AN INVESTIGATION INTO THE PHASE STABILITY OF MANGANESE OXIDE USING QUANTUM MONTE CARLO AND INSIGHTS INTO MATERIALS PREDICTION IN THE BARIUM-RUTHENIUM-SULFUR PHASE SPACE

BY

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THESIS

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Abstract

We present an analysis of the polymorphic energy ordering and properties of the rock salt and zincblende structures of manganese oxide using fixed node diffusion Monte Carlo (DMC). Manganese oxide is a correlated, antiferromagnetic material that has proven to be challenging to model from first principles across a variety of approaches. Unlike conventional density functional theory and some hybrid functionals, fixed node diffusion Monte Carlo finds the rock salt structure to be more stable than the zincblende structure, and thus recovers the correct energy ordering. Analysis of the site-resolved charge fluctuations of the wave functions according to DMC and other electronic structure descriptions give insights into elements that are missing in other theories. While the calculated band gaps within DMC are in agreement with predictions that the zincblende polymorph has a lower band gap, the gaps themselves overestimate reported experimental values. Additionally, a preliminary analysis of a structure search in the barium-ruthenium-sulfur phase space using the evolutionary algorithm USPEX is presented. We identify find challenges to discovering new materials using an evolutionary algorithm as well as a potential new candidate structure, BaRu$_2$S$_2$ with space group 139.
To my family, who continue to support me in whatever endeavor I pursue and through whichever hardship.
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When studying any material on the atomic scale, there is typically a trade-off between accuracy and computational complexity. With increasing accuracy of a calculation, fewer approximations can be made and more computational resources are required. Given the limitations of resources, one is often forced to choose between one or the other depending on the requirements of the investigation. The research presented in this thesis can be thought of as two opposite ends of this modeling spectrum. On one end, the material properties and energetic ordering of a known compound, manganese oxide, was studied using high-accuracy techniques. On the other end of the spectrum, a broad search of many different potential structures was carried out for an unknown compound in the barium-ruthenium-sulfur phase space using more approximate methods.

The first topic covered in this thesis is the polymorphic energy ordering of the two phases of manganese oxide. This compound, found in nature with a rock salt structure, is counterintuitively predicted to be in the zincblende structure when modeled using conventional density function theory (DFT) techniques [2, 3]. The odd behavior of this compound is thought to be due to DFT’s treatment of electron exchange and correlation effects. Subsequent attempts to correct this phenomenon have necessitated empirically parameterized calculations [3]. It is therefore desirable to find a technique that can address the electron exchange and correlation effects directly without introducing spurious approximations. In this work, fixed-node diffusion Monte Carlo (FN-DMC) was used to address these issues. With minimal approximations and a many-body stochastic approach to solving the Schrödinger equation, FN-DMC demonstrates potential for tackling difficult-to-model, correlated materials like MnO.

The second topic covered in this thesis is the search for novel compounds within the barium-ruthenium-sulfur ternary phase space. There have been many structures found within the barium-ruthenium-oxygen ternary phase space, yet despite their valence similarities, none have been identified for which sulfur is introduced instead of oxygen. Given this curious disparity in known structures, it stands to reason that there may be undiscovered materials yet to be found. In this work, an evolutionary algorithm was used to search the energy landscape parameterized by the barium-ruthenium-sulfur phase space in order to identify such a compound.
Computational Tools and the Theory Underpinning Them

To understand the methods used within this thesis, one must first have a brief understanding of the physical problem this research seeks to solve. Once the physical problem has been brought to bear will the importance and theory of the computational procedures can be illustrated.

2.1 A Brief Introduction to Solid State Physics

2.1.1 Schrödinger’s Equation

The Schrödinger Equation can be thought of as the fundamental equation to solve when exploring a physical phenomenon within the quantum mechanical regime. It is a differential equation from which a wave function describing the system of one or more bodies can be determined. This wave function can be further used to determine observable properties of the system at hand. The time-dependent, non-relativistic Schrödinger equation is as follows:

\[ i\hbar \frac{\partial \psi(r,t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r,t) = \hat{H} \psi(r,t) \] (2.1)

