Density Functional Theory Studies of Energetic Materials

by

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For Kathy, Larry, Corey, and Colleen
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First-principles calculations employing density functional theory (DFT) were performed on the energetic materials PETN, HMX, RDX, nitromethane, and a recently discovered material, nitrate ester 1 (NEST-1). The aims of the study were to accurately predict the isothermal equation of state for each material, improve the description of these molecular crystals in DFT by introducing a correction for dispersion interactions, and perform uniaxial compressions to investigate physical properties that might contribute to anisotropic sensitivity.

For each system, hydrostatic-compression simulations were performed. Important properties calculated from the simulations such as the equilibrium structure, isothermal equation of state, and bulk moduli were compared with available experimental data to assess the agreement of the calculation method. The largest contribution to the error was believed to be caused by a poor description of van der Waals (vdW) interactions within the DFT formalism.

An empirical van der Waals correction to DFT was added to VASP to increase agreement with experiment. The average agreement of the calculated unit-cell volumes for six energetic crystals improved from approximately 9% to 2%, and the isothermal
EOS showed improvement for PETN, HMX, RDX, and nitromethane. A comparison was made between DFT results with and without the vdW correction to identify possible advantages and limitations.

Uniaxial compressions perpendicular to seven low-index crystallographic planes were performed on PETN, HMX, RDX, nitromethane, and NEST-1. The principal stresses, shear stresses, and band gaps for each direction were compared with available experimental information on shock-induced sensitivity to determine possible correlations between physical properties and sensitivity. The results for PETN, the only system for which the anisotropic sensitivity has been thoroughly investigated by experiment, indicated a possible correlation between maximum shear stress and sensitivity. The uniaxial compressions that corresponded to the greatest maximum shear stresses in HMX, RDX, solid nitromethane, and NEST-1 were identified and predicted as directions with possibly greater sensitivity. Experimental data is anticipated for comparison with the predictions.
CHAPTER 1  INTRODUCTION

1.1 Motivation and Research Objective

The United States Department of Defense is actively pursuing the development of insensitive munitions to reduce the risk for loss of life and property by accidental explosions of EMs. While methods for safe handling and transportation of EMs applications are effectively utilized, the reduction of sensitivity would greatly diminish the cost of such methods. An obstacle to the design of insensitive materials is the fact that the microscopic events that lead to detonation are not well understood. Also poorly understood are the mechanisms responsible for anisotropic sensitivity of EMs such as PETN, which, if clarified, might aid in grasping the mechanisms of initiation. While modeling and simulation offer the ability to capture the miniscule time and length scales associated with initiation, modern techniques exhibit disadvantages ranging from prohibitive computational expense to inaccurate descriptions of atomic-level interactions.

This study aims to address three important problems in EMs research: (1) first-principles calculations of isothermal equations of state for important energetic materials, (2) an improvement to the description of intermolecular interactions in density functional theory calculations of energetic solids in the form of molecular crystals, and (3)
simulations of uniaxial compression aimed at understanding anisotropic sensitivity in single-crystal energetic materials.

The first focus of this work is to calculate from first-principles the isothermal equations of state (EOSs) for important energetic materials. The EOS of an energetic material is a very important quantity obtained from hydrostatic compression, allowing the calculation of the bulk modulus and its pressure derivative. From these quantities, the accessible states of a material, also termed the Hugoniot locus, after a weak shock can be calculated [1]. Accurate and reliable first-principles predictions of the EOS for energetic materials are highly desired because of both the highly reactive nature of the materials and the cost associated with experiments.

The second aim of the project is the introduction of an empirical correction to account for dispersive van der Waals (vdW) interactions in DFT calculations for EMs. The initial calculations of this study were performed with uncorrected DFT, and the unit-cell volumes were calculated with undesirably large error as compared with experiment. The source of the error is believed to be the poor (or lacking) description of dispersion interactions by exchange-correlation functionals commonly used in DFT calculations, which is a well-known problem in condensed-matter theory. To correct for the missing intermolecular interactions, a dispersion correction is used in this study that is based on the work of Neumann and Perrin [2], which showed a significant improvement in the prediction of equilibrium unit-cell volumes for molecular crystals. The method was chosen to allow for quick, efficient calculations without the sacrifice of accuracy. In this study, a DFT computer code with and without the empirical correction (referred to below as pure DFT and vdW-DFT, respectively) is used to calculate the equilibrium unit-cell
structure and to simulate the hydrostatic compression of PETN-I, β-HMX, α-RDX, solid nitromethane, and NEST-1. A comparison of the results is made to evaluate the improvement in the predictive capabilities of DFT with the empirical vdW correction.

The final task is to use density functional theory to study the anisotropic response of these materials to compression. The uniaxial compression of PETN is an important task for the study because the anisotropic sensitivity of this material has been studied in several experiments. By performing uniaxial compressions in the known sensitive and insensitive directions of PETN, it might be possible to gain an understanding of the physical properties that contribute to the anisotropy. Similar simulations and analysis are applied to HMX, RDX, nitromethane, and NEST-1, important EMs that have not been investigated for anisotropic sensitivity to shock, to predict the anisotropic response to compression. The anisotropic constitutive relationships between stress and strain for these materials calculated from the simulations can also be useful for simulations of EM grains at greater length scales. Further, DFT is a suitable tool for this study because it has shown success in the description of EMs at high pressure at a reasonable computational expense.

An important result of the simulations in this work is the prediction of the EOS for NEST-1, a recently discovered EM for which hydrostatic-compression experiments have yet to be performed. Further, the EOSs for several important EMs have been calculated in exceptional agreement with experimental results, demonstrating the utility of DFT calculations in the predictive characterization of EMs.
Another significant outcome of this work is that the empirical dispersion correction reduced the average error in the prediction of equilibrium unit-cell volumes from 9% by pure DFT to about 2%. In addition, vdW-DFT provides, on average, better agreement with experiment than pure DFT in the prediction of the isothermal equation of state, as well as the lattice constants as functions of pressure. These findings support the use of vdW-DFT as an effective tool for use in EMs research.

An additional major finding of this work is the possible existence of a correlation between shear stress and sensitivity in PETN. From the uniaxial-compression simulations, the sensitive directions, <110> and <001>, showed greater shear stress-values than the insensitive directions, <100> and <101>, at high compression. Further, the insensitive directions exhibited non-monotonic dependence of shear stress on strain. For the other EMs of the study, compression directions that exhibited behavior similar to the sensitive and insensitive directions of PETN were identified. If the sensitivity of these materials is linked with the shear stresses in a similar manner as observed in PETN, this work could serve as a prediction for directions of greater (and/or) lesser sensitivity.

In the following sections, the energetic materials used in this study are introduced along with their properties that are relevant for this study. The utility of theoretical tools for the study of EMs is also briefly noted.
1.2 Energetic Materials

One of the key properties of materials employed in chemical explosives is the ability to detonate. Detonation is a combustion process that travels in the form of a shockwave at a supersonic speed through an explosive material. The chemical reactions behind the self-sustaining detonation front release gaseous products at high pressure and temperature, typically resulting in destructive effects on the surroundings. Hence, energetic materials capable of detonation are utilized for the purposes of commercial demolition as well as warfare.

Energetic materials (EMs) store large amounts of chemical energy that can be released. The EMs used in commercial and military explosives applications may be classified as primary and secondary explosives. Primary explosives detonate when subject to relatively weak stimuli in the form of heat or shock. A secondary explosive is typically more powerful than a primary explosive, but will require much stronger stimuli for initiation of detonation. In a typical application, a primary explosive will be used to initiate detonation in a more powerful secondary explosive.

Secondary explosives are typically formed by organic molecules. Under ambient conditions, these materials condense to form molecular solids or liquids. Of particular interest for this work are the molecular crystals formed by the secondary explosives PETN, HMX, RDX, nitromethane, and NEST-1.
Pentaerythritol tetranitrate (PETN) is an explosive nitric ester with chemical formula $\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$ and is known to form a molecular crystal with three polymorphs. The polymorph that is stable at ambient conditions is PETN-I, and a phase transition [3] to the second polymorph PETN-II occurs at a temperature [4] of 403 K. The discovery of a third polymorph PETN-III was recently made at high pressure [5]. PETN-I, the stable polymorph at ambient conditions, forms with space group $P\overline{4}2_1c$, and the lattice constants of the tetragonal unit cell [6] are provided in Table I. There are 2 molecules per unit cell, shown in Figure 1, with the total number of atoms per unit cell equal to 58.
1.2.2 HMX

Cyclotetramethylene tetranitramine (HMX) has the chemical formula $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$, and forms molecular solids of at least four polymorphs; $\alpha$-, $\beta$-, $\gamma$-, and $\delta$-HMX. The $\beta$ polymorph is used in explosives applications because it is both stable at ambient conditions and the least sensitive to impact [7]. The space-group symmetry of the $\beta$ polymorph is $P2_1/c$, which forms a monoclinic unit cell. The lattice constants[8] of $\beta$-HMX are listed in Table I. The unit cell is displayed in Figure 2, and it contains two molecules or, equivalently, 56 atoms.
1.2.3 RDX

Cyclotrimethylene trinitramine (RDX) is a molecule specified by $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ that forms solids of three polymorphs; $\alpha$-, $\beta$-, and $\delta$-RDX. The $\alpha$ polymorph is stable at ambient conditions, but a phase transition occurs near 4 GPa to $\delta$-RDX [9-14]. The $\alpha$ polymorph of RDX has the $\text{Pbca}$ space-group symmetry with an orthorhombic unit cell [15]. The lattice constants [15] of $\alpha$-RDX are shown in Table I. The unit cell of $\alpha$-RDX, exhibited in Figure 3, is the largest of the study, holding 168 atoms within a total of 8 molecules.
1.2.4 Nitromethane

Nitromethane molecules are relatively simple for energetic materials, having the formula CH$_3$NO$_2$. Unlike the other materials of this study, nitromethane is a liquid at ambient conditions, but becomes a solid at lower temperature [16] and/or higher pressure [17]. Several studies [17-19] indicate that solid nitromethane does not undergo a phase transition to another polymorph for pressures below approximately 27 GPa, but this has been debated in recent work [20, 21]. Nitromethane forms a solid with $P2_12_12_1$ symmetry at low temperature and ambient pressure. The lattice constants of solid nitromethane are displayed in Table I. The nitromethane unit cell is shown in Figure 4, and it is the smallest of the study, holding only 28 atoms (4 molecules).
1.2.5 NEST-1

In the work [22] revealing its discovery, Chavez et al. call the new explosive nitrate ester 1. We have shortened the name of the material, calling it NEST-1 to be concise. The NEST-1 molecule has a somewhat similar shape to that of PETN, and its chemical formula is \( \text{C}_6\text{H}_8\text{N}_6\text{O}_{16} \). The crystal [22] has a \( P2_1/n \) symmetry with a monoclinic unit cell. The lattice constants [22] of NEST-1 are provided in Table I. The unit cell, illustrated in Figure 5, is relatively large, containing 144 atoms (4 molecules).
1.3 Sensitivity to Shock

One of the common methods to detonate an explosive is through a mechanical shock wave, a very fast compression at high pressure. Energetic materials (EMs) that detonate at relatively low shock pressures are said to be more sensitive to shock, whereas EMs which require much stronger shocks to cause detonation are insensitive to shock. Owing to the fact that explosives can be initiated by different stimuli, such as heat, shock, friction, and electric spark, one must specify the stimulus when discussing sensitivity. For shock compression, experiments have shown that shock sensitivity in an EM can have directional dependence [23, 24].

The energetic material PETN exhibits strongly anisotropic sensitivity to shock. Initiation occurs for compression in one crystallographic direction at approximately 4
GPa [24], while shocks in excess of 30 GPa were needed to detonate the sample in another direction [25]. Meanwhile, other directions exhibit sensitivity between these extremes [24]. An understanding of the difference in the physical properties of PETN when compressed in different directions might contribute to an understanding of anisotropic sensitivity in EMs. On a broader scale, knowledge of the contributing factors to anisotropic sensitivity might help the energetic materials research community gain insight into the elusive microscopic events that precede detonation.

1.4 Theory in EM Research

The use of theoretical techniques allows for the study of atomic-scale events that cannot be resolved in experimental measurements. Further, the freedom of simulation design allows researchers to manipulate systems in ways that are difficult, if not impossible, to accomplish via experiment. Clear advantages of theory also include the reduced expense of research equipment and the use of “virtual” explosives without risk of accidental explosion.

As discussed above, the response of EMs to mechanical compression is an active area of EMs research. A quantum-mechanical theoretical tool, density functional theory (DFT), has been successful in the description of EMs at extreme conditions with exceptional accuracy, and the speed of modern computational technology has allowed this success to be achieved at a reasonable computational expense. On the other hand, the description of explosive molecular crystals by DFT at ambient conditions does not show
the same quality in agreement with experimental data. It is commonly believed that the deficiency of DFT for these materials is the poor description of weak intermolecular interactions. An ambition in modern DFT research is to improve the predictive ability for systems with weak interactions, where the successful accomplishment of the goal will have a great impact on EMs research, along with many other research fields involving soft matter.

1.5 Outline

In Chapter 2, an overview is provided of practical density-functional-theory calculations, covering the salient features of the methods employed in this work. In Chapter 3, a description is given of the method used to empirically account for van der Waals interactions in DFT calculations. Chapter 4 provides an account of hydrostatic-compression simulations, as well as a comparison of DFT calculations with and without the empirical vdW correction for each EM of the study. Chapter 5 discusses the uniaxial-compression simulations and the calculated anisotropic properties that might correlate with sensitivity to shock. In Chapter 6, the conclusions of the research are summarized.
CHAPTER 2  FIRST-PRINCIPLES CALCULATIONS

First-principles calculations approach the study of systems at the atomic level from the fundamental equations of quantum mechanics rather than fitting parameters to empirically describe the system. Hence, first-principles calculations are also called ab initio methods, meaning literally “from the beginning.” The most widely used theoretical tool implemented in first-principles calculations for the ground state of condensed-phase systems is density-functional theory (DFT). Approaches based on DFT have been used in several areas of research, including solid-state and biological physics, chemistry, and materials science. DFT is an attractive tool because it enables the treatment of the many-body electronic problem with feasible cost and reasonable accuracy despite the approximations made in the handling of electron-electron interactions. Further, the advance of computational technology has allowed first-principles DFT calculations to accurately describe systems composed of hundreds of atoms. The method was such a scientific breakthrough that the 1998 Nobel Prize in Chemistry was awarded to Walter Kohn, who provided the recipe for practical calculations using DFT.

In this study, first-principles DFT calculations were performed to provide a quantum-mechanical description of energetic materials (EMs) at extreme conditions. This chapter is aimed to provide the reader with a concise picture of the ideas involved in the theoretical framework of DFT and the practical methods for first-principles calculations
with a specific emphasis on the methods employed in the project. Readers with an interest in a thorough discussion of the methods described below are directed to references with more information on aspects of the first-principles methodology.

2.1 Density-Functional Theory (DFT)

The study of a system at the atomic level begins with the consideration of a system of interacting electrons and nuclei. Contributions to the energy of this fundamental system include the kinetic energy of the electrons $T_e$ and nuclei $T_n$ in addition to the potential energy describing the nuclei-nuclei, electron-nuclei, and electron-electron interactions ($V_{nn}$, $V_{ne}$, and $V_{ee}$, respectively). The Schrodinger equation for this system is

$$\hat{H}\Psi = (\hat{T}_e + \hat{T}_n + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee})\Psi = E\Psi,$$  

(2.1)

where the many-body wavefunction $\Psi$ is an eigenstate of the Hamiltonian operator $\hat{H}$ that yields the energy of the system $E$ as an eigenvalue. Following the Born-Oppenheimer approximation [26], one neglects the kinetic energy $T_n$ of the relatively massive nuclei. Consequently, the electrons are in the instantaneous ground state corresponding to the geometrical arrangement of the surrounding nuclei, and the electrons interact with the static external potential $V_{e,ext}$ of the nuclear configuration. With this consideration, the electron-nuclei interaction can be expressed as [27]
In addition, the Coulomb interaction between nuclei $V_{nn}$ can in many cases be treated classically, and corresponding energy term, referred to as $E_{nn}$ below, is calculated with relative ease.

The electronic terms require a QM treatment, and an approach to the solution is to find the many-body wavefunction for the system of interacting electrons in an external potential. A monstrous difficulty with this problem is that the wavefunction depends on the position of each electron, where the number of coordinates in the wavefunction depends exponentially on the number of electrons in the system. This approach is simply not feasible for systems composed of hundreds of atoms.

2.1.1 Changing the Approach to the Many-Body Problem

Density-functional theory avoids the troubles of the many-body wavefunction by instead approaching the problem with the electron density $\rho = \rho(\mathbf{r})$ of the system, a function of only a single position. The elimination of the dependence on the coordinates of each electron and the potential for linear dependence of calculation cost on system size for DFT provides a tremendous advantage over the many-body wavefunction approach [28].

Hohenberg and Kohn found that the ground-state energy of a system of interacting electrons in an external potential is a unique functional of the electron density

$$V_{ne} = \int d^3 r \ V_{ext}(\mathbf{r}) \rho(\mathbf{r}).$$

(2.2)
A functional maps a function to a number, and in this case the position-dependent function representing the electron density is mapped to the energy via an energy functional

\[ E[\rho] = T_0[\rho] + V_{ee}[\rho] + \int d^3r \, V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + E_{\text{xc}} \tag{2.3} \]

One can find the exact ground-state energy \( E_{GS} \) and the corresponding electron density by minimizing the energy functional with respect to the electron density (taking care to preserve the total number of electrons in the minimization) [28]

\[ E_{GS} = \text{Min}_\rho E[\rho]. \tag{2.4} \]

The missing but vital information is the mathematical form of the functional to find the exact ground-state energy. Combining aspects of the work of Hohenberg and Kohn with the work of Kohn and Sham, the functional can be expressed as

\[
E[\rho] = 2 \sum_i \left\langle \psi_i \left| -\frac{\nabla^2}{2} \right| \psi_i \right\rangle + \frac{1}{2} \int d^3r \, d^3r' \, \frac{\rho(\mathbf{r})\rho'(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \\
+ \int d^3r \, V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + E_{\text{xc}}[\rho]. \tag{2.5}
\]

The first term represents the kinetic energy of independent electrons (with a factor of 2 for spin degeneracy), the second term is the classical Coulomb interaction of the electron density (also termed the Hartree energy), and the third term in the electron-nuclei interaction discussed above. The fourth term is the exchange-correlation (xc) term that is defined are whatever terms are necessary to make (2.5) equal to the exact ground-state energy. Hidden in \( E_{\text{xc}} \) are the terms that are difficult and/or unknown. These include the effects of both exchange and correlation, which contribute to both the kinetic and
potential energies of the electrons [28]. Because the mathematical form of the exact xc functional is not known, approximations for this functional are necessary to make use of the method. Fortunately, these approximations are still able to predict ground-state materials properties with reasonable accuracy.

An important step to lead to practical calculations using this theoretical framework was developed by Kohn and Sham [30]. In their work, the interacting system is replaced by a system of non-interacting electrons, as observed in (2.5), with the same density as the real system. The many-body problem is therefore reduced to single-particle wavefunctions, where $E_{\text{xc}}$ accounts for the missing many-body effects.

2.1.2 Functionals of Exchange and Correlation

The initial xc functional used in DFT calculations was the local density approximation (LDA), where the exchange and correlation of a system is approximated by that of a homogenous electron gas. For an electron density without rapid variation, the xc functional of the LDA can be expressed as an integral [31]

$$E_{\text{xc}}[\rho] = \int d^3r \, \rho(r) \varepsilon_{\text{xc}}(\rho),$$

(2.6)

where $\varepsilon_{\text{xc}}$ represents the energy per electron due to exchange and correlation. Note that the xc energy density, $\varepsilon_{\text{xc}} = \varepsilon_x + \varepsilon_c$, is a sum of the exchange and correlation energies. The LDA was later improved to account for spin in the local spin-density approximation (LSDA), making the xc energy density a function of the density for each spin, $\varepsilon_{\text{xc}}(\rho^\uparrow, \rho^\downarrow)$. 
Going a step beyond using the local approximation, corrections to the LSDA functional for both exchange and correlation have been developed to include the magnitude of the gradient of the density $|\nabla \rho|$. With these corrections, the xc energy density takes the form $\varepsilon_{xc}(\rho^\uparrow, \rho^\downarrow, |\nabla \rho^\uparrow|, |\nabla \rho^\downarrow|, \ldots )$. Several gradient-corrected functionals exist, each showing strengths for certain types of systems (see Refs. [27, 31] and references therein).

The explicit mathematical expressions used for exchange and correlation, as found in Ref. [27] (Chapter 8 and Appendix B), are quite complex. For the purposes of this study, it suffices to mention that the expressions for exchange and correlation depend on the local density, where the addition of the density gradient dependence introduces a semilocal approximation. Meanwhile, the weak intermolecular interactions prevalent in molecular crystals are insufficiently described by these functionals because of their nonlocal character. The method introduced to remedy the DFT calculations in this study is discussed in Chapter 3.

2.2 Methods for Practical Calculations

To make use of DFT, approximations and other “tricks” must be introduced to make the solution process feasible. Several of these important considerations for practical DFT calculations are briefly discussed below. For a more thorough discussion of the methods used in the solution of the KS equations, see Ref [27].
2.2.1 Self-Consistent Solution of KS Equations

The independent-electron equations of Kohn and Sham must be solved numerically by finding the electron density and effective potential that are consistent. In the solution process [27], an initial guess is made for the spin-dependent density of electrons, $\rho^\uparrow(r)$ and $\rho^\downarrow(r)$. From this input density, an effective potential is calculated from the electron density [27],

$$V_{\text{eff}}^\sigma = V_{\text{ext}}(r) + V_{\text{Hartree}}[\rho] + V_{\text{xc}}[\rho^\uparrow, \rho^\downarrow].$$  \hspace{1cm} (2.7)

and used in the Kohn-Sham (KS) equation [27],

$$\left[ -\frac{\nabla^2}{2} + V_{\text{eff}}^\sigma (r) \right] \psi_i^\sigma(r) = e_i^\sigma \psi_i^\sigma,$$  \hspace{1cm} (2.8)

to solve for independent-electron states. Note that the dependence of the potential terms on spin have been denoted with the superscript $\sigma$. From the independent-electron wavefunctions, the output electron density may be calculated as

$$\rho^\sigma(r) = \sum_i f_i^\sigma |\psi_i^\sigma(r)|^2,$$  \hspace{1cm} (2.9)

where $f_i^\sigma$ denotes the occupation of the corresponding state [27]. At this step in the solution process, the guessed input density may be compared with the output density to check for self-consistency. In the event that input and output densities are not equal within a desired tolerance, a strategic “guess” (see Ref. [27], Chapter 9 for details) is made for the subsequent input density. When the input density sufficiently matches the
output density, self-consistency is reached. From the self-consistent solutions, the output quantities of interest such as energy, forces, stress, and eigenvalues are calculated.

Reaching self-consistency does not truly occur in practical calculations because it is both expensive and unnecessary to continue the solution process until the input and output densities are exactly the same. For practical purposes, the densities must match within a tolerance value, usually specified by a user within DFT computer codes. This tolerance is typically in the form of an energy value, wherein the solution is acceptable when the difference in energy between the input and output densities is less than the specified tolerance.

2.2.2 Wavefunctions of Independent Electrons

DFT requires the consideration of the electron density rather than the many-body wavefunction, but wavefunctions are not disregarded completely. The calculation of independent-electron wavefunctions is clearly needed for the solution of the Kohn-Sham (KS) equations. Different approaches exist for the solution of the KS equations, and a manner of classifying the methods is through the type of basis used for expansion of the independent-electron wavefunctions. The expansion of a wavefunction in a basis can be performed in a number of ways, but a convenient choice for solids is to have an orthonormal basis set that obeys periodic boundary conditions. Plane waves are a widely used basis set for DFT calculations of solids, and their use provides several advantages. Some of the benefits include completeness, the same treatment of all space, the
independence of the basis on atomic positions, simplicity in mathematical form and in the
calculation of derivatives in reciprocal space, and the ease by which convergence can be
achieved [32].

The Fourier expansion of such a wavefunction yields the desired plane-wave
expansion [27],

\[ \psi_i(r) = \sum_q c_{i,q} \times \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{q} \cdot \mathbf{r}) \equiv \sum_q c_{i,q} \left| \mathbf{q} \right\rangle \] (2.10)

Exploiting the orthonormality of the basis set yields a Schrödinger equation for each
eigenstate [27],

\[ \sum_q \langle \mathbf{q} | \hat{H} | \mathbf{q} \rangle c_{i,q} = \varepsilon_i \sum_q \langle \mathbf{q}' | \mathbf{q} \rangle c_{i,q} = \varepsilon_i c_{i,q}'. \] (2.11)

By defining \( \mathbf{q} = \mathbf{k} + \mathbf{G}_m \) and \( \mathbf{q}' = \mathbf{k} + \mathbf{G}_{m'} \), where \( \mathbf{G} \) is a lattice vector in reciprocal
space, the Schrödinger equation can be written for a point \( \mathbf{k} \) in reciprocal space as [27]

\[ \sum_{m'} \left( \frac{1}{2} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}) \right) c_{i,m'} = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}). \] (2.12)

A difficulty that must be faced is the large number of plane waves that are
required to describe a rapidly varying wavefunction. Such variations occur in the region
of the core electrons, near the nucleus of an atom. Fortunately, pseudopotential methods
have been developed, and a benefit of these methods is that the variation of the
wavefunction is “smoothed out” near the nucleus. As a result, fewer plane waves are
required for the calculations. The pseudopotentials smooth the variations by forming an
effective potential that incorporates the effects of both the core electrons and nuclei.
Because of the relatively insignificant contribution of the core states to chemical bonding and other properties of the solid state [33], pseudopotentials are great approximations for DFT calculations that possess the additional advantage of reducing the computational expense of calculations. A number of methods exist to form these potentials, and a summary of these techniques may be found in Ref. [27], Chapter 11.

With plane waves, the convergence of a physical quantity calculated from the DFT formalism can be achieved simply by increasing the number of plane waves in the basis until the quantity no longer varies or, in practice, varies less than a desired error with increased cutoff. With the proper treatment to produce a wavefunction without rapid variation, the wavefunction can effectively be expanded in a finite number of plane waves. Noting that regions of rapid variation of the wavefunction are characterized by high kinetic energy, a maximum kinetic energy, typically called the cutoff energy, can be set to indicate the magnitude of the maximum wavevector used in the expansion of the wavefunction. The cutoff energy and the maximum wavevector are related by the expression [33]

\[ E_C = \frac{\hbar^2}{2m}(k + G)^2 \]  \hspace{1cm} (2.13)

which is the energy of a free electron with the corresponding wavevector.
2.2.3 Calculation of Physical Quantities

The calculation of several important physical quantities such as the energy per unit cell requires the integration over a continuous variable \( k \) within the Brillouin zone. Fortunately, these integrals can effectively be reduced in most cases to an average over a small number of \( k \)-points without much loss on accuracy. The number of points needed for accurate integration is greater for integrands with rapid variation. For insulators such as those of this study, the bands are filled, and integration can be done with a small number of “special points”. For metals, many more points are needed to sufficiently sample the Fermi surface, where the occupation of bands changes quickly.

There are several methods for the calculation of special points for the use of integration within the Brillouin zone [34]. Overall, the methods are aimed to use crystal symmetry to approximately find the point where the integral and integrand are equal [27]. A popular choice is the Monkhorst-Pack method [35], which is convenient because the special points can be found for any crystal type with a simple formula [27]:

\[
k_{n_1,n_2,n_3} = \sum_i \frac{2n_i - N_i - 1}{2N_i} \mathbf{G}_i
\]  

(2.14)

The sum is performed over three dimensions, where \( \mathbf{G}_i \) are the lattice vectors in reciprocal space. These points form a uniform grid of \( N_1 \times N_2 \times N_3 \) points in reciprocal space that is translated off of the \( \Gamma(k = 0) \) point.

The forces and stress in a system are important physical quantities to extract from DFT calculations. The force conjugate to any parameter within the Hamiltonian of a
system may be calculated with the Hellman-Feynman theorem [27, 36]. The force on an atom and the stress tensor from first-principles can be found from derivatives of the energy with respect to atomic coordinates and strain components, respectively. The force on atom $I$ can be found by the derivative of the energy with respect to the coordinates of atom $I$ [27]:

$$F_I = -\frac{\partial E}{\partial \mathbf{R}_I}$$

(2.15)

Separating the terms in the energy that require a quantum-mechanical treatment into the Hamiltonian $\hat{H}$ and the energy of the classical nuclei-nuclei interaction $E_{nn}$, the expression for the force on an atom $I$ in the ground state can be written as [27]

$$F_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \mathbf{R}_I} \right| \Psi \right\rangle - \frac{\partial E_{nn}}{\partial \mathbf{R}_I}.$$

(2.16)

This expression is a result of first-order perturbation theory, where the derivatives of the wavefunction $\Psi$ with respect to the atomic coordinate $\mathbf{R}_I$ vanish in the ground-state because the wavefunction is at extrema with respect to variations in the parameters describing the system [27]. Similarly, a system in equilibrium will have a stress calculated by taking the derivative of the energy with respect to strain per unit volume,

$$\sigma_{ij} = -\frac{1}{V} \frac{\partial E}{\partial \epsilon_{ij}},$$

(2.17)

where $\epsilon_{ij}$ is given by the scaling $\mathbf{r}_i$ to $(\delta_{ij} + \epsilon_{ij})\mathbf{r}_i$.

The numerical differentiation of the energy to calculate the forces and stress in this study is accomplished within the routines of the VASP computer code [37].
The commonly used exchange-correlation functionals of the local density approximation (LDA) and the generalized gradient approximation (GGA) do not yield the correct asymptotic behavior of long-range interactions. The improper description of these interactions by DFT gives poor results for the structure of sparse systems, where long-range interactions are vital for structure determination. Examples of sparse systems that are poorly described by DFT include molecular crystals, vdW complexes, proteins, DNA, and other biomolecules. Energetic materials, which are usually molecular crystals at ambient conditions, fall into this category, and DFT results for these systems with LDA and GGA functionals are insufficiently accurate [38]. For example, the unit-cell volumes of energetic materials are predicted with an error of roughly 10% [38]. Owing to the fact that several important properties of materials such as the detonation velocity are functions of the density (or powers of the density), the error in volume prediction desired by experimentalists is less than 1% [38].

The cause of the error for sparse systems is commonly believed to be due to long-range interactions. Because the commonly used xc functionals depend on the local or semilocal density, only effects at this range are well described. For neutral systems, an important long-range interaction that cannot be described by common DFT functionals is
dispersion, and the resulting intermolecular forces are typically called van der Waals forces or London forces.

\section{3.1 Dispersion Interactions}

Dispersion forces are a quantum-mechanical effect where fluctuations in electron density separated in space interact with one another. These forces are a type of polarization force between molecules in that their origin is from the polarization of one molecule by another \cite{31} and can be expressed by second-order Rayleigh-Schrödinger perturbation theory (see Ref \cite{31}, Section A3.3).

The dispersion interaction can be expressed as a multipole expansion of the form \cite{31}:

\begin{equation}
E_{\text{dispersion}} = - \sum_{n=6}^{\infty} \frac{C_n}{r^n}, \tag{3.1}
\end{equation}

where the sum includes only even powers of $r$ for interacting atoms separated by the interatomic distance $r$. The values of $C_n$ are termed the dispersion coefficients.

An important consideration is that the leading term that describes instantaneous dipole-dipole interactions can account for most of the dispersion interaction. In fact, at separations of about 10 bohr (~5.3 Å), the error introduced by using the dipole-dipole term is less than 20\% \cite{31}, and the error decreases at larger separations.
3.2 Empirical van der Waals Correction to DFT Calculations

Two common methods are employed to treat vdW forces in DFT calculations: the first-principles approach and the empirical approach. First-principles approaches [39-51] maintain the “spirit” of DFT calculations by avoiding any fitting to experimental data, and this approach shows great promise. However, first-principles methods for a dispersion correction to DFT are currently too expensive for large systems. Further, the results from first-principles approaches have not shown a significant increase in accuracy that would justify the computational expense. On the other hand, the empirical approach [2] has recently been shown to significantly improve the accuracy of calculations involving molecular crystals [2] at a much smaller cost than first-principles methods. Although the empirical method deviates from the first-principles methodology and requires experimental data, it is currently able to predict unit-cell volumes within an error that the first-principles methods are still striving to achieve.

In this work, an empirical approach based on the work of Neumann and Perrin [2] is used for the simulation of energetic materials. For the molecular crystals in their study, the average error in the prediction of unit-cell volume was reduced from 20.4% by pure DFT to about 1% with the empirical vdW correction [2]. This result is a significant improvement over previous works on the use of empirical vdW corrections for the prediction of equilibrium unit-cell structures of molecular crystals.
Following the work of Neumann and Perrin [2], the salient points of the approach are summarized below. The total energy of the unit cell is a sum of two parts, the energy calculated by DFT and the energy from the vdW correction [2]

$$E_{\text{total}} = E_{\text{DFT}} + E_{\text{vdW}}.$$  \hfill (3.2)

The Vienna Ab Initio Simulation Package (VASP) [37, 52] is a DFT code used to calculate the energy and its derivatives for the DFT component. Although VASP is treated as a “black box” in the calculation method, the parameters for calculations must be chosen properly. The details of the VASP parameters used in this work are provided in Chapter 4.

The dispersion component of the approach $E_{\text{vdW}}$ is formed by interaction potentials between pairs of atoms [2]:

$$E_{\text{vdW}} = \sum_i \sum_j \sum_k \frac{1}{2} v_{t_i,t_j}(r_{i,j,k}).$$  \hfill (3.3)

The first two sums include the atoms within the unit cell, and the third sum includes all real-space lattice vectors. The primed sum is an indication that the self-interaction $(i = j; k = 0)$ must be avoided, and the factor $(1/2)$ is introduced to avoid double counting. The pair potentials depend on the type of the interacting atoms $t_i$ and $t_j$, and the type depends on both the atomic number of the atom and the number of its covalent bonds. The interatomic distance $r_{i,j,k}$ is specified as the distance between atom $i$, translated by the lattice vector $k$, and atom $j$. Only atoms separated by 18 Å or less are considered in order to truncate the infinite sum, and a spline function brings the potentials to zero smoothly between 15 and 18 Å.
The pair potentials are formed by a product of two terms [2]:

\[ v_{AB}(r) = d_{AB}(r) \frac{C_{6,AB}}{r^6}. \]  

(3.4)

The leading term in the multipole expansion of the dispersion interaction is \( C_{6,AB}/r^6 \) (referred to as the dispersion term below), and it is multiplied by a damping function that controls the distance-dependent influence of the vdW pair potential. At long distances, the dispersion term alone properly describes the asymptotic behavior, and the damping function appropriately takes a value of one. At short distances, the damping function must prevent the divergence of the dispersion term. A breakthrough of the approach is the improvement of the damping function at intermediate distances. Because the GGA functionals PW91 [53, 54] and PBE [55] can provide an accurate description of short-range interactions consistent with ionic and covalent bonds, it is crucial for the vdW correction potential to properly “turn on” at longer distances where the GGA functional description begins to fail. The damping function takes the form [2]

\[ d_{AB}(r) = \left( 1 - \exp \left[ - \left( \frac{r}{R_{AB}} \right)^{3/n} \right] \right)^{2n}, \]  

(3.5)
where the form factor $n$ was introduced to add flexibility to the similar potential by Mooij et al. [56] used in a previous empirical vdW approach [57]. The parameter $R_{NN}$ is the crossover distance, and it denotes the interatomic distance where the dispersion term intersects the constant value taken by the pair potential at very small interatomic
distances. In Figure 6, the empirical vdW pair potential for interacting nitrogen atoms is shown to illustrate the influence of the damping function.

The number of fitting parameters is reduced by simple rules to calculate heteroatomic parameters from homoatomic parameters. For the crossover distances, the values for different atoms of type A and B are found by the average of the homoatomic values according to [2]

$$R_{AB} = \frac{1}{2}(R_{AA} + R_{BB})$$ (3.6)

The heteroatomic $C_6$ coefficients are calculated from homoatomic $C_6$ coefficients via the combination rule [2]

$$C_{6,AB} = \frac{2(C^2_{6,AA}C^2_{6,BB}N_{eff,A}N_{eff,B})^{1/3}}{(C^2_{6,AA}N^2_{eff,B})^{1/3} + (C^2_{6,BB}N^2_{eff,A})^{1/3}}$$ (3.7)

devised by Wu and Yang [57]. The effective number of electrons is represented by the parameter $N_{eff}$, and these values are taken from the work of Halgren [58].

The empirical nature of the correction is in the fitting of the parameters $C_6$, $n$, and $R_{AR}$ to experimental data. Using the molecular $C_6$ coefficients calculated from the dipole oscillator strengths measured by Meath and co-workers [59-64], a form is made for the calculation of atomic $C_6$ coefficients assuming that molecular coefficients simply added [2]:

$$C_{6,\alpha\beta} = \sum_{i\in\text{molecule} \alpha} \sum_{j\in\text{molecule} \beta} C_{6,i,j}$$ (3.8)
The molecules are denoted by the Greek subscripts \( \alpha \) and \( \beta \), and the molecular \( C_6 \) coefficients are formed by a sum over the \( C_6 \) coefficients for interacting atoms on the different molecules. Using this form and the combination rule, the homoatomic \( C_6 \) coefficients are found by minimizing the function [2]

\[
F = \sum_i \left( \frac{C_{6, \text{calculated},i} - C_{6, \text{experiment},i}}{C_{6, \text{experiment},i}} \right)^2.
\]  

(3.9)

The crossover distances and the form factor are fit by a single quantity that accounts for the difference in both lattice constants and angles as compared to experimental structures [2]. The fitting procedure is covered in detail in the appendix of Ref. [2], but a brief explanation is provided below.

A transformation between predicted and experimental lattice vectors is cleverly formed by a product of a rotation matrix and a symmetric matrix with orthogonal eigenvectors. The eigenvalues \( d_i \) of the symmetric matrix represent compressions along the corresponding orthogonal eigenvectors, and the rotation matrix does not alter the unit-cell geometry. From the eigenvalues \( d_i \), a quantity is defined as [2]

\[
\Delta = \frac{1}{2} \left( \sum_{i=1}^{3} |d_i - 1| + \sum_{i=1}^{3} \left| \frac{1}{d_i} - 1 \right| \right)
\]  

(3.10)

to represent the difference between the predicted and experimental lattice. Essentially, the crossover distances and the form factor are determined by the minimization of \( \Delta \) for the molecular crystals of the study. The experimental data set includes the unit-cell structures of 31 molecular crystals obtained at low-temperature [2].
The homoatomic parameters used for the model are shown in Table II [2, 58].

Note that heteroatomic parameters can be calculated from the values shown. The $C_6$ coefficients depend on the atom type, which includes both the chemical element and the number of its covalent bonds. Only one type was used for nitrogen because of limited availability of experimental data for molecules containing nitrogen [2]. The crossover distances and effective electron numbers, however, depend only on the chemical element. For all interactions, the form factor $\eta=0.25$ was used.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Number of covalent bonds</th>
<th>Homoatomic $C_6$ coefficient (eV Å$^6$)</th>
<th>Homoatomic crossover distance $R$ (Å)</th>
<th>Effective number of electrons, $N_{eff}$</th>
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</thead>
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<tr>
<td>Carbon</td>
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<td>3.884</td>
<td>2.49</td>
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<td>3.15</td>
</tr>
<tr>
<td>Oxygen</td>
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<td>2.837</td>
<td>3.15</td>
</tr>
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<tr>
<td>Hydrogen</td>
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<td>3.200</td>
<td>0.8</td>
</tr>
</tbody>
</table>
CHAPTER 4 HYDROSTATIC-COMPRESSION SIMULATIONS OF ENERGETIC MATERIALS

The application of hydrostatic pressure to a system is analogous to the compression of a static fluid, wherein shear stresses are absent and the compressive stresses, i.e. the diagonal stress-tensor elements, are equal. The application of hydrostatic pressure to a material may be used to investigate its equation of state (EOS), a relation between thermodynamic state variables such as the pressure, volume, and temperature of the material. The EOS of a material is of critical importance for a multitude of practical problems. For energetic materials, an example application of the EOS from hydrostatic-compression data it allows one to calculate the bulk modulus and its pressure derivative, which can be used to calculate the linear relationship between shock and particle velocities for weak shocks in a material [1]. For this study, the temperature will be restricted to 0 K because DFT is a ground-state theory. Hence, this work involves the simulation of hydrostatic compression on PETN, HMX, RDX, nitromethane, and NEST-I to calculate the isothermal EOS, relating pressure and volume. Also investigated are the pressure-induced structural changes in the unit cell.
4.1 Previous Work

The hydrostatic compressions of PETN, HMX, RDX, and solid nitromethane have been performed in both experimental and theoretical studies by other research groups. A brief review of the relevant previous works is provided in the following subsections.

4.1.1 Experimental

Hydrostatic compression experiments on the EMs of interest have been carried out using diamond anvil cells. In the experiments, a very small sample is placed inside of a hole drilled in a metal gasket along with a pressure-distributing medium that (ideally) creates hydrostatic conditions under pressure. The pressure is applied by diamond anvils on either side of the sample/medium mixture. X-rays can pass through the apparatus at desired pressures for analysis of the sample.

Hydrostatic compression experiments on PETN up to 10 GPa at room temperature were completed by Olinger et al. [12]. Yoo et al. [14] also studied the hydrostatic compression of PETN, extending the pressure up to 15 GPa.

Experiments of hydrostatic and non-hydrostatic compression on HMX have been performed by Yoo and Cynn [65], and later by Gump and Peiris [66]. Yoo and Cynn argued from their x-ray diffraction and Raman spectroscopy results that HMX undergoes
a phase transition at the pressures of 12 and 27 GPa from $\beta$-HMX to $\epsilon$- and $\varphi$-HMX, respectively [65]. A lower pressure regime up to 5.8 GPa was studied in the experiments of Gump and Peiris, where HMX remained in the beta phase during the application of hydrostatic pressure at 30, 100, and 140 °C [66]. However, their samples converted to the $\delta$ phase upon decompression.

Olinger et al. [13] and Yoo et al. [14] have reported the isothermal EOS of RDX from experiments of hydrostatic compression. Both studies observed phase transitions near 4 GPa from $\alpha$- to $\gamma$-RDX [13, 14]. The transition has been investigated with Raman spectroscopy experiments by Ciezak et al. [9] and Dreger and Gupta [11]. The structure of the $\gamma$-polymorph was recently identified by Davidson et al [10].

The EOS has been reported from experiments of hydrostatic compression on solid nitromethane done by Cromer et al. [17], Yarger and Olinger [19], and Citroni et al. [18]. Cromer studied compression up to 6.0 GPa, Yarger and Olinger up to 15 GPa, and Citroni et al. up to 27.3 GPa, nearly approaching the detonation threshold pressure[17-19]. Each of the studies report that solid nitromethane maintains its crystal symmetry throughout its respective pressure range. However, Courtecuisse et al. [20] have reported X-ray diffraction results indicating solid-solid phase transitions at approximately 3, 7.5, 13.2, and 25 GPa. It has been argued [21] that these results are indicative of changes in molecular structure rather than phase transitions.
4.1.2 Theoretical

Modeling techniques have also been employed to study the hydrostatic compression of PETN, HMX, RDX, and nitromethane.

DFT calculations to simulate the hydrostatic compression of PETN have been performed by Gan et al. [67] and Byrd and Rice [68]. In the work of Gan et al., the PBE xc functional was used with a Gaussian basis set [67]. Byrd and Rice have studied the compression of PETN (as well as HMX, RDX, and other important EMs) with a plane-wave basis using the PW91, PBE, and LDA xc functionals at different energy cutoffs [68]. Hydrostatic compression has also been modeled at the Hartree-Fock level by Brand [69].

Several theoretical investigations of the hydrostatic compression of HMX have been reported in the literature. Using a rigid-molecule approximation and classical interatomic potentials fit to near-ambient conditions, Sewell [70] has completed Monte Carlo simulations of beta HMX under hydrostatic pressures up to 7.5 GPa. Sorescu et al. [71] have performed molecular-packing and molecular-dynamics simulations on HMX, as well as RDX, under hydrostatic compression with the constraint of a rigid-molecule approximation. Another study by Sewell [72] investigated the compression of the pure phases of HMX via molecular dynamics calculations, predicting the isotherms and elastic moduli for each polymorph. Hartree-Fock calculations of compression on HMX have been done by Zerilli and Kuklja [73]. DFT studies of hydrostatic compression of HMX have also been executed with the LDA xc functional up to 40 GPa [74].
As mentioned above, Byrd and Rice [68] have performed hydrostatic compression simulations on HMX and RDX. While theoretical investigations of HMX are abundant, the size of the RDX unit cell is most likely a source for the low number of calculations involving hydrostatic compression for this EM. The computational expense for first-principles calculations of systems as large as RDX is prohibitive.

In contrast to RDX, solid nitromethane has a very small unit cell, and is commonly regarded as a prototype EM for simulation. The hydrostatic compression of nitromethane was studied via Hartree-Fock calculations by Zerilli [75] and with DFT by Liu et al. [76] up to 20 GPa. Reed et al. [77] have performed extensive DFT calculations on solid nitromethane, which include hydrostatic compression up to very high pressures.

The uniqueness of the calculations of the present study for EM research is the implementation of the vdW correction into DFT codes to study these important systems both at equilibrium and under hydrostatic compression. The lacking proper description of dispersion forces in DFT has been noted for EMs and other molecular crystals at low pressure, and the empirical vdW correction has been shown to remedy the predictive ability of DFT for systems such as nitromethane [2]. However, the agreement of results with the vdW correction has not been studied for other EMs, and has not been studied for any molecular crystals under hydrostatic pressure. Through the comparison of the vdW-corrected results with both pure DFT and experiment, the ability of the empirical correction to properly describe dispersion effects with pressure can be investigated. Further, the hydrostatic-compression calculations serve as a method to assess the predictive ability of our DFT approach because experiments have been performed with data available for comparison. However, it is not possible to compare the physical
quantities obtained from the uniaxial-compression simulations described in Chapter 5 (page 61) with experiment, simply because they either have not been performed or experimental techniques were not used (or in existence) to probe the quantities of interest.

Some of the results below have appeared in previous publications [78-80] and are shown below with permission where appropriate.

4.2 Computational Details

The first-principles DFT [29, 30] calculations to model hydrostatic compression were performed for the EMs using the Vienna Ab-Initio Simulation Package (VASP) [37, 52]. Tests were completed to determine the parameters of the calculations that would provide sufficient accuracy while minimizing computational expense. Parameters that significantly contribute to the accuracy of the results include the exchange-correlation functional, pseudopotential, k-point set, and energy cutoff.

The combination of exchange-correlation functional and pseudopotential was chosen to provide the best agreement with experimental structure. The functionals tested were the PW91 [53, 54] and PBE [55, 81] functionals. Both functionals were tested with the PAW potentials [82, 83] as implemented in VASP, and the PW91 functional was also tested with ultra-soft pseudopotentials (USPs) [84, 85]. In the initial tests, each combination of functional and potential was used in the relaxation of the experimental structure of PETN. The parameters of each relaxation included a reasonably high energy cutoff of 1,000 eV and Monkhorst-Pack (MP) grid of 2x2x2 (spacing: 0.07 Å⁻¹). For
these calculations and all others in the study, an energy tolerance of $10^{-6}$ eV was used as the criteria for self-consistent solution of the Kohn-Sham equations. The PBE functional with the PAW potential showed the best agreement with experiment, and this combination was chosen for the DFT component of all calculations.

Tests were subsequently performed to determine the k-point sampling density for the calculations. The k-point sampling was tested first by setting the energy cutoff to the high value of 1,000 eV and executing total-energy calculations on the experimental structure, both at 50% volume compression and without compression. The half-compressed structure was constructed by scaling the lattice constants by $0.5^{1/3}$ and keeping the atoms in fractional coordinates. The rationale for the tests at the two compressions is that the Brillouin zone expands when its real-space counterpart is compressed, and the k-point sampling density for a fixed number of k-points will decrease with compression. The tests were aimed to be sure that the accuracy of the calculations was sufficient for all compression values of the study. For PETN, it was found that an average k-point sampling density of 0.08 Å$^{-1}$ at half compression yielded convergence by less than 1 meV in energy per atom and 0.05 GPa in pressure. The other EMs of the study yielded similar convergence results, and the average sampling density of 0.08 Å$^{-1}$ at half-compression was used to determine the MP grid for the hydrostatic-compression simulations of each EM in the study.

Kinetic-energy cutoff tests were performed with the parameters specified above to find the minimum plane-wave basis set that provided sufficient accuracy. Total energy calculations of the experimental structures at ambient conditions were performed at cutoff values of 400, 500, 700, and 1,000 eV. The 700 eV calculation for PETN gave
convergence better than 0.4 GPa in pressure and 1.5 meV per atom in energy. Similar convergence values were obtained for the other EMs of the study at an energy cutoff of 700 eV, which was the cutoff chosen for the hydrostatic-compression simulations of the work. The chosen cutoff is 1.75 times larger than the default cutoff specified by the PAW potentials in VASP, which is usually necessary for molecular crystals to obtain sufficient convergence.

The experimental structures of each EM were relaxed via the conjugate gradient algorithm as implemented in VASP to obtain the theoretical equilibrium structure. In the energy minimization, the unit cell volume, shape, and symmetry as well as the atomic coordinates were allowed to relax until the maximum force on any atom was less than 0.03 eV/Å. It is expected that the error from the choice in force tolerance is much smaller than the error from the chosen energy cutoff.

The hydrostatic-compression simulations were completed by scaling the volume of the unit cell in increments of 2% from the calculated equilibrium volume $V_0$ to $V/V_0 = 0.60$. At each step, the conditions of hydrostatic pressure were simulated by holding the unit-cell volume constant while relaxing the atomic coordinates and unit-cell shape. In the relaxations, the symmetry of the unit cell was not constrained.

### 4.3 Equilibrium Properties

The calculated equilibrium structures for PETN, HMX, RDX, solid nitromethane, and NEST-1 using both pure DFT and the empirical vdW correction are displayed in
Table III: Comparison of Experimental and Calculated Equilibrium Unit-Cell Volumes

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental</th>
<th>Pure DFT</th>
<th>Pure DFT %error</th>
<th>DFT-vdW</th>
<th>DFT-vdW %error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETN-I</td>
<td>589.50 (Ref. [6])</td>
<td>620.11</td>
<td>+5.2%</td>
<td>567.27</td>
<td>-3.8%</td>
</tr>
<tr>
<td>β-HMX</td>
<td>519.39 (Ref. [86])</td>
<td>556.07</td>
<td>+7.1%</td>
<td>500.77</td>
<td>-3.6%</td>
</tr>
<tr>
<td>α-RDX</td>
<td>1633.86 (Ref. [15])</td>
<td>1775.95</td>
<td>+8.7%</td>
<td>1591.21</td>
<td>-2.6%</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>275.31 (Ref. [16])</td>
<td>304.22</td>
<td>+10.5%</td>
<td>270.00</td>
<td>-1.9%</td>
</tr>
<tr>
<td>NEST-1</td>
<td>1456.01 (Ref. [22])</td>
<td>1649.48</td>
<td>+13.3%</td>
<td>1464.18</td>
<td>+0.6%</td>
</tr>
</tbody>
</table>

Table III along with the percent error as compared to the experimental volumes. The unit-cell volumes predicted by pure DFT (GGA-PBE) are approximately 9% larger on average than experiment. As described in Chapter 3, it is commonly believed that a poor description of vdW forces within GGA xc functionals is the main source of the error in the prediction of equilibrium structures for molecular crystals, where intermolecular forces are significant. With the vdW correction, the calculated unit-cell volumes are less than experiment by 2.3% on average.

### 4.4 Hydrostatic-Compression Results

From the hydrostatic-compression simulations, the isothermal equation of state (EOS) and bulk moduli were calculated. The lattice constants were also calculated as a
function of pressure. The results from the simulations are compared with experimental data for PETN, HMX, RDX, and nitromethane.

4.4.1 Isothermal Equation of State

The isothermal EOS of PETN is shown in Figure 7 and compared with the experimental data of Olinger et al. [12]. With respect to the experimental data, the
The EOS for HMX is displayed in Figure 8 with the results of two hydrostatic compression experiments [65, 66]. In the low-pressure regime, the volume of the unit cell at a given pressure is overestimated by pure DFT and underestimated by the vdW correction when compared to the experimental data. For the study by Yoo and Cynn [65], the vdW results appear to agree well at pressures between 5-25 GPa. The discrepancy in agreement is clearly increased with the addition of the vdW correction. The EOSs from some other experiments are not provided because volume ratios ($V/V_0$) were reported in the absence of absolute volumes and/or equilibrium volumes.

Figure 8: Isothermal EOS for β-HMX.
between all DFT calculations and experiment at higher pressures increases, most likely because of a phase transition[65] to φ-HMX near 27 GPa. This phase transition was measured to have a 4% change in unit-cell volume [65]. In fact, another phase transition was predicted at 12 GPa, but the resulting change in volume was negligible [65]. From the simulation data, no phase transitions were observed: the space-group symmetry remains the same for all structures during the compression.

The EOS for RDX is provided in Figure 9, along with the data from the experiments of Olinger et al. [13]. Below the phase-transition pressure of 4 GPa, the
agreement of the EOS with experiment is improved with the addition of the vdW correction. The experimental data show a reduction in unit-cell volume after the transition, however the transition was not observed in the simulation.

The EOS for solid nitromethane is displayed in Figure 10, and experimental data from Refs. [17-19] are shown for comparison. At low pressure, the vdW-corrected DFT data appear to agree well with the experimental data [17, 18] of Citroni et al. and Cromer et al., but the pure DFT data show better agreement with the data [19] of Yarger et al. At pressures above 10 GPa, however, the Citroni and Yarger experiments approach the EOS
calculated with pure DFT by showing a greater pressure at a given volume. Meanwhile, the Cromer experiment shows the opposite trend, yielding a significantly smaller pressure at a given volume. As discussed in Ref [19], the greater compressibility measured by Cromer et al. might be a result of the geometrical alignment of the x-ray beam along the axis of the diamond anvil cell.

The EOS for NEST-1 is shown in Figure 11. There are no known hydrostatic compression experiments for comparison. Based upon the results for the other systems, it is likely that the experimental data will reasonably agree with the results obtained from

Figure 11: Isothermal EOS of NEST-1.
the vdW calculations provided that NEST-1 does not undergo a phase transition in the pressure interval studied.

4.4.2 Lattice Changes Under Pressure

The lattice parameters of PETN as a function of pressure from the hydrostatic-compression simulations are compared with experimental data [12] in Figure 12. Below 5
50 GPa, the vdW-corrected DFT data show better agreement with experiment than pure DFT. Above 5 GPa, the pure DFT data for the lattice constant $a$ appears to show slightly better agreement than the vdW-DFT data. On the other hand, vdW-DFT clearly shows better agreement with experiment for the $c$ lattice constant.

The calculated and experimental [65, 66] lattice constants of HMX are shown in Figure 13. It is difficult from the plot to evaluate the improvement in agreement obtained with the use of vdW-DFT. The predictions for the $a$ and $c$ lattice constants via both methods are in similar agreement with experiment. The vdW-DFT data appear to agree
slightly more with the experimental data of Yoo and Cynn, while the pure DFT look to agree more with pure DFT. A similar trend is shown for the EOS calculation in Figure 8.

The calculated lattice parameters of RDX are displayed in Figure 14 along with experimental data from Ref [13]. The vdW-corrected data clearly show better agreement with experiment than pure DFT for the $a$ and $c$ lattice constants up to the phase-transition pressure of about 4 GPa. Meanwhile, the agreement for both calculation methods is similar for the $b$ lattice constant up to about 4 GPa. Overall, the vdW correction yields pressure-dependent lattice constants with better average agreement that pure DFT.
The calculated lattice constants of solid nitromethane are displayed in Figure 15 along with experimental data [17-19]. The $b$ lattice constant calculated with the vdW correction agrees more with the experimental data than pure DFT, but the opposite is true for the $c$ lattice constant. Meanwhile, both calculation methods predict the lattice constant $a$ in good agreement with experiment. Similar to the case of HMX, an evaluation of the improvement in the prediction of lattice constants of nitromethane provided by the vdW correction is difficult to assess.

The calculated lattice constants $a$ and $c$ of NEST-1 from the hydrostatic-compression simulations are displayed in Figure 16. Owing to the larger length of lattice
constant $b$, it was plotted separately in Figure 17. As mentioned above, there are currently no experimental data available for comparison.
4.4.3 Bulk Moduli

The bulk modulus is defined as $B = -V \left( \frac{\partial P}{\partial V} \right)$, and it is a measure of the stiffness of a material. The bulk modulus and its derivative with respect to pressure can be calculated by fitting hydrostatic compression data to equations of state for pressure as a function of volume. The bulk moduli for each EM of the study were calculated by fitting $(V, P)$ data to three common equations of state; the Birch-Murnaghan, Murnaghan, and Vinet EOS forms. The Birch-Murnaghan equation is given by
the Murnaghan equation is given by

\[ P = \frac{3}{2} B_0 \left[ \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} - \left( \frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} \left[ B'_0 - 4 \right] \left[ \left( \frac{V}{V_0} \right)^{-\frac{3}{2}} - 1 \right] \right\}, \tag{4.1} \]

\[ P = \frac{B_0}{B'_0} \left[ \left( \frac{V}{V_0} \right)^{B'_0} - 1 \right], \tag{4.2} \]

and the Vinet equation is given by

\[ P = 3B_0 \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} \left[ 1 - \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \right] \exp \left\{ \frac{3}{2} \left[ B'_0 - 1 \right] \left[ 1 - \left( \frac{V}{V_0} \right)^{\frac{1}{2}} \right] \right\}. \tag{4.3} \]

The calculated bulk moduli are shown in Table IV along with reported experimental values obtained by various methods. For consistency with reported experimental values, the hydrostatic-compression data were fit to the EOS forms up to different pressures for each system. PETN was fit up to 10 GPa, HMX up to 12 GPa, RDX up to 4 GPa, and nitromethane up to 15 GPa. The data for NEST-1 was fit up to 5 GPa. The lower pressure was chosen because the fitting forms provided very similar results in this pressure range. Also, it is not known if NEST-1 experiences a phase transition to a different polymorph in the pressure range studied. By choosing a lower pressure for fitting, there is a better chance that the undesirable case might be avoided wherein the maximum pressure chosen for fitting is above the transition pressure.
Table IV: Bulk moduli of PETN-I, β-HMX, α-RDX, Nitromethane, and NEST-1. The superscripts BM, M, and V indicate that the value was obtained by fitting data to the Birch-Murnaghan, Murnaghan, and Vinet EOS, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>DFT without vdW</th>
<th>DFT with vdW</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_0$</td>
<td>$B'_0$</td>
<td>$B_0$</td>
</tr>
<tr>
<td>PETN-I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.0$^{BM}$</td>
<td>8.6$^{BM}$</td>
<td>14.2$^{BM}$</td>
</tr>
<tr>
<td></td>
<td>10.4$^{M}$</td>
<td>5.9$^{M}$</td>
<td>16.0$^{M}$</td>
</tr>
<tr>
<td></td>
<td>9.2$^{V}$</td>
<td>7.9$^{V}$</td>
<td>14.7$^{V}$</td>
</tr>
<tr>
<td>β-HMX</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.0$^{BM}$</td>
<td>8.4$^{BM}$</td>
<td>19.3$^{BM}$</td>
</tr>
<tr>
<td></td>
<td>12.3$^{M}$</td>
<td>6.1$^{M}$</td>
<td>20.8$^{M}$</td>
</tr>
<tr>
<td></td>
<td>11.2$^{V}$</td>
<td>7.9$^{V}$</td>
<td>19.5$^{V}$</td>
</tr>
<tr>
<td>α-RDX</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.0$^{BM}$</td>
<td>7.2$^{BM}$</td>
<td>15.9$^{BM}$</td>
</tr>
<tr>
<td></td>
<td>10.4$^{M}$</td>
<td>6.2$^{M}$</td>
<td>16.4$^{M}$</td>
</tr>
<tr>
<td></td>
<td>10.0$^{V}$</td>
<td>7.1$^{V}$</td>
<td>15.9$^{V}$</td>
</tr>
<tr>
<td>Nitromethane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.9$^{BM}$</td>
<td>7.2$^{BM}$</td>
<td>11.7$^{BM}$</td>
</tr>
<tr>
<td></td>
<td>8.0$^{M}$</td>
<td>5.1$^{M}$</td>
<td>12.9$^{M}$</td>
</tr>
<tr>
<td></td>
<td>6.8$^{V}$</td>
<td>7.2$^{V}$</td>
<td>11.7$^{V}$</td>
</tr>
<tr>
<td>NEST-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.8$^{BM}$</td>
<td>7.3$^{BM}$</td>
<td>15.9$^{BM}$</td>
</tr>
<tr>
<td></td>
<td>9.2$^{M}$</td>
<td>6.0$^{M}$</td>
<td>16.4$^{M}$</td>
</tr>
<tr>
<td></td>
<td>8.8$^{V}$</td>
<td>7.3$^{V}$</td>
<td>15.9$^{V}$</td>
</tr>
</tbody>
</table>
4.5 Discussion

The equilibrium structures calculated with the vdW correction clearly show an improvement over pure DFT in the agreement with experiment. By pure DFT, the average error compared with the experimental data chosen for comparison is about 9%, and the vdW correction shows an improved error of approximately 2.3%. On the other hand, the results of Neumann and Perrin for 31 molecular crystals showed an error of approximately 20% for pure DFT and about 1% with their vdW correction [2]. The difference could be the result of several changes that were made to the vdW correction for this work. It is expected that the change of functional from PW91 to PBE would not contribute largely to the difference, as these functionals are commonly believed to provide very similar results. However, there were changes in this work for the energy cutoff, $k$-point sampling density, and the tolerance for structural optimization that may be mostly responsible for the difference between the average results. The energy cutoff was 700 eV, yielding a larger basis than the 500 eV calculations of Neumann and Perrin. In addition, this work has a greater $k$-point sampling density, which was approximately 0.05 Å$^{-1}$ near equilibrium conditions. The changes introduced for the energy cutoff and $k$-point sampling in this work improve the accuracy of the DFT contribution. Also, the structural optimization in this work was set via a maximum force on any atom, but their work involved a tolerance of 0.01-0.02 kcal/mol in absolute energy. The different tolerance criteria could also contribute to the difference because the energy tolerance of 0.01-0.02 kcal/mol (0.4-0.8 meV) for several systems was reached before the maximum force on any atom was less than 0.03 eV/Å. If relaxations were ceased at a total energy
convergence of 0.4 meV, the calculated unit-cell volumes in most cases would be slightly greater. Further, the damping-function parameters of the vdW approach were not re-fit to adjust for the changes made in this work. It was expected that these parameters would not differ significantly with the changes made to the approach in the DFT component, but the contribution might be greater than expected. In either case, the vdW correction is a step towards improving the predictive power of DFT for these systems.

For the hydrostatic-compression calculations, the vdW correction shows an improvement in the agreement with the experimental EOS. While pure DFT overestimates the volume at a given pressure, the vdW correction gives a slightly lower pressure at a given volume. One must consider that the experimental data for most of the systems studied were taken at room temperature, but a comparison is made with DFT, a ground-state theory that gives results corresponding to 0 K. If thermal expansion on the 0 K results were accounted for, it is expected that the pressure at a given volume would increase. Hence, an accurate prediction at 0 K should predict a slightly smaller pressure at a given volume than an experiment at 300 K. Zerilli and Kuklja have provided an estimate of the pressure difference in the EM, FOX-7, to account for the corresponding temperature difference of ground-state electronic structure calculations and experiment at 300 K [73], and the estimate at a density of 1900 kg/m³ was approximately 0.6 GPa. If a pressure increase on this order of magnitude were added to the vdW-DFT results for the EOS, the agreement with most experimental studies would be much improved.

The greatest contributing factor to the uncertainty in the DFT calculations of the EOS is most likely the error in the pressure from the energy cutoff, which is approximately 0.4 GPa for the systems in this study. On the pressure scale of the EOS
plots, this uncertainty is roughly the same size as the symbols for the data points. Meanwhile, the error in the equilibrium-structure calculations from the cutoff choice should also be considered. As shown in Ref [38], the equilibrium volume has a significant dependence on the basis, i.e. the energy cutoff, for several energetic molecular crystals. Convergence of unit-cell volume with cutoff is notoriously slow for these systems, where the trend in approaching convergence is that volume increases with cutoff. Performing the calculations with a higher energy cutoff would decrease the error and most likely yield results for the vdW correction in better agreement with experiment, but this would incur a tremendous cost. Overall, the choice of the parameters was considered as a reasonable balance between accuracy and expense for the purposes of this study.

It was expected that the influence of dispersion is only significant at low pressure for molecular crystals. From the results of the study, it is observed that the discrepancy between pure DFT and vdW-DFT is greatest at low pressure, and the curves representing the EOS results for pure DFT and vdW-DFT appear to approach one another with increasing pressure. However, the difference in pressure at a given volume is still significant at much higher pressures than expected. Although the damping function proposed by Neumann and Perrin is a breakthrough for equilibrium-structure calculation, further refinement of the damping function might be necessary for calculations at high pressure.

The bulk modulus predictions exhibit a few trends. The values calculated with the vdW correction are greater than those obtained with pure DFT. This result is expected since the vdW correction predicts a smaller volume for the unit cell of each system, and
the denser unit cell is most likely more resistant to changes in volume. Further, the experiments of Gump and Peiris indicate that the bulk modulus decreases with increasing temperature [66]. If one were to account for the temperature difference between the simulations and experiment, it is possible that the vdW results would show better agreement with experimental values. Another trend exhibited is that the vdW correction appears to have little influence on the calculated value of the pressure derivative of the bulk modulus.

An evaluation of the results obtained for the bulk modulus by comparison with reported experimental results is a difficult task. The values from experiment seldom agree within an experimental uncertainty, and the discrepancy in the values measured (without uncertainty) is reflected in Table IV. This could be the result of several factors, including the fitting forms used as well as a lack of low-pressure data [1]. For this reason, it is not clear whether the vdW correction improves or weakens the predictive ability of DFT in the prediction of these elastic properties.
CHAPTER 5  UNIAXIAL-COMPRESSION SIMULATIONS OF ENERGETIC MATERIALS

Single-crystal samples of explosives can respond quite differently to stimuli in comparison with polycrystalline samples. In the case of PETN, single crystals have shown greater initiation sensitivity, and this behavior is also highly anisotropic. By investigating the factors that contribute to the anisotropic sensitivity of single-crystal PETN, it might be possible to gain insight into the poorly understood atomic-scale events that lead to detonation.

Following the discovery of unexpected shock response of PETN [91], the anisotropic sensitivity of PETN has been studied in several experiments [23, 24, 92-95] by Dick. The initial works [23, 93] employed wedge-tests that delivered plane shocks to samples of single-crystal PETN in the <100>, <001>, <110>, and <101> orientations (the notation \(<hkl>\) specifies a direction that is perpendicular to a crystallographic plane with similar Miller indices [93]). Reflected light from the free surface of the sample was used to determine the time after impact and distance into sample when and where, respectively, detonation took place. The results show heavy directional dependence of sensitivity. The <110> and <001> directions were found to be sensitive. The <110> direction exhibits the greatest sensitivity, where longitudinal stresses as low as approximately 4 GPa have caused detonation [93]. The <001> direction also has been described as sensitive because it has shown[23] a transition to detonation near 12 GPa.
On the other hand, the other two directions studied in the experiments, <100> and <101>, are relatively insensitive. The initial works of Dick [23, 93] showed an intermediate velocity transition for the <101> direction, which indicated decomposition without detonation. The <100> direction, however, showed no such transition [23, 93], and detonation was not observed for this direction until a later study by Yoo et al. [25]. The shock-to-detonation transition was achieved for <100> only near the detonation pressure of approximately 31 GPa [25].

Other energetic materials might also have anisotropic sensitivity properties, but there are no systems other than PETN for which the anisotropy has been sufficiently studied. Single-crystal experiments of uniaxial compression have been performed on HMX [96] and RDX [97], but the focus of the experiments was to obtain data on the elastic response to weak shocks. However, both works [96, 97] state that the anisotropic sensitivity of these materials will be investigated. Also, anisotropic sensitivity has been observed in a DAC experiment [98] on solid nitromethane, but the sensitive directions have not clearly been identified [99].

The mechanisms responsible for the anisotropic sensitivity of PETN are not fully understood, though several works have suggested possibilities. The discoverer of the anisotropy, Dick, reasoned that directions with fewer available slip systems do not possess the ability to effectively relieve shear stress, and these directions may be more sensitive than others [23, 24, 92-94]. Commonly called the steric-hindrance hypothesis, compression studies of PETN as well as other EMs have been designed based upon the available slip systems of the studied uniaxial-compression directions [96, 97, 100]. Gruzdkov and Gupta [101] built upon the hypothesis of steric hindrance by suggesting
that hindered shear in PETN causes conformational changes in the PETN molecules which lead to local polarization of the crystalline lattice. The work assumes that these local changes can lead to ionic reactions, i.e. initiation, under shock conditions.

Another suggestion for the anisotropic sensitivity in PETN was provided by Jindal and Dlott [102]. In their work, it is hypothesized that the anisotropic heating of the crystal as a result of uniaxial compression might be responsible for the observed directional dependence of sensitivity. Their results from an anharmonic potential for the molecular crystal naphthalene indicate that the difference in temperature at pressures of approximately 10 GPa can lead to reaction rate constants that differ by orders of magnitude for different compression directions.

Further, it has been proposed that the electronic band gap of EMs under compression might play a significant role in the initiation of detonation. In several works, Kuklja and co-workers [103-107] have investigated the possible role of electronic excitations in the initiation of EMs. The effect of dislocations in the initiation of EMs is central to the work, where reduction of the band gap by compression is a co-requisite. Further, Reed et al. performed theoretical studies of nitromethane, concluding that dynamics outweigh static effects in the reduction of the bandgap [77] and a transient metallic layer is formed at the detonation front [108].

In this work, DFT is employed to investigate the response of EMs to uniaxial compression. Of particular interest is the compression of PETN in the directions studied by in the experiments of Dick [23, 24]. Using the available experimental data regarding the anisotropic sensitivity of PETN, a comparison of the physical properties for each
compression direction may be useful for identifying physical quantities that may be correlated with greater (or lesser) sensitivity.

An aim of the study was to compare and contrast the shear stress during compression for several directions in each EM. The steric-hindrance hypothesis emphasizes the role of shear in initiation, but other evidence also suggests its importance. For example, molecular dynamics simulations of uniaxial compression of RDX in the $<100>$ direction by Cawkwell [100] show zones of high shear as regions of energy localization. The melting of the RDX occurs at 45° to the compression direction, where the shear stress is at a maximum. One may deduce that these regions of high shear stress have an associated localization of energy that could, according to hot spot theory [109], serve to overcome energy barriers for highly exothermic chemical reactions.

In addition, the band gap under compression can be calculated from DFT. While the method described below captures only the static effects that contribute to the reduction of the band gap, it is important to investigate the anisotropic nature of these static effects. This work investigates the band gap of each system under uniaxial compression to predict the anisotropic band-gap changes.

Finally, simulations of EMs at the mesoscale require quantum-mechanical calculations of anisotropic constitutive relationships. Menikoff and Sewell [110] have emphasized the need of anisotropic stress-strain relationships for mesoscale simulations of HMX to accurately model the concentration of stress between explosive grains, an effect that is believed to generate hot spots for detonation. In this work, these anisotropic constitutive relationships are predicted for several important EMs for compression in
several low-index crystallographic directions at pressures that are expected to be useful as input for simulation at greater length scales.

Some of the results of this study have appeared in previous publications [79, 80, 111-113] and appear below with permission where applicable.

5.1 Computational Details

The uniaxial compressions were performed on the EMs in the low-index crystallographic directions <100>, <010>, <001>, <110>, <101>, <011>, and <111>. It is important to note that the compression directions specified by \( <hkl> \) are defined as perpendicular to crystallographic planes referred to by Miller indices \( (hkl) \), following the notation of Dick [24]. Clearly, a direction specified by this notation is not equal (for general crystal symmetry) to the direction \( [hkl] \), which in popular notation corresponds to the direction along \( \mathbf{r} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c} \), where \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \) are the lattice vectors.

To simulate uniaxial compression, the unit cell was first rotated such that the desired direction was aligned with the \( x \) axis. The compression was carried out in steps of 2% of the calculated equilibrium volume by first scaling the \( x \)-components of the lattice vectors to reduce the volume of the unit cell by 2%, and then the atomic coordinates were relaxed. During the relaxations, the unit-cell shape and atomic coordinates were held constant. Uniaxial-compression simulations were performed in each of the seven low-index directions from 100% to 70% of the calculated equilibrium volume. With the exception of the constraints during relaxation, the parameters for the VASP DFT
uniaxial-compression calculations are the same as those previously described on page 40 for hydrostatic compression. Note that the uniaxial-compression calculations were performed without the vdW correction unless otherwise indicated.

5.2 Stress-strain relationships

The constitutive relationships between stress and strain in the unit cells of the uniaxially compressed EMs of this study are discussed below.

5.2.1 Principal stresses

The stress tensor is used to describe the state of stress in a material. Owing to the fact that the elements of a tensor depend on the chosen coordinate axes, it is informative to extract invariant information on the stress state. This can be accomplished by diagonalizing the stress tensor to find its eigenvalues. The eigenvalues of the stress tensor are the principal stresses, and these quantities describe purely compressive stress on the corresponding orthogonal eigenvectors, i.e. the principal axes.

The principal stresses have been defined in this work as $\sigma_1$, $\sigma_2$, and $\sigma_3$, where the subscripts are assigned in decreasing order. The greatest of the principal stresses $\sigma_1$ corresponds to the longitudinal stress along the compression direction, while $\sigma_2$ and $\sigma_3$ correspond to the stresses along mutually perpendicular directions.
The principal stresses $\sigma_1$, $\sigma_2$, and $\sigma_3$ of PETN under uniaxial compression are

Figure 18: Principal stress $\sigma_1$ as a function of volume ratio for seven low-index uniaxial compressions. The hydrostatic pressure is shown for comparison.
shown in Figure 18, Figure 19, and Figure 20, respectively. The principal stress $\sigma_1$ clearly shows the anisotropic response of PETN to mechanical compression. There are directions with very similar behavior, and this response is expected because of the crystal symmetry. In particular, the $<100>$ and $<010>$ compressions, as well as the $<101>$ and $<011>$ compressions, have almost identical principal-stress values. The tetragonal symmetry of PETN indicates that the lattice constants $a$ and $b$ are equal, and one might expect these directions to exhibit similar response to compression.
The greatest longitudinal stress for PETN is observed at high compression along the <001> direction. The <110>, <101>, and <011> compressions show similar values at a volume ratio near 0.70. The smallest longitudinal stress is observed for the <100> and <010> directions. For the other principal stresses, the values of $\sigma_2$ are relatively isotropic with respect to the other stresses. However, the values of $\sigma_3$ for the insensitive direction <100> and <010> are slightly smaller than the other directions of the study.

Figure 20: Principal stress $\sigma_3$ as a function of volume ratio for uniaxial compression in seven low-index crystallographic directions of PETN. The pressure from the hydrostatic-compression simulations is shown for comparison.
The principal stresses $\sigma_1$, $\sigma_2$, and $\sigma_3$ of HMX are shown in Figure 21, Figure 22, and Figure 23, respectively. In contrast to the behavior shown by PETN, the longitudinal stresses $\sigma_1$ from the uniaxial-compression simulations of HMX have very similar values at a volume ratio of 0.70. However, the $\langle 110 \rangle$ direction exhibits slightly greater values of $\sigma_1$ than the other directions at high compression. Also, the $\langle 011 \rangle$ direction shows relatively larger stress at lower compression, but non-monotonic behavior is observed near a volume ratio of 0.80 that reduces the stress to values that are similar to the other
Figure 22: Principal stress $\sigma_2$ of HMX as a function of volume ratio for uniaxial compression in seven low-index crystallographic directions. The pressure from the hydrostatic-compression calculations is shown for comparison.

directions. With the exception of the increase in stress shown for the $<100>$ and $<001>$ directions near a volume ratio of 0.76, the values of $\sigma_2$ for HMX are mostly isotropic. The values of principal stress $\sigma_3$ are also relatively similar, where the $<100>$ direction yields a slightly smaller stress than the other compression directions.
The principal stresses $\sigma_3$ of RDX upon uniaxial compression are shown in Figure 24, Figure 25, and Figure 26, respectively. At high compression, the $\langle 011 \rangle$, $\langle 100 \rangle$, $\langle 001 \rangle$, and $\langle 010 \rangle$ compressions show relatively greater stress. The $\sigma_3$ values for RDX, like PETN and HMX, are relatively similar for the compression directions studied. There is a noticeable drop in the value of $\sigma_2$ observed for the $\langle 110 \rangle$ direction near a volume ratio of 0.76. For the values of $\sigma_3$, the $\langle 011 \rangle$ compression is
Figure 24: Principal stress $\sigma_1$ (longitudinal stress) of RDX as a function of volume ratio for uniaxial compression in seven low-index crystallographic directions. The pressure from the hydrostatic-compression calculations is shown for comparison.

significantly smaller than the values obtained for the other compression directions, which are relatively similar.
Figure 25: Principal stress $\sigma_2$ of RDX as a function of volume ratio for uniaxial compression in seven low-index crystallographic directions. The pressure from the hydrostatic-compression calculations is shown for comparison.
Figure 26: Principal stress $\sigma_3$ of RDX as a function of volume ratio for uniaxial compression in seven low-index crystallographic directions. The pressure from the hydrostatic-compression calculations is shown for comparison.

The principal stresses $\sigma_1$, $\sigma_2$, and $\sigma_3$ of solid nitromethane from uniaxial-
compression simulations are shown in Figure 27, Figure 28, and Figure 29, respectively. The <001> direction stands out from the other directions as having the greatest value of the longitudinal stress $\sigma_1$. As observed for the other systems, the $\sigma_2$ values for the uniaxial compressions of nitromethane are relatively similar. On the other hand, the <010> compression has a significantly higher value of principal stress $\sigma_3$ than the other compression directions.
Figure 28: Principal stress $\sigma_2$ of nitromethane as a function of volume ratio for uniaxial compression in seven low-index crystallographic directions. The pressure from the hydrostatic-compression calculations is shown for comparison.
The principal stresses $\sigma_1$, $\sigma_2$, and $\sigma_3$ of NEST-1 are shown in Figure 30, Figure 31, and Figure 32, respectively. Note that the NEST-1 uniaxial-compression calculations were performed with the vdW correction, but the other systems were treated with pure DFT. The values of $\sigma_1$ for the uniaxial compressions of NEST-1 are relatively similar for most of the compression range studied, but the directions $<010>$ and $<110>$ display non-
monotonic behavior near a volume ratio of 0.74. The <011> direction also shows a change in the trend of the data that reduces the stress near this volume ratio.

Figure 30: Calculated maximum principal stress $\sigma_1$ of NEST-1 using vdW-DFT for uniaxial compressions. The pressure from the hydrostatic-compression simulations is shown for comparison.
Figure 31: Calculated maximum principal stress $\sigma_3$ of NEST-1 using vdW-DFT for uniaxial compressions. The pressure from the hydrostatic-compression simulations is shown for comparison.
5.2.2 Shear stresses

The maximum shear stress is calculated from the principal stresses. The principal stresses are the eigenvalues of the stress tensor, and therefore they are the elements of a diagonalized stress tensor. By transforming the stress tensor to find the axes where the non-diagonal elements, i.e. the shear stresses, are maximal, one discovers that the

Figure 32: Calculated maximum principal stress $\sigma_3$ of NEST-1 using vdW-DFT for uniaxial compressions. The pressure from the hydrostatic-compression simulations is shown for comparison.
maximum shear occurs near 45° to the principal axes, i.e. the eigenvectors corresponding
to the principal stresses.

To demonstrate the calculation of the shear stresses, the transformation of the
stress tensor has the form

\[ \sigma'_{ij} = \sum_{kl} a_{ik} a_{jl} \sigma_{kl}, \]  

(5.1)

where \( a_{mn} \) are direction cosines and \( \sigma'_{nm} \) are stress tensor components in the transformed
coordinates. Since the stress tensor with principal-stress values is diagonal,
\( \sigma_{kl} = \sigma_{kl} \delta_{kl} = \sigma_{kk} \). Keeping the notation of the principal stresses, \( \sigma_{kk} \) is denoted as
principal stress \( \sigma_k \). As an example, one of the shear stresses is obtained by
counterclockwise rotation of the \( x \) and \( y \) axes around the \( z \) axis by 45°. By transformation,
the maximum shear stress can be calculated as

\[ \tau_{12} = \sigma'_{12} = \left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}} \right) \sigma_1 + \left( \frac{-1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}} \right) \sigma_2 + (0) \sigma_3 = \left( \frac{\sigma_1 - \sigma_2}{2} \right) \]  

(5.2)

The shear stress is equal in magnitude but opposite in sign for a clockwise rotation, hence
only the magnitude of the shear stress is considered below. The quantities of interest from
rotation of the principal axes are therefore \( |\sigma_1 - \sigma_2| / 2, |\sigma_2 - \sigma_3| / 2, \) and \( |\sigma_1 - \sigma_3| / 2 \).
The greatest of these shear stresses is referred to as \( \tau_1 \) below, and the values of \( \tau_2 \) and \( \tau_3 \)
are assigned in order of decreasing magnitude. Note that the smallest shear stress
maximum \( \tau_3 \) is typically much smaller than the other two. Owing to this fact, the values
of \( \tau_3 \) for the uniaxial-compression simulations are expected to be of relatively minor
importance, but are shown below to give a more complete picture of the state of stress in the materials.

The shear stresses $\tau_1$, $\tau_2$, and $\tau_3$ for each uniaxial compression direction of PETN are shown in Figure 33, Figure 34, and Figure 35, respectively. The $<001>$ compression calculations show much greater shear stress $\tau_1$ than the other directions, which have similar values near a volume ratio of 0.70. The $<101>$, $<011>$, and $<111>$ directions show non-monotonic dependence of stress on strain below a volume ratio of 0.80.
Figure 34: Maximum shear stress $\tau_2$ for uniaxial compressions of PETN.
The ordering of the principal stresses by value masks the relation of the stress to crystal orientation, which is a very important consideration for PETN. To illustrate this point, the shear stresses $\tau_{xy}$ and $\tau_{rr}$ defined by

$$
\tau_{ij} = \frac{\sigma_{ii} - \sigma_{jj}}{2}
$$

are shown in Figure 36 and Figure 37, respectively. A few ideas should be considered for these stresses. First, the stress tensors obtained from the uniaxial compressions of PETN were approximately diagonal, so the values $\sigma_{ii}$ correspond to the principal stresses with orientational ordering. Several of the other systems did not yield nearly diagonal stress
Figure 36: Shear stress $\tau_{xy}$ from uniaxial-compression simulations for directions of known sensitivity in PETN.

tensors, and the principal-stress analysis was introduced to treat each system in an equal
Next, note that the compression direction in all cases is the $x$-direction, and therefore the shear stresses $\tau_{xy}$ and $\tau_{xz}$ reflect the maximum shear stress at $45^\circ$ to the compression direction ($\tau_{yz}$ is considered to be of minor importance). In Figure 36 and Figure 37, these maximum shear stresses are shown for the directions of known sensitivity in PETN. Recall that the $<110>$ and $<001>$ directions are sensitive, while the $<100>$ and $<101>$ directions are insensitive to shock compression. Although the $\tau_{xy}$ values do not appear to largely differ between the high and low sensitivity directions,
there is a clear distinction in the values of $\tau_{xz}$ between the sensitive and insensitive directions. At a volume ratio of 0.70, the insensitive directions exhibit much lower values of shear stress $\tau_{xz}$ than the sensitive directions. Further, both of the insensitive directions have non-monotonic dependence of shear stress $\tau_{xz}$ on volume ratio. These observations indicate that there might be a correlation between shock sensitivity and maximum shear stresses in EMs.

The maximum shear stresses $\tau_1$, $\tau_2$, and $\tau_3$ from the uniaxial-compression simulations of HMX are shown in Figure 38, Figure 39, and Figure 40, respectively.
Compression in the <110> direction yields large values of both $\tau_1$ and $\tau_3$. According to the possible correlation of sensitivity with greater shear stress observed in PETN, an investigation into the relative sensitivity of the <110> direction in HMX would be enlightening. Also, all of the directions show non-monotonic dependence in one or both of the larger two shear stresses except for the <010> and <001> directions. In PETN, non-monotonicity of the shear stresses as a function of volume ratio was observed for the insensitive directions, and this behavior might also reflect insensitivity in HMX.

Figure 39: Maximum shear stress $\tau_2$ from uniaxial-compression simulations of HMX.
Figure 40: Maximum shear stress $\tau_3$ from uniaxial-compression simulations of HMX.
The maximum shear stresses $\tau_1$, $\tau_2$, and $\tau_3$ from the uniaxial-compression simulations of RDX are shown in Figure 41, Figure 42, and Figure 43, respectively. The directions with greater shear stress, and possibly greater sensitivity, at high compression are $<100>$, $<010>$, $<001>$, and $<011>$. Also, the $<101>$ and $<111>$ directions show much smaller shear stresses upon compression, and therefore might be relatively insensitive directions.
Figure 42: Maximum shear stress $\tau_2$ from uniaxial-compression simulations of RDX.
Figure 43: Maximum shear stress $\tau_3$ from uniaxial-compression simulations of RDX.
The maximum shear stresses $\tau_1$, $\tau_2$, and $\tau_3$ from the uniaxial-compression simulations of nitromethane are shown in Figure 44, Figure 45, and Figure 46, respectively. The directions that stand out from the others are the $\langle 001 \rangle$ direction, which shows much greater shear stresses $\tau_1$ and $\tau_3$, and the $\langle 010 \rangle$ direction, which yields smaller shear stresses than the other compression directions. The other directions reveal relatively similar behavior.
Figure 45: Maximum shear stress $\tau_2$ from uniaxial-compression simulations of nitromethane.
Figure 46: Maximum shear stress $\tau_3$ from uniaxial-compression simulations of nitromethane
The maximum shear stresses $\tau_1$, $\tau_2$, and $\tau_3$ from the uniaxial-compression simulations of NEST-1 are shown in Figure 47, Figure 48, and Figure 49, respectively. All directions show non-monotonic behavior, but the $<100>$ and $<001>$ directions show greater shear stress values for $\tau_1$ and $\tau_3$ at high compression.
Figure 48: Maximum shear stress $\tau_2$ for uniaxial compressions of NEST-1 using vdW-DFT.
5.3 Band Gaps

As discussed above, the reduction of the electronic band gap in EMs during compression has been identified as a possible contributing factor to initiation. From the compression simulations, the band gap was approximately calculated to determine if the gap was reduced significantly and to estimate the anisotropy in the band-gap reduction caused by compression.
For the band gap calculations, only the $k$-points used in the VASP calculations were included. It is expected that the few points used for sampling provide a reasonable estimate of the band gap. In other words, it is assumed that there are not large variations in the band structure for these materials.

The band gaps as functions of volume ratio for the uniaxial-compression simulations of PETN are shown in Figure 50. From a comparison with the band gap from the hydrostatic-compression simulations, the uniaxial compressions lower the calculated...
band gap of PETN more than hydrostatic compression. However, it is clear that none of
the band gaps approach a value typical of a conductor. In addition, the calculated band
gap does not appear to correlate with sensitivity. The most sensitive direction, <110>,
shows the least change in band gap, and the least sensitive direction, <100>, has only a
slightly greater reduction. Further, the sensitive direction <001> has a greater reduction
in band gap than <100>, but the insensitive direction <101> has the greatest change in
band gap of the directions in the study.
The band gaps as functions of volume ratio for the uniaxial-compression simulations of HMX are shown in Figure 51. The <011> direction displays a much greater reduction in the band gap than the other directions. On the other hand, the <001> and <101> directions show less of a reduction in the band gap than hydrostatic compression. While the calculations indicate a significant anisotropy in the band gap for HMX, it does not approach a metallic state.
The band gaps as functions of volume ratio for the uniaxial-compression simulations of RDX are shown in Figure 52. The <100> direction exhibits a greater reduction than the other directions. Also, the <011>, <010>, and <001> compressions display a greater gap than hydrostatic compression at intervals within the compression range shown. Note that the band gap at equilibrium conditions is similar to that of HMX, and the minimum gap at high compression is also approximately equal.

Figure 52: Band gap of RDX from uniaxial-compression simulations. The band gap from the hydrostatic-compression simulations is shown for comparison.
The band gaps as functions of volume ratio for the uniaxial-compression simulations of nitromethane are shown in Figure 53. Note the increase in band gap from equilibrium to the first compression step for some directions. This behavior is assumed to be caused by the error in the approximation used to calculate the band gap. The equilibrium calculations were performed with the $k$-points used for the hydrostatic compressions, but each uniaxial compression had different points used for sampling. Hence, the increase in band gap is most likely a result of the change in $k$-points, and the energy difference between the band gap from the hydrostatic calculations at a volume.
The band gaps as functions of volume ratio for the uniaxial-compression simulations of NEST-1 are shown in Figure 54. At high compression, the <110> direction exhibits a relatively greater reduction in the band gap as compared to the other directions. The <101> and <111> directions show an unexpected increase in the band gap near a volume ratio of 0.80. For all directions, the reduction of the band gap is below 1 eV.
5.4 Discussion

The principal and shear stresses, as well as the band gap, as a function of volume ratio were examined for uniaxial compressions of PETN, HMX, RDX, nitromethane, and NEST-1. Because the anisotropic shock sensitivity of PETN has been studied by experiment, the response of PETN was examined for correlations with sensitivity. It was observed that the insensitive <100> and <101> directions in PETN exhibited lower maximum shear stresses, as well as non-monotonic dependence on strain, and the sensitive <110> and <001> directions clearly showed greater maximum shear stress values. Although further work is needed to validate a correlation, the results present convincing evidence that a correlation is possible. If, in fact, there is a correlation and it can be extended to other EMs, it would be valuable to identify directions in other systems that display similar behavior to the sensitive and insensitive directions in PETN. Hence, the anisotropic shear stresses of HMX, RDX, nitromethane, and NEST-1 were calculated, and directions with relatively greater (and lesser) shear stress were identified. The impending results of experiments by other groups [96, 97] for these materials will provide a means to accept or reject the possible correlation.

The band gap of the materials was also examined for a correlation with sensitivity in PETN, but it was found to be unlikely from the results. Meanwhile, the EMs of the study exhibit anisotropic reduction of the band gap with compression. Overall, the calculated band gaps reduced by roughly 1 eV, clearly not enough to cause metallization. As discussed above, the simulations do not provide a complete picture for reductions in
the band gap because of the static nature of the calculations [77] and because the calculations involve defect-free unit cells [104].

The uniaxial-compression calculations performed on NEST-1 differ from the other systems because they were performed with the vdW correction. Calculations have been performed to compare the results between pure DFT and the vdW correction for the principal and shear stresses. A preliminary inspection of the results indicate that the vdW correction gives higher values for the principal stresses (and, consequently, the shear stresses), but the relative differences in stresses between the compression directions are similar. Hence, it is expected that directions showing greater principal and/or shear stress from pure DFT calculations would also exhibit greater relative values with the vdW correction. Meanwhile, the pure DFT calculations for all systems were not repeated with the vdW correction for a thorough comparison owing to the large expense of the calculations and because a significant difference in the relative behavior was not expected.

In the stresses and band gaps for some uniaxial compressions, abrupt changes are observed, such as the onset of non-monotonic behavior and sudden large increases. While an analysis of the changes in molecular structure that accompany these interesting changes would be valuable, this investigation has not yet been thoroughly performed. However, it is expected that those in collaboration with this study will examine how changes to molecular structure influence the electronic structure and stress in these EMs.
CHAPTER 6  CONCLUSION

In this work, density functional theory was used to study the energetic materials (EMs) PETN-I, β-HMX, α-RDX, solid nitromethane, and a recently discovered EM referred to as NEST-1. The empirical van der Waals correction of Neumann and Perrin [2] was used along with the DFT code VASP in an effort to improve the description of the molecular crystals of the study. The empirical method was used in the prediction of equilibrium unit-cell structures and hydrostatic-compression simulations, and a comparison was made between the corrected and uncorrected results.

For the prediction of equilibrium unit-cell volumes, the pure DFT results provided an error of about 9% when averaged over each of the five EMs of the study, whereas the error was reduced to approximately 2% with the vdW correction. Although this is a significant improvement, the average percent error from the work of Neumann and Perrin is greater for the pure DFT results and smaller for the corrected results. It was concluded that a large contribution to the discrepancy was likely caused by the changes in this study to the DFT portion of the empirical method. The changes were introduced with the intent to improve the quality of the DFT portion. A worthwhile study would be to repeat the fitting of the vdW potential parameters with altered VASP settings to investigate whether a similar agreement of 1% is obtained [2].
The isothermal equations of state (EOSs) at 0 K for each EM were calculated from the hydrostatic-compression simulations and compared with available experimental data. For PETN and RDX, there is a clear improvement in the agreement with experiment. For HMX and nitromethane, there are data from two or more experiments for comparison, and the agreement is similar to, if not better than, the agreement yielded by pure DFT. Meanwhile, the vdW correction predicts a smaller volume at a given pressure, which is physically consistent with the difference between the simulation and experimental temperatures. Note that experimental data on the hydrostatic compression of NEST-1 are not currently available for comparison.

The calculated lattice constants \( a, b, \) and \( c \) from the hydrostatic-compression simulations were also compared with experiment. With the exception of a few cases, the vdW correction increases the agreement with experiment. The correction therefore shows an improvement in the agreement on average for the EMs studied.

The bulk modulus and its pressure derivative were calculated from the hydrostatic compression data and compared with available experimental data. The Birch-Murnaghan, Murnaghan, and Vinet EOSs were used to fit the simulation data. Owing to the lack of agreement in experimental results, it was difficult to make a sound conclusion regarding the improvement of the vdW correction in the prediction of the bulk moduli. However, trends were observed for the results; the pure DFT approach predicted a smaller value for the bulk modulus than experiment in many cases, whereas the vdW-DFT approach yielded greater values than experiment on average.
For the comparison, the temperature difference must be considered between the simulations and the experimental data. The experimental data were taken at room temperature, but the ground-state results represent the conditions at absolute zero. Thus, it is expected that the theoretical results should predict a smaller volume (and lattice-vector lengths, correspondingly) at a given pressure than experiment. The vdW-correction results are consistent with this expectation, whereas the pure DFT results are not. Meanwhile, it remains to be shown that the difference in volume between the experimental data and the vdW-DFT results at a given pressure is consistent with the temperature difference. A suggestion for future research is the addition of methods to account for temperature to the simulations, which would allow a more suitable comparison with experiment and enable further exploration into the equation of state for EMs.

Uniaxial-compression simulations were also performed in seven low-index crystallographic directions for the EMs of this study. The calculations were designed to investigate the anisotropic response of the materials to compression, with particular interest in the shock-sensitive directions of PETN.

The constitutive relationships between stress and strain were calculated for the EMs under uniaxial compression. Specifically, the principal stresses and the maximum shear stresses were calculated for uniaxial compression up to a volume ratio of $V/V_0=0.70$. The predicted behavior of stress for each material is clearly anisotropic.

Unlike the other EMs of the study, the anisotropic sensitivity of PETN to shock has been studied thoroughly by experiment [23, 24]. From a comparison of the maximum
shear stresses at about 45° to the compression direction, greater shear stresses were found for the sensitive <110> and <001> directions than for the insensitive <100> and <101> directions. Further, both insensitive directions exhibited non-monotonic dependence of shear stress on strain, and this behavior was not shown by the sensitive directions. It was concluded from these observations that the maximum shear stresses might have a correlation with shock sensitivity. For this reason, the directions corresponding to greater and lesser shear stresses, as well as non-monotonic dependence of shear stress on strain, were identified in HMX, RDX, nitromethane, and NEST-1. The results of experiments on the sensitivity of these materials is highly anticipated to determine if the sensitive (insensitive) directions from experiment correspond to directions with greater (lesser) shear stress from the simulations.

The electronic band gap was also calculated for each of the uniaxially compressed EMs. These results also indicate anisotropy, but the calculated band gaps do not appear to be correlated with the anisotropic sensitivity in PETN. Further, the band gap reduces by approximately 1 eV at most for each EM at a volume ratio up to 0.70, which is not nearly enough to render the systems metallic. Owing to the expectation that dynamic effects and crystalline defects might be responsible for greater band-gap reduction [77, 103], it was anticipated that the band gaps calculated in this study would not decrease significantly.

The stresses and band gaps as functions of volume ratio exhibited abrupt changes with uniaxial compression for some directions. The relation of these changes to the underlying molecular structure is not analyzed in this work, but this investigation will be the subject of future research.
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