencies (wider phonon spectrum ranges) lead to stronger electron-phonon coupling and larger magnitudes for $\Delta E_{g}^{ZP}(\Gamma - \Gamma)$. For example, panels Figure 4.10(a) and Figure 4.10(b) indicate that the highest optical phonon frequency in graphite ($\sim 1600$ cm$^{-1}$) is larger than that in diamond ($\sim 1300$ cm$^{-1}$). Also the $\Delta E_{g}^{ZP}$ of graphite is larger than that of diamond. The situation is similar for the bulk BN polymorphs. Among them, h-BN has the highest maximum optical phonon frequency ($\sim 1450$ cm$^{-1}$), while w-BN has the lowest ($\sim 1250$ cm$^{-1}$), as seen in Figure 4.11(a), Figure 4.11(b) and Figure 4.11(c). The Si allotropes follow the same pattern. Si has a slightly smaller phonon frequency range than silicene, and $\Delta E_{g}^{ZP}(\Gamma - \Gamma)$ for Si is roughly 25 meV smaller than it is for silicene. Additionally, Si and silicene have much narrower phonon frequency ranges than the C and BN materials, and their electron-phonon induced renormalizations are substantially smaller. Comparing bulk C allotropes and BN polymorphs, the trend that materials with higher maximum optical frequencies have larger ZPR magnitudes still, roughly, holds true. This observation is in line with the fact that stronger electron-phonon coupling is often caused by stronger atomic interactions.

Figure 4.9: The calculated phonon spectra and density of states for two Si allotropes: (a) Si and (b) silicene. The phonon density of states (DOS) is in unit of states/atom/cm$^{-1}$.

Figure 4.12 maps out $\Delta E_{g}^{ZP}(\Gamma - \Gamma)$ as a function of frequency for the combined structures. Using this representation of the data, it is clear that there is a general increase over the structures as the phonon frequency range becomes wider. The notable outliers include 2D-
Figure 4.10: The calculated phonon spectra and density of states for three C allotropes: (a) diamond, (b) graphite, and (c) graphene. The phonon density of states (DOS) is in unit of states/atom/cm$^{-1}$.

BN and graphene. There is not enough evidence to determine if silicene is expressing behavior similar to graphene as the sample size of the Si allotropes is too small. It is possible that, due to its characteristic buckling, silicene may be showing characteristics of a 3D structure in this case. Figure 4.10(b) and Figure 4.10(c) show that the phonon frequency ranges of graphite and graphene are similar, but $\Delta E_{g}^{ZP}$ in graphene is about three times smaller in magnitude than that of graphite. This may be a result of differences in the EPC behavior due to the interlayer interactions in graphite that are absent in graphene. The opposite behavior is seen in h-BN and 2D-BN, however. Like graphite and graphene, the phonon frequency range of the two structures is comparable, but unlike the C allotropes, $\Delta E_{g}^{ZP}(\Gamma - \Gamma)$ for h-BN in slightly smaller ($\sim 60$ meV) than that of 2D-BN. This may be an affect of the
Figure 4.11: The calculated phonon spectra and density of states (in unit of states/atom/cm\(^{-1}\)) for four BN polymorphs: (a) zincblende; (b) hexagonal; (c) monolayer; and (d) wurtzite.

convergence of the ZPR calculations as the two numbers are not as dramatically different as they are with graphite and graphene. There is also the possibility that the deviation in 2D-BN from the behavior of the bulk BN materials is due to a lack of out-of-plane interactions. While we might expect graphene and 2D-BN to show similar outlying behavior if this were the case, the fact that graphene is a semimetal and 2D-BN is a semiconductor could explain the variation in their trends.

The evidence presented in the phonon dispersions and Figure 4.12 suggests that crystal structure in combination with phonon frequency data can be used to make rough predictions about the significance of electron-phonon induced renormalization of band gaps. The cubic structures, diamond and z-BN are both dense stable materials with maximum phonon
frequencies in the intermediate range of this data set, and we have calculated non-negligible band gap renormalizations for both. Si is isoelectronic to diamond and z-BN, but its frequency range is substantially smaller as is its calculated value of $\Delta E_{g}^{ZP}$. The hexagonal layered structures, graphite and h-BN, have the largest phonon frequency ranges that accompany significant ZPR values at $\Gamma$. Furthermore, $\Delta E_{g}^{ZP}$ for w-BN is the smallest of the BN polymorphs, which is consistent with it frequency range as compared to h-BN and z-BN. 2D-BN exhibits behavior that deviates slightly from the bulk materials. It also has a high maximum phonon frequency paired with a large ZPR, but its $\Delta E_{g}^{ZP}$ magnitude is larger than that of h-BN despite having a slightly lower optical phonon frequency range. Graphene is the most striking outlier. Despite having a phonon frequency range nearly identical to
graphite, its ZPR is appreciably smaller. Given the many unique qualities of graphene, it is not surprising that its behavior in this case is also divergent. Further studies on the EPC in graphene would be useful to fully understand its differences from bulk and other 2D structures, such as an examination of the van der Waals interaction and a more in-depth dimensional analysis of carbon materials, including 1D structures.

4.5 Temperature-dependent band gaps

Having thoroughly analyzed the renormalizations of each considered structure at zero temperature, $T = 0$ K, it is instructive to perform calculations of the temperature dependence of those renormalizations. While zero-point motion in materials is significant and useful, many experiments and calculations are done at non-zero temperatures. As such, it is helpful to know how the eigenenergy renormalizations change as $T$ increases.

In section 4.4.1, we established that non-adiabatic corrections to the ZPR can be substantial depending on the material and crystal structure under consideration. The temperature dependent adiabatic and non-adiabatic renormalizations were also calculated for each structure to compare temperature trends and EPC characteristics for $T > 0$. Figure 4.13 shows the $\Delta E_g(\Gamma - \Gamma)$ temperature profiles for each structure with the non-adiabatic calculations in black and the adiabatic calculations in red. As expected from our previous ZPR results (Table 4.3), Si, silicene, and diamond exhibit negligible differences between their adiabatic temperature profiles and their non-adiabatic corrections. For z-BN, w-BN, and 2D-BN the adiabatic and non-adiabatic renormalizations are closer in magnitude at temperatures below 300 K and diverge as $T$ increases so that the difference between the treatments is more dramatic at high temperatures. For graphite, graphene, and h-BN the non-adiabatic temperature profile is shifted uniformly such that the difference in values due to the correction is roughly the same at each temperature. Overall the non-adiabatic corrections do not have a dramatic effect on the the relative temperature trends, so for our structural comparison, we will look at temperature profiles calculated with the non-adiabatic treatment.
Figure 4.13: The adiabatic and non-adiabatic electron-phonon renormalizations of $\Delta E_{g}^{ZP}(\Gamma)$ as a function of temperature for (a) Si, (b) silicene, (c) diamond, (d) graphite, (e) graphene, (f) z-BN, (g) w-BN, (h) h-BN, and (i) 2D-BN. The non-adiabatic calculations are denoted by the solid black curves, and the adiabatic calculations are given by the dashed red curves.

The temperature ($T$) dependence of $\Delta E_{g}$, calculated with non-adiabatic corrections, at the direct band gap is plotted for the Si allotropes, the C allotropes, and the BN polymorphs in Figure 4.14. The $\Delta E_{g}$ temperature profiles in most of these materials are similar: at low to room temperature, the ZPR dominates the total energy shift and $\Delta E_{g}(T)$ changes very gradually as a function of $T$. In these cases, one needs only consider phonon renormalization caused by the zero-temperature lattice vibrations up to room temperature. The exceptions to this are silicene and graphene, both of which have a more linear profile such that the magnitude of the renormalization steadily increases from the ZPR. This is particularly pronounced in silicene, which increases more than tenfold from 0 K to 1000 K, and at 300 K,
the renormalization is no longer negligible at $\Delta E_g \sim 400 \text{ meV}$ . As this behavior is unique for our set of structures, silicene’s buckled structure may be a contributing factor. The other 2D materials are flat and have no out-of-plane atomic interactions, and the bulk materials have consistent atomic interactions in all three directions. Silicene, on the other hand, has a slight deviation in its planar structure, and even though it is electronically stable, the EPC could be complicated by intricacies due to the slight out-of-plane buckling. This dramatic temperature profile may also be the result of a convergence issue. As our calculations for silicene were preliminary, further studies are required to explore the origins of its intense temperature dependence in the EPC induced renormalization.

![Graphs](image)

**Figure 4.14:** The electron-phonon renormalization at the $\Gamma$-point as a function of temperature for (a) Si and silicene(2D-Si); (b) diamond(d-C), graphite(h-C), and graphene(2D-C); and (c) z-BN, w-BN, h-BN, and 2D-BN.

At high temperatures ($T \gtrsim 400 \text{ K}$), $\Delta E_g(T)$ increases dramatically as $T$ rises in each of the structures. We also find that for bulk materials with a large ZPR, $\Delta E_g(T)$ increases
slightly faster than it does in bulk materials with smaller ZPR’s. The above can be easily understood by a simple Debye [123]:

\[ \Delta E_g(T) = -a \left[ 1 + \frac{2}{e^{\Theta/T} - 1} \right], \]  

(4.2)

where \( a \) and \( \Theta \) are fitting parameters. When \( T = 0 \) in equation 4.2, the magnitude of \( \Delta E_g(T) \) is dependent on the magnitude of \( a \). The larger \( a \) is, the faster \( \Delta E_g(T) \) will grow as \( T \) increases.

This is not the case for 2D materials, however, as is particularly clear in Figure 4.14(c) for h-BN and 2D-BN. The monolayer structure has a larger ZPR than the layered structure, but at \( T \gtrsim 300 \text{ K} \), \( \Delta E_g \) for h-BN begins to increase more quickly than it does for 2D-BN. In the cases of silicene and graphene, it is more difficult to make a definitive statement about the relationship between the ZPR and the temperature dependent rate of increase in the renormalization; however, a characteristic difference of the electron-phonon renormalization temperature dependence is indicated between the 2D and bulk materials.

### 4.6 Summary

In this chapter, we have investigated electron-phonon renormalization of eigenenergies in two Si allotropes, three C allotropes, and four BN polymorphs using DFPT. Our analysis demonstrates that \( \Delta E_g \) is sensitive to crystal structure and dimension, and that it can be substantial in electronic structure calculations for some materials. This is the first direct comparison of eigenenergy renormalizations in isoelectronic structures as well as 3D and 2D materials. We discovered that the magnitudes of the total renormalization at the band gap, \( \Delta E_g^{ZP}(\Gamma) \), is directly related to the structural stiffness of a given 3D material. Low-dimensional structures such as planar 2D materials do not follow this trend indicating significant differences in their EPC behavior.

Very few first-principles calculations of phonon renormalization have been carried out because of their prohibitive computational cost. The major issue in these calculations is slow convergence, requiring extremely large and fine \( \mathbf{q} \)-meshes. We compared two implemen-
tations: the unofficial QE+EPW code, based on the Allen-Heine theory, and the ABINIT package using the original mathematical formalism with Sternheimer equations [78]. Our calculations suggest that the ABINIT implementation converges faster than QE+EPW, though it is highly memory intensive.

Analysis of the adiabatic and non-adiabatic treatments of AHC theory in ABINIT confirmed the conclusions of previous studies [31, 207] that certain materials and crystal structures cannot be accurately described by the adiabatic, Born-Oppenheimer approximation [72]. Our results confirm that polar BN materials and semimetallic materials tend to have significant variations in their adiabatic and non-adiabatic ZPR’s, suggesting a failure of the adiabatic approximation. Temperature dependent $\Delta E_g^{ZP}$ calculations also confirm that this disparity between the two treatments continues at higher temperatures. In different materials the adiabatic renormalizations have various deviations from the non-adiabatic results as temperature increases, indicating that the relative accuracy of adiabatic temperature dependent renormalization profiles is not reliable for all materials.

Next we considered the ZPR values in concert with the phonon dispersions of each structure and found that bulk materials with wide phonon frequency ranges tend to have strong EPC and a sizable $\Delta E_g$. These calculations suggest that high optical phonon frequency is a good indicator of whether or not the electron-phonon renormalization should be included the in electronic structure calculations. However, this relationship does not always hold in monolayer structures, particularly graphene, where the magnitude of $\Delta E_g$ is diminished compared to graphite even though the top optical phonon bands in graphene are located in roughly the same range as its layered counterpart. The departure from the behavior of the bulk structures may be a result of reduced DOS of the optical phonons in 2D materials, or, possibly, the absence of out-of-plane atomic interactions.

Our general observations of the behavior of electron-phonon energy band renormalizations in bulk materials tended to be contradicted by the 2D structures. EPC and ZPR have been previously shown to be enhanced in nanoscale structures [177]; however, here we find
that the magnitude of ZPR is significantly reduced in graphene while it is slightly enhanced in 2D-BN and silicene. The temperature dependent profiles also indicate substantial differences between the 2D and 3D structures as temperature increases. Thus it is imperative and pertinent to study the effects of lattice vibrations and temperature dependence in 2D materials and nanostructures, including phonon mediated electronic and optical properties.
Crystal symmetry is an essential part of every electronic structure calculation and experiment. For a familiar material, inferences can be made about the crystal structure, the electronic characteristics, the atomic configuration, the elemental makeup, and the band structure because the electronic characteristics are determined by these aspects of a solid. So, it follows that the phonon characteristics would be likewise dependent on crystal structure as would the interaction between the electrons and phonons. This conclusion is intuitive, and there are abundant examples of this dependence scattered throughout the literature. Our purpose has been to use a significant sampling of structures to compare EPC characteristic and identify useful patterns in the relationships between crystal structures and their phonon-mediated properties.

In section 1.5 of Chapter 1, we posed several questions, which began our research.

(i) Our first question was “Does sodium, like lithium, become a superconductor in any of its high pressure phases (cI16, tI19, or cI24)?” We discovered that Na is not a superconductor in any of its high pressure phases. This was not previously known. Prior studies have calculated superconducting critical temperatures for bcc-Na and fcc-Na [20, 18], but no calculations of $T_c$ or electron-phonon coupling strength, $\lambda$, had been performed for the higher pressure phases, cI16, tI19, and cI24. The lack of increased electron-phonon strength and raised $T_c$ in Na was, at first, surprising. After all, previous theoretical studies of Cs, K, Rb, and Li all reveal substantial increases in the both $\lambda$ and $T_c$ associated with their pressurized fcc phases [16, 17, 20, 18, 21, 22, 23]. Superconductivity has also been confirmed experimentally in both tetragonal-Cs and cI16-Li [158, 129, 126, 130]. Given this evidence, we postulated that the commonalities between the alkali metals would lead to a likelihood of superconductivity in some
pressurized phase of Na. This is not the case. Due to the sustained nearly-free-electron-like behavior in Na at pressures up to 260 GPa resulting in the absence of electronic orbital hybridization, the electron-phonon coupling strength peaks at $\lambda = 0.5$ in $cI16$-Na. As for the ultra-high pressure $cI24$ phase of Na, while $T_c = 12$ K, the electron-phonon coupling strength does not surpass $\lambda = 0.46$. This suggests that Na is not a scientifically interesting superconductor in any of it’s metallic phases up to 30 TPa.

(ii) Our second question was “Is Wannier interpolation a superior technique for converging the electron-phonon matrix elements as compared to the homogeneous phonon wavevector sampling method of the ABINIT[131] DFPT implementation?” As to this, we found that the EPW+QE [108] Wannier interpolation method we used was not superior to the ABINIT method. To our knowledge, this is the first direct comparison of ZPR convergence using a Wannier interpolation method (QE+EPW) and a homogeneous phonon wavevector sampling method (ABINIT). Our results showed that the total ZPR’s at the $\Gamma$-point ($\Delta E_g$) for both Si and diamond converged more slowly with the QE+EPW code than with the ABINIT method. We also found that the renormalization magnitudes calculated with ABINIT were in much better agreement with previous studies [31, 181, 9, 32] than those calculated with QE+EPW. For both techniques the convergence is difficult and time consuming. QE+EPW requires that the summation in the self-energy terms (Eqs. 2.20 and 2.21) be done over many unoccupied energy bands, but it has the advantage of efficient parallelization and is less disc-space intensive than the ABINIT method. On the other hand, the Sternheimer equations [78] used in ABINIT allow summations to be done only over occupied bands, which significantly decreases the computational demand. However, the homogeneous $\mathbf{q}$-point sampling requires large amounts of disc-space. In the end the ABINIT method was preferable to the QE+EPW code due to its faster convergence and overall accuracy.
(iii) The next question we asked was “How is the EPC induced eigenenergy renormalization related to crystal symmetry and composition for various carbon and silicon allotropes and boron nitride polymorphs?” The answer here is that, for 3D materials, the stiffness of the structure is directly related to the magnitude of the zero-point eigenenergy renormalization of the band gaps ($\Delta E_{gz}^{ZP}$). We performed calculations for a number of structures and found that, where stiffness is indicated by high phonon frequencies, the magnitude of $\Delta E_{gz}^{ZP}$ for the bulk Si, C, and BN materials was found to increase with increasing frequency (Figure 4.12). This relationship has not been explicitly shown before. In addition, it may be useful in predicting the significance of the eigenenergy renormalizations in 3D materials as well as for revealing outlining structures with exotic EPC behavior.

(iv) Our final question was “Is the EPC induced eigenenergy renormalization affected by the lower-dimensionality of 2D structures?” Our $\Delta E_{gz}^{ZP}$ frequency relationship reveals that the eigenenergy renormalizations are significantly affected by lower-dimensionality. This is clear from the outlying behavior of graphene and 2D-BN. These materials do not follow the same trends as the bulk structures. For example graphene has a $\Delta E_{gz}^{ZP}(\Gamma)$ about three times smaller in magnitude than that of graphite, but its phonon frequency range is roughly the same. In the case of 2D-BN, $\Delta E_{gz}^{ZP}$ is slightly larger than that of h-BN despite the fact that its phonon frequency range is slightly smaller. As this study is the first to compare EPC induced eigenenergy renormalization in 3D and 2D structures, the divergent behavior of 2D structures will require further investigation to fully understand the effects of dimensionality on EPC properties.

In order to investigate the questions above, we reviewed the relevant literature on the history and current development and applications of ab initio EPC calculations in Chapter 1, and in Chapter 2 we discussed the theoretical and computational techniques employed in this project. Two primary EPC induced properties were our focus: superconductivity and the renormalization of electronic eigenenergies. To examine the relationship of EPC
induced superconductivity to crystal structure, we identified five stable crystal phases of Na, and calculated the electron-phonon coupling constant and critical temperature as functions of pressure for each structure. In contrast, we analyzed and compared EPC induced eigenenergy renormalization for different materials and varying structures. Eigenenergy renormalizations were calculated for the band gaps and around the Fermi energies of two Si allotropes, three C allotropes, and four BN polymorphs, including a 2D structure of each composition. This allowed for a cross comparison of EPC characteristics in isoelectronic structures and materials with reduced dimensionality. In total, fourteen structures have been examined through DFT-based calculations of electron-phonon coupling phenomena.

Historically, \textit{ab initio} EPC calculation began with metals \cite{39} and evolved to include limited studies of semiconductors \cite{43, 44} and ionic crystals \cite{45, 46}. Each of these steps led to advances in computational techniques and theoretical approximations aimed at accurately and efficiently solving the coupled electron-phonon hamiltonian (eq. 1.1). It has become clear that this requires the calculation of electron-phonon matrix elements \cite{1}, which was first done using \textit{ab initio} calculations nearly forty years ago \cite{35}. Since then, theoretical and computational methods along this line have evolved quickly to include “frozen phonon” calculations and density functional perturbation theory.

Today DFT and DFPT \cite{71} make up the standard procedure for calculating electron-phonon matrix elements in the harmonic and adiabatic approximations; however, advances in this field are ongoing and rapid. Recent studies have explored anharmonic effects \cite{32, 89, 87, 88, 85, 86} and non-adiabatic corrections \cite{73, 74, 32} in EPC studies. GW corrections \cite{7, 97, 98} have also been used to calculated accurate quasiparticle energies and improve calculations of EPC induced energy band shifts \cite{9}. In the vein of computational improvements, the use of Sternheimer equations \cite{78} and Wannier interpolation methods \cite{28, 30, 108} has reduced the strain and cost of calculating electron-phonon matrix elements by improving the speed and efficiency of DFPT calculations. While these developments may not be a complete numerical field theory, they do provide more accurate methods and practical solutions for the complex
task of studying electron-phonon interactions.

The theoretical and computational methods used in this study are the current standard for EPC analysis using DFT and DFPT linear response calculations. We have not included GW corrections, which are computationally demanding, nor have we looked at the effects of anharmonicity as these are beyond the scope of our present inquiries. The connection between the two parts of our study lies in the electron-phonon matrix elements. Both the superconductivity and eigenenergy renormalization studies begin with calculating these matrix elements using DFPT implemented in the ABINIT [131] package. To determine the phonon-mediated superconductivity parameters of the various phases of Na, we used Migdal-Eliashberg theory [82, 81] in addition to the McMillan equation [110] as modified by Allen and Dynes [111]. For the calculations of the EPC induced eigenenergy renormalizations we used Allen-Hein-Cardona theory [24, 25, 26] in the adiabatic approximation as well as with the non-adiabatic corrections implemented by Poncè et al. [31]. The inclusion of non-adiabatic calculations was necessary due to previous evidence of the adiabatic approximation’s failure for polar materials [31, 32], such as BN, and semimetals [74], such as graphene.

In Chapter 3, the possibility of superconductivity in pressurized Na was investigated. Looking closer at the effects of pressure on the electronic and phonon characteristics in Na, it is clear that, unlike Li, Cs, K, and Rb, the contributions to Na’s density of states comes primarily from $s$ states between 0 and 260 GPa, which results in nearly-free electrons and spherical Fermi surfaces. The other alkali metals exhibit either $s$-$p$ or $p$-$d$ orbital hybridization in their fcc phases [20]. Na does not start to show $p$-$d$ electron hybridization until it reaches its $cI24$ phase at 16 TPa. In addition, the density of states as Fermi surface $[N(\varepsilon_F)]$ decreases over Na’s structural phases as the pressure rises. This is in stark contrast to previous studies on the other alkali metals and is a factor in decreased $\lambda$. We also note that the average phonon frequency fluctuates in the pressure range from 0 to 260 GPa, but steadily increases above 16 TPa. Our calculations and analysis suggest that the structural transitions of pressurized Na are not enough on their own to induce electron-phonon mediated superconductivity despite
their similarities to those of other superconducting alkali metals. It is necessary to look at the DOS, phonon dispersions, and electron-phonon coupling strengths to see that Na inhabits an elemental “anti-Goldilocks” position: It is just heavy enough that s-p hybridization does not occur and it is too light to exhibit p-d hybridization. It is not until extreme pressures, above16 TPa, are applied that cI24-Na shows signs of p-d hybridizations; however, the stiffening of the structure related to the phonon frequency increase along with the considerably reduced DOS lead to a weak electron-phonon coupling.

In Chapter 4 we analyzed the relationship of crystal structures to a second EPC induced effect: renormalization of electronic energy bands. While the EPC induced renormalizations are often ignored in electronic structure calculations, our results indicate that these effects cannot be disregarded in all cases. In our examination of two Si allotropes (Si and silicene), three C allotropes (diamond, graphite, and graphene), and four BN polymorphs (z-BN, w-BN, h-BN, and 2D-BN), only Si and silicene had negligible renormalizations at $T = 0$. The calculations, performed using the adiabatic and non-adiabatic treatments of AHC theory, were consistent with previous results and studies for diamond, silicon, and z-BN [108, 181, 9, 32, 31]. Our work has expanded the database of ZPR calculations to include the semiconductors w-BN, h-BN, and 2D-BN as well as the semimetals silicene, graphene, and graphite. We found that the convergence of the zero-point renormalization requires a large $q$-mesh, and that differences in the results of adiabatic and non-adiabatic calculations larger than $\sim 2\%$ correspond to semimetals and polar materials with a non-zero Born effective charge, for which the adiabatic approximation is known to fail [31, 74]. Phonon dispersions and densities of state were analyzed as were temperature dependent renormalization profiles, which show expected trends for each of our materials in that the magnitude of the energy shifts increases with increasing temperature.

The inclusion of semimetals like graphite, graphene, and silicene has been, primarily, for continuity in our comparisons between allotropes and polymorphs. In the cases of graphene and silicene, scientific interest usually focuses on the Dirac points as the gap at $\Gamma$ is not
particularly significant to the interesting electronic properties. In this study, however, we are focusing on the gap at $\Gamma$ for each material in order to achieve a direct comparison of EPC induced ZPR in 2D and 3D structures, which is one of our main purposes. The methods used to calculate renormalizations for these material will also be useful in similar studies of modified graphene and other 2D structures, in which a gap is opened at the $K$-point.

By comparing total ZPR’s of the band gaps ($\Delta E^{ZP}_g$) at the $\Gamma$-point with the phonon dispersions, we were able to identify patterns in our sample set. There is a clear relationship between the phonon frequency ranges and the size of $\Delta E^{ZP}_g(\Gamma)$ that has not been explicitly demonstrated prior to this research. This relashionship holds for all of the bulk materials we tested. This departure of 2D materials from this trend may be a result of reduced DOS of the optical phonons in 2D materials, or, possibly, the absence of out-of-plane atomic interactions. Overall, we have shown that high optical phonon frequencies are related to large eigenenergy renormalizations around the Fermi surface. As high phonon frequencies are also associated with stiffer structures, there is a correlation between a material’s hardness and the significance of the distortion of its band structure due to EPC.

All of these calculations are limited, not only by computational capabilities, but also by approximations and assumptions. The McMillan equation [110] is known to overestimate peak $T_c$ values and is sensitive to the choice of semiempirical Coulomb repulsion parameter, $\mu^*$. Additionally, all of the electron-phonon matrix elements are calculated in the harmonic approximation, and though there are no indications that this approximation is invalid for our calculations, anharmonic effects are known to alter renormalization magnitudes in some cases [32]. However, the most significant limitation for these computations is the extremely difficult convergence. Interpolation techniques [108, 31] have made some progress in overcoming the complications of this issue, but the calculations still require fine $\mathbf{q}$-point grids that take significant time and disk space. This is particularly complicated for nano-structures, such as nanowires and nanotubes, that have many atoms in their primitive cells. Convergence of the EPC renormalizations in these structures will likely to require interpolation methods.
The results of our analysis and comparisons have revealed several key insights into the relationship between EPC and crystal structure that were not previously known. We have found that, despite the structural commonalities between Na and the superconducting alkali metals, Na is not a likely superconductor in any of its phases between 0 and 30 TPa. This satisfies the questions about superconductivity in Na from previous studies, which have only looked at its bcc and fcc phases. In the case of eigenenergy renormalization, our sample set of structures revealed a clear correlation between the phonon frequency range and the size of the energy band renormalizations. This is useful in assessing the possibility of a non-negligible band gap renormalization and identifying exotic EPC behavior in specific materials.

A continuation of this work would build on its main discoveries; namely, that (i) even at ultra-high pressures, Na has weak electron-phonon coupling making superconductivity unlikely, (ii) convergence of EPC properties is highly demanding and requires large \( q \)-grids to sample the BZ, (iii) structural stiffening associated with high phonon frequencies is related to large EPC induced eigenenergy renormalizations in bulk materials, and (iv) low-dimensionality affects EPC behavior drastically. Advancement in the study of phonon-mediated properties will require more accurate methods to calculate electron-phonon matrix elements. This will allow for further studies into the dimensional aspect of structures necessary to explore the differences in EPC characteristics shown by 2D structures such as graphene, 2D-BN, and silicene as well as 1D materials and other nano-structures. Currently we are working on EPC renormalization calculations in one-dimensional C and BN nanotubes as well as Si nanowires, to continue and strengthen our study of dimensional effects on phonon-mediated properties.
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