In this equation, \( \hbar \) is modified Planck’s constant, \( \psi(r,t) \) is the wave function with position vector \( r \), \( t \) is time, \( m \) is mass and \( V(r) \) is the potential in the studied system. \( \hat{H} \) refers to the Hamiltonian operator, which conveys the energy of the system. It is possible to further transform this equation by making the assumption that this Hamiltonian is independent of time (i.e. the system is in equilibrium). From this assumption, we can decompose the wave function into spacial and temporal parts, \( \psi(r,t) = \psi(r)\phi(t) \). Using this, it is possible to construct the time-independent, non-relativistic Schrödinger equation:

\[ E\psi(r) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) = \hat{H}\psi(r) \] (2.2)

In this case, we can solve for the energy of the system, \( E \), in terms of time-independent wave function. It should be noted that this is an eigenvalue problem with corresponding time-independent wave function eigenstates and eigenenergies. For the sake of completeness, the time-dependence of the wave
function can be determined as:

$$\phi(t) = e^{-iEt}$$  \hspace{1cm} (2.3)$$

For the remainder of this thesis, attempts to solve the Schrödinger equation will revolve around solving this time-independent form. As for most systems of interest there is no analytical solution to this equation, this becomes a nontrivial task.

### 2.1.2 Bloch Waves

For certain types of systems, where the potential $V(r)$ is periodic, it is possible to determine the form of the solution before even solving the Schrödinger equation. Felix Bloch, a Swiss-born American physicist, discovered that wave functions in a periodic potential take the following form [4]:

$$\psi(r) = e^{ik \cdot r} \mu(r)$$  \hspace{1cm} (2.4)$$

In this equation, $e^{ik \cdot r}$ is a phase defined in part by the vector $k$ and $\mu(r)$ is function with the same periodicity of the lattice. The vector $r$ refers to the position vector. The domain containing $k$ is often called k-space, reciprocal space or the Brillouin Zone (BZ). In the event that one knows that the solution to the Schrödinger equation takes the form of a Bloch wave, one can simply select a point in k-space and solve the differential equation. Repeating this process for all k-points in reciprocal space defines a band structure for the material. In an ideal world, to determine the total energy of an infinitely large solid, one would simply integrate over all points in the BZ up to the Fermi level of the material (accounting for spin states as well). As this is computationally infeasible, in practice one builds a mesh in the BZ to calculate energies at each point. The total energy can then be determined using standard quadrature methods.

### 2.1.3 The Variational Principle

The last important physical detail to keep in mind is the variational principle. Given a wave function comprised of some number of parameters, this principle simply states that the parametric values that give the lowest energy eigenvalue when acted upon by $\hat{H}$ represents the ground state of the system and this given energy represents the ground state energy [5].
2.1.4 The Many-Body Problem for Crystalline Solids

When dealing with a crystalline material, we can define the Schrödinger equation as follows:

\[ \hat{T}_e + \hat{T}_n + \hat{V}_{nn} + \hat{V}_{en} + \hat{V}_{ee} \] \[ \psi(r, R) = E \psi(r, R) \]  

\[ \hat{T}_e = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{r_i}^2 \]
\[ \hat{T}_n = -\sum_{i=1}^{M} \frac{1}{2\mu_i} \nabla_{R_i}^2 \]
\[ \hat{V}_{nn} = \sum_{i=1}^{M} \sum_{j=1}^{i-1} \frac{Z_i Z_j}{|R_i - R_j|} \]
\[ \hat{V}_{en} = \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{|r_i - R_j|} \]
\[ \hat{V}_{ee} = \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{1}{|r_i - r_j|} \]

In this equation, \( N \) is the number of electrons, \( M \) is the number of nuclei, \( r_i \) is the position of electron \( i \), \( R_i \) is the position of nucleus \( i \), \( Z_i \) is the charge of nucleus \( i \), \( \mu_i \) is the mass of nucleus \( i \) and \( E \) is the total energy. Note, atomic units \( (m = 4\pi\varepsilon_0 = \hbar = e = 1) \) have been used to simplify the equation.

We can simplify this equation further by taking advantage of the Born-Oppenheimer Approximation [4], whereby we assume the much more massive nuclei are fixed and only the electrons move. This approximation is valid due to the disparate time scales of the electron and nucleus motion, with the nuclei much slower than the electrons. Consequently, \( \hat{T}_n = 0 \) in this approximation. Moreover, the potential due to the nuclear Coulombic interactions with the electrons become solely dependent on the positions of the individual electrons as the nuclear positions have now been fixed. Likewise, the Coulomb energy due to the nuclear-nuclear interactions becomes a constant. In light of this, \( \hat{V}_{nn} \) is usually removed from the equation for computational purposes and its energy is simply added in at the end. Thus, the problem to solve becomes:

\[ \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} \] \[ \psi(r) = E \psi(r) \]

This problem, while it may seem simple, is quite difficult to solve. First, there is no analytical method for solving this equation for all systems. Second, there are multiple terms that require integration over a \( 3N \) dimensional space, where \( N \) is the number of electrons. Coupled with existing computational
methods, solving such a system would be unreasonably difficult and time consuming without further simplifying approximations. Consequently, there have been many attempts to develop methods to minimize the computational cost of solving these systems, while maximizing the accuracy.

2.2 Hartree-Fock Theory

One of the earliest theories for solving the many-body Schrödinger equation is with Hartree-Fock. In this method, a wave function ansatz is created in the form of a Slater determinant. A Slater determinant takes the following form [6]:

\[
\Psi(x_1, \ldots, x_N) = \det \begin{bmatrix} \psi_1(x_1) & \psi_1(x_2) & \cdots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \cdots & \psi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \cdots & \psi_N(x_N) \end{bmatrix}
\] (2.7)

In this determinant, \( \{\psi_i\} \) refer to functions corresponding to the electron orbitals and the \( \{x_i\} \) refer to the electron coordinates. In this form, the wave function retains the antisymmetric property of electrons, whereby exchanging any two electrons negates the wave function. This is due to the property of exchanging columns in a determinant. If we assume an orthonormal and normalized set of functions \( \psi \), the Hamiltonian becomes [6]:

\[
\left[ -\frac{1}{2} \nabla^2 + \sum_{j=1}^{M} \frac{Z_j}{|r - R_j|} \right] \psi_i(r) + \sum_{j} \int \frac{|\psi_j(r')|^2}{|r - r'|} \psi_i(r) dr' \\
- \sum_{j} \delta_{\sigma_i, \sigma_j} \int \frac{\psi_j^* (r') \psi_i (r')}{|r - r'|} \psi_j (r) dr' = \epsilon_i \psi_i (r) \quad (2.8)
\]

In this case, the \( \epsilon_i \) refers to the Lagrange multiplier for function \( \psi \), which can be considered the Hartree-Fock orbital. The total energy of the system is then given as \( E = \sum_i \epsilon_i \). We can see that the interacting electron Coulomb term has become a non-interacting sum dependent on the single particle densities. The final term is known as the exchange term and arises due to the use of a Slater determinant as an ansatz solution of the wave function.

Hartree-Fock theory is useful in that it manages to accurately capture the exchange effects of the quantum system due to its use of a Slater determinant. However, where it excels in capturing electron exchange properties, it suffers from poor modeling of the electron-electron correlation. A consequence of this is that calculations using Hartree-Fock tend to have electrons that are more localized than they would be otherwise, increasing calculated lattice constants.
and band gaps among other shortcomings. While the Hartree-Fock method is not used on its own in this study, it is utilized for some calculations using density functional theory.

2.3 Density Functional Theory

2.3.1 Foundations of Density Functional Theory

Currently, the predominant method for quantum mechanical modeling of atomic-scale systems is known as density functional theory (DFT). It has been shown to frequently produce some of the most accurate descriptions of atomic scale systems while necessitating a reasonable amount of computational resources. The foundations of DFT were laid out in the 1960s by the physicists Pierre Hohenberg and Walter Kohn in what are known as the Hohenberg-Kohn theorems. The theorems state [7]:

Theorem 2.3.1 The ground-state energy from Schrödinger’s equation is a unique functional of the electron density.

Theorem 2.3.2 The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

These two theorems state that it is possible to transform a 3N-dimensional system, where N is the number of electrons, to a 3-dimensional system by utilizing the electron density instead of the electron themselves. Moreover, the second theorem acts as an extension to the variational principle, ensuring that it is possible to determine ground state properties by varying the electron density. The many-body problem then reduces to the following:

\[
E = -\frac{1}{2} \sum_i \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} + \sum_j \int \frac{Z_j}{|\mathbf{r}_j - \mathbf{r}|} n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{nn} + E_{XC}[n(\mathbf{r})] \tag{2.9}
\]

\[
n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \tag{2.10}
\]

Again, atomic units are assumed in this equation. The term \(n(\mathbf{r})\) represents the electron density, which is simply a sum of the single electron orbital densities with a factor of 2 accounting for spin. The Coulomb interactions between nuclei are represented in the term \(E_{nn}\). This is usually ignored until final energies
need to be calculated. The $E_{XC}$ represents the newly introduced exchange-correlation term, which is itself a functional of the electron density.

### 2.3.2 The Kohn-Sham Equations

Shortly after Hohenberg and Kohn proved these theorems, Walter Kohn and Lu Jeu Sham derived a set of differential equations for determining this electron density. These equations are known as the Kohn-Sham equations\cite{8}:

\[
\begin{align*}
-\frac{1}{2} \nabla^2 - \sum_j \frac{Z_j}{|\mathbf{r}_j - \mathbf{r}|} + \frac{1}{2} \int \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{XC}(\mathbf{r}) \end{align*}
\]

The first term represents the kinetic potential, the second is the potential due to electron-nuclei interaction and the third is potential due to electron-electron interaction, known as the Hartree potential. One of the drawbacks of the Hartree potential is that it contains spurious electron self-interaction due to the approximation of the electrons as a one-body density. This and other effects are corrected in the last term, the exchange-correlation potential. The determination of the exchange-correlation potential remains one of the most difficult parts of DFT. This potential is defined as a functional derivative of the exchange-correlation energy:

\[
V_{XC} = \frac{\delta E_{XC}}{\delta n(\mathbf{r})}
\]

The exact form for $V_{XC}$ is not currently known. The Kohn-Sham equations do not represent any physical system nor do the Kohn-Sham orbitals represent physical orbitals. Instead, they are used as tools to construct the fictitious one-body electron wave function. Upon inspection of the equations, one can plainly see that there is a circular methodology involved. That is, solutions to the Kohn-Sham equations depend on the electron density, which in turn depend on the orbitals determined from the Kohn-Sham equations. Hence, to determine the ground state electron density, one needs to cyclically solve for the electron density and orbitals. This type of calculation is known as a self-consistent field (SCF) and each cycle is known as an SCF loop or cycle. An illustration of the SCF cycle can be seen in Figure 2.1.
Figure 2.1: The SCF loop for a DFT calculation is demonstrated graphically. One can see the cyclical nature of a typical calculation. Once the electron density converges to within a desired threshold, the SCF ends and the desired properties are calculated.
2.3.3 Basis Sets

In solving the Kohn-Sham equations, one must first define a basis set to construct the Kohn-Sham orbitals. The most common basis set that is used is the set of plane waves satisfying the periodicity of the system. The Kohn-Sham orbitals then become like waves in a Fourier transform. More explicitly, the wave function takes the following form:

\[
\phi(r) = \sum_{G} c_{G} e^{iG \cdot r} \tag{2.12}
\]

\[
\psi_{k}(r) = \sum_{G} c_{G+k} e^{i(G+k) \cdot r} \tag{2.13}
\]

with \( G \) representing a linear combination of reciprocal lattice vectors and \( k \) representing a point in reciprocal space. The set of reciprocal lattice vectors, \( \{b_{j}\} \), for a set of real space lattice vectors, \( \{a_{i}\} \), are defined such that \( a_{i} \cdot b_{j} = 2\pi \delta_{ij} \). They are determined as follows:

\[
b_{1} = 2\pi \frac{a_{2} \times a_{3}}{V} \tag{2.14}
\]

\[
b_{2} = 2\pi \frac{a_{3} \times a_{1}}{V} \tag{2.15}
\]

\[
b_{3} = 2\pi \frac{a_{1} \times a_{2}}{V} \tag{2.16}
\]

\[V = a_{1} \cdot (a_{2} \times a_{3}) \tag{2.17}\]

To determine the specific set of plane waves to be used, it is very common to set a threshold based on the kinetic energy term. The idea is that lower energy terms contribute more to the description of the wave function than higher energy terms. The infinite set of plane waves is truncated at values for \( G \) and \( k \), such that the kinetic energy term is below a cutoff energy. In atomic units, this can be expressed as follows:

\[
E_{\text{kinetic}} = \frac{|k + G|^{2}}{2} \tag{2.18}
\]

\[
E_{\text{cutoff}} \geq \frac{|G_{\text{cutoff}}|^{2}}{2} \tag{2.19}
\]

The benefit to using plane waves is that they offer an easily scalable method for constructing a wave function. Moreover, due to the nature of plane waves, they ensure a complete basis for representation of the wave function in the limit of \( G_{\text{cutoff}} \rightarrow \infty \). The disadvantage is that calculations require numerous plane waves, which require a significant amount of computational resources.

An alternative method for constructing a basis set is by using localized functions. In this case, the basis consists of functions, \( \{g_{i}(r - r_{a})\} \), centered on each
atomic site $r_n$ that decay to zero as $r - r_n \to \infty$. In this way, they mimic some of the attributes of physical orbitals. Periodicity for localized basis sets is enforced through boundary conditions. One of the most common types of localized basis sets is one composed of gaussian-type orbitals (GTO). A GTO takes the following form:

$$g(r) = Ye^{-\alpha |r|^2} \quad (2.20)$$

In this case, $Y$ represents the angular portion of the GTO and can, for instance, be a polynomial function of $(x, y, z)$ or spherical harmonic of $(\theta, \phi)$. The constant, $\alpha$ then can be determined by the variational theorem. Using such a basis set allows for much smaller matrices during computation. Additionally, integration is easier as the integral for gaussian functions is known analytically. The drawback to this method is that it can often times be difficult to determine the exponential constants and required number of GTOs. Moreover, GTOs do not satisfy the cusp condition at $r = 0$ and the decay much faster than radial components of orbitals would otherwise. Consequently, it makes sense to construct an orbital out of a combination of GTOs to better satisfy these conditions. Such orbitals are called contracted Gaussian-type orbitals. A contracted GTO would then be:

$$g_i(r) = Y_i \sum_k c_{i,k} e^{-\alpha_{i,k} |r|^2} \quad (2.21)$$

A typical Kohn-Sham orbital is comprised of combination of contracted and uncontracted GTOs so as to adequately describe its “core”, while allowing for some variability in its diffuseness (the “valence” portion). These are known as split-valence basis sets. Developed by John Pople’s group, a common notation for these is of the form, $N-XY\!ZG[9]$. The $N$ represents the number of primitive GTOs in the core, while the $X$, $Y$ and $Z$ represent the number primitive GTOs in each valence orbital. In this case, there are three valence orbitals ($X, Y, Z$), so this would be known as split valence, triple-zeta basis set. The $G$ simply means that the component functions are gaussians.

### 2.3.4 Exchange-Correlation Functionals

As mentioned earlier, perhaps the most crucial part of a DFT simulation that utilizes the Kohn-Sham equations is the exchange-correlation functional ($E_{xc}$). It contains information about the wave function that is not captured by the kinetic or potential terms. There are many different functionals that have been developed by the community. The three types this thesis will cover are: ones based on the local density approximations (LDA), ones based on the generalized
gradient approximation (GGA) and hybrid functionals.

**Local Density Approximation**

The initial functionals were developed with the approximation that the exchange-correlation effects of electron solids can be accurately modeled by using the properties of a homogenous electron gas with an equivalent electron density. This is known as the local density approximation (LDA) or, if including spin, the local spin density approximation (LSDA). The exchange-correlation functional then becomes [10]:

\[
E_{LSDA}^{xc} = \int n(\mathbf{r}) \xi_{xc}^{\text{hom}}(n^{+}(\mathbf{r}), n^{-}(\mathbf{r})) d^{3}r
\]

\[
= \int n(\mathbf{r}) \left[ \xi_{xc}^{\text{hom}}(n^{+}(\mathbf{r}), n^{-}(\mathbf{r})) + \epsilon_{c}^{\text{hom}}(n^{+}(\mathbf{r}), n^{-}(\mathbf{r})) \right] d^{3}r
\]

where \( n(\mathbf{r}) \) is the electron density and \( \epsilon_{xc}^{\text{hom}}(n^{+}(\mathbf{r}), n^{-}(\mathbf{r})) \), \( \epsilon_{c}^{\text{hom}}(n^{+}(\mathbf{r}), n^{-}(\mathbf{r})) \) are, respectively: the exchange-correlation energy, exchange energy and correlation energy of the homogenous electron gas as a function of the spin dependent electron densities. In this case the exchange and correlation effects have been separated. The exchange energy can be determined analytically per atom of spin \( \sigma \) as [10]:

\[
\epsilon_{x}^{\sigma} = -\frac{3}{4} \left( \frac{6}{\pi} n^{\sigma} \right)^{1/3}
\]

The remaining correlation effect is then calculated using other means, such as quantum Monte Carlo which David Ceperley and Berni Alder notably used to achieve a high degree of accuracy [11]. Once this functional has been established, it then becomes computationally simple to calculate \( E_{XC} \). The main drawback to LDA is that it has a tendency to mimic the properties of the homogenouse electron gas, which causes solids to appear more metallic than they would otherwise be. Moreover, there is still a self-interaction term that can become problematic in more localized systems [10].

**Generalized Gradient Approximation**

Further improvement was made to LDA by accounting for the gradient in the electron density. Initial attempts simply used the electron density in conjunction with an unmodified density gradient. This formulation is known as a gradient expansion approximation (GEA) and did not show much improvement to existing LDA techniques. Consequently, modifications to GEA were made to alter the behavior of the exchange-correlation functional at large gradients.
These types of functionals fall under the umbrella of the generalized gradient approximation (GGA). Although there are many different approaches to creating a GGA functional, the general form appears as follows [10]:

\[ E_{xc}^{GGA} = \int n(r)F_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|, ...)d^3r \]  

(2.25)

The term \( F_{xc} \) is dimensionless and determined by the methodology outlined by the technique that is used. The GGA functional that is used within this paper was developed by Perdew, Burke and Enzerhof (PBE).

Hybrid Functionals

The last major group of functionals covered are hybrid functionals. These consist of a combination of exchange energy extracted from Hartree-Fock theory and the exchange-correlation energy in either LDA or GGA. A very commonly used hybrid functional is PBE0 [12]:

\[ E_{xc}^{PBE0} = \frac{1}{4}E_{c}^{HF} + \frac{3}{4}E_{xc}^{PBE} + E_{c}^{PBE} \]  

(2.26)

where \( E_{c}^{HF} \) is the Hartree-Fock exchange energy, \( E_{xc}^{PBE} \) is the PBE exchange energy and \( E_{c}^{PBE} \) is the PBE correlation energy. It can be seen that the exchange-correlation energy in this scheme incorporated 25% Hartree-Fock exchange, with the rest coming from the PBE GGA functional. More generally, one can write style of functional as PBE1_ω:

\[ E_{xc}^{PBE1_\omega} = \omega E_{c}^{HF} + (1 - \omega)E_{xc}^{PBE} + E_{c}^{PBE} \]  

(2.27)

In this case, \( \omega \) is a weighting in between 0 and 1. There are other types of hybrid functionals that have been developed as well, such as (but not limited to) the Heyd-Scuseria-Enzerhof (HSE) [13] or Becke, three-parameter, Lee-Yang-Parr (B3LYP) [14]. The former takes into account screening of the exchange energy at long ranges, while the latter uses an empirically defined combination of other functionals and exact exchange energy.

2.3.5 Pseudopotentials

Oftentimes, some of the sets of constants, \( c_i, \alpha_i \) that describe core orbitals for specific atomic species, do not differ much between the isolated atoms and the bonded solid. This is because core states are usually not very active in bonding. Consequently, it is possible to improve the computational efficiency by replacing
these core orbitals with an effective core pseudopotential. With a pseudopotential, one can effectively model fewer electrons, reducing the complexity of the problem. Typically, pseudopotentials are non-local, dependent on the angular momentum channel. In plane wave basis set calculations, the pseudopotential often times takes the form of a projector augmented basis (PAW). PAW pseudopotentials do not actually replace any electrons, but merely modify orbitals in the core regions so as to make the behavior more suitable for computation [10].

2.4 Quantum Monte Carlo

Although DFT has been used historically to great success for a variety of problems, there are instances where the approximations in the approach can result in improper descriptions of a given material. In cases where the exchange-correlation energy is not modeled accurately by a homogeneous electron gas, DFT can cause materials to exhibit more metallic properties. Therefore, it is beneficial to utilize a method that can correct for the deficiencies present in the one-body technique. For this, it is possible to turn to Quantum Monte Carlo (QMC). Within the realm of QMC methods, two methods have been used in this study: variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC).

2.4.1 Variational Monte Carlo

Perhaps the simpler of the two QMC methods described here, VMC utilizes Monte Carlo integration in conjunction with the variational principle to evaluate an expectation value of a given trial wave function, \( \Psi_T^*(\mathbf{R}) \). Given a parameterized trial wave function, one can determine the set of parameters that results in the lowest energy ground state wave function. This energy then represents an upper bound on the exact ground state energy. More explicitly, we can define the expectation value of the energy as:

\[
E_T = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}} \geq E_0
\]

(2.28)

where \( E_0 \) represents the ground state energy, \( \hat{H} \) represents the Hamiltonian operator and \( \Psi_T(\mathbf{R}) \) is a trial wave function. This is rewritten as:

\[
E_T = \frac{\int |\Psi_T(\mathbf{R})|^2 |\Psi_T(\mathbf{R})^{-1} \hat{H} \Psi_T(\mathbf{R})| d\mathbf{R}}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}}
\]

(2.29)

In a standard Monte Carlo integration scheme, we have the form:
\[ V = \int P(x)f(x)dx \quad (2.30) \]

One simply averages samples of the function \( f(x) \) with distribution defined by \( P(x) \) to determine the value \( V \). With this in mind, it is clear that in the VMC scheme, \( P(x) = \frac{|\Psi_T(x)|^2}{\int |\Psi_T(x)|^2 dx} \) and \( f(x) = \Psi_T(x)^{-1} \hat{H} \Psi_T(x) = E_T \). As the number of samples approaches infinity, the Monte Carlo integration approaches the energy of the trial wave function. With this method of determining the total energy of a trial wave function, the task remains of determining the optimal form of such a wave function. A common form of a trial wave function takes the form of a Slater-Jastrow type function [15]:

\[ \Psi(R) = e^{J(R)}D(R) \quad (2.31) \]

The term \( D(R) \) is a Slater determinant and \( J(R) \) is the Jastrow factor whose parameters can be used to optimize the wave function (produce the lowest ground state energy or variance). The orbitals in the Slater determinant are often taken from DFT calculations. While this method allows for improvement to existing DFT calculations, there is another QMC algorithm that permits further refinement with less dependence on the trial wave function.

### 2.4.2 Diffusion Monte Carlo

Diffusion Monte Carlo (DMC) provides an alternative method for solving the many-body Schrödinger equation with less dependence on the trial wave function. With DMC, one solves the imaginary-time form of the Schrödinger equation using an energy offset:

\[ \frac{d\Psi(R, t)}{dt} = (\hat{H} - E_T)\Psi(R, t) \quad (2.32) \]

Representing this as an integral utilizing a Green’s function gives:

\[ \Psi(R, t + \tau) = \int G(R \leftarrow R', \tau)\Psi(R', t) dR' \quad (2.33) \]

\[ G(R \leftarrow R', \tau) = <R|e^{-\tau(\hat{H} - E_T)}|R'> \quad (2.34) \]

In the limit as \( \tau \) approaches zero, the exponential operator in the Green’s function, \( G(R \leftarrow R', \tau) \), projects out the ground state energy, while exponentially dampening all other energy eigenvalues. By solving the Schrödinger equation for \( N \) electrons with the Trotter-Suzuki approximation, one will find
that the Green’s function is:

\[
G(\mathbf{R} \leftarrow \mathbf{R}', t + \tau) \approx (2\pi\tau)^{-3N/2} e^{-(\mathbf{R}-\mathbf{R}')^2/2\tau} e^{-\tau(V(\mathbf{R})+V(\mathbf{R})-2E_T)/2} \tag{2.35}
\]

If one treated this problem as a random walk of Brownian particles, \( G(\mathbf{R} \leftarrow \mathbf{R}', t + \tau) \) acts as the transition probability density of a walker to move from \( \mathbf{R} \) to \( \mathbf{R}' \). To make use of this, one uses the factor \( P = e^{-\tau(V(\mathbf{R})+V(\mathbf{R})-2E_T)/2} \) in conjunction with a branching/birthing/death algorithm to propagate a set of walkers. By following this algorithm and tweaking the offset \( E_T \), one can accurately determine the ground state energy.

Perhaps the primary drawback of DMC is that absent of any restriction, the algorithm trends towards a bosonic description of the wave function. To preserve the fermionic properties of the system, the fixed-node (FN) approximation is introduced. With FN approximation, the nodes of the trial wave function remain static and walkers are disallowed from crossing these nodes. When using DMC, it also necessary to choose a small enough time step for which their is sufficiently small time step error. For both VMC and DMC, trial waves must be created for all k-points of interest. These values are then twist averaged.

### 2.5 Universal Structure Predictor: Evolutionary Xtallography

Released in 2005 by the Oganov Group, USPEX is a crystal structure prediction program, utilizing an evolutionary algorithm combined with \textit{ab-initio} atomistic calculations [16, 17, 18, 19, 20, 21]. While there have been various other evolutionary algorithms, USPEX is flexible, easy to to use and has demonstrated to be successful in a number of studies[22, 23, 24, 25, 26, 27].

USPEX identifies minima on a fitness landscape parameterized by the crystal’s ionic positions and lattice parameters by evolving a population of structures analogous to its biological counterpart. However, unlike a genetic algorithm, which stores information about the structure in the form of binary 1s and 0s, USPEX’s evolutionary algorithm treats properties as physical numbers. Through a combination of breeding to promote fitter offspring and mutations to introduce variability, the algorithm is designed to trend towards a crystal structure that is “most fit.” Fitness is most often characterized by lower enthalpies, but attributes like hardness, band gap and magnetization can be used as well. USPEX also makes use of external atomistic simulation software to improve the efficiency of the algorithm. By using these simulations for local relaxations, USPEX effectively decreases the combinatorial complexity of the problem as structures that relax to the same configuration become clustered together.

USPEX has a few methods to introduce variability into the population:
- Lattice Mutations: a structure’s cell shape is distorted.
- Rotation Mutation: if the structure is a molecular crystal, individual molecules may be rotated.
- Permutation: two different chemical species are interchanged.
- Soft Mutations: ionic positions are translated along directions of soft phonon modes.

While the fraction of offspring affected by these mutations may be set manually, USPEX offers its own “autofrac” mechanism to control these on its own. In addition to these mutations, existing structures can be preserved for the next generation or bred with other fit structures. USPEX creates child structures by combining slabs of two parent structures, while ensuring that the user-imposed stoichiometric restrictions are maintained in the process. After some number of generations, the fittest individuals are expected to survive and continue producing offspring.
3 Stability of Manganese Oxide Polymorphs

3.1 A Literature Review of Manganese Oxide Stability

Transition-metal oxides exhibit a rich variety of intriguing phenomena, including metal-to-insulator transitions\([28, 29]\), high-temperature superconductivity\([30, 31]\), colossal magnetoresistance\([32]\), and colossal dielectric constants\([33]\). These properties are closely related to the strongly correlated nature of the localized \(d\)-orbital electrons. The presence of electron correlations also render transition metal oxides very challenging to model from first principles. One classic example of a correlated metal oxide is manganese oxide (\(\text{MnO}\)), which is of interest for several potential applications including solar energy conversion \([34]\), photoelectrochemical water splitting \([35, 36]\), and as a magneto-piezoelectric semiconductor \([37]\). While the ground state of \(\text{MnO}\) is rock salt (RS), a few years ago metastable wurtzite (WZ) was grown by thermal decomposition on a carbon template \([38]\). More recently, predictions of a reduced band gap and favorable hole transport properties in the wurtzite phase \([34, 3]\) have been verified in experiment \([39]\).

Manganese oxide possesses a \(d^5\) electronic structure, and exhibits antiferromagnetic ordering of the Mn atoms. Several recent first-principles studies have explored in detail the properties of two polymorphs of \(\text{MnO}\): rock salt (RS) and zincblende (ZB)\([3, 2, 40, 41]\). Within the RS and ZB polymorphs, there is antiferromagnetic ordering along the [111] (AF2) and [001] (AF1) directions, respectively\([2]\). Although rock salt is the ground state structure, the generalized gradient approximation (GGA) and some hybrid functionals (HSE06) erroneously predict that the zincblende structure is lower in energy\([3, 2]\). The failure of conventional DFT and even some hybrids to obtain the correct energetic ordering shows the importance of correlation in the phase stability of these materials. The challenges in describing correlated materials within DFT arise from its approximate treatment of electron correlation and exchange. This is true whether one uses the local density approximation\([10]\), the generalized gradient approximation\([10]\), or a hybrid functional\([42, 43, 13]\). The accuracy and transferability of a given approximation across a spectrum of materials, or even for different polymorphs of the same material, must ultimately be justified \textit{a posteriori}, by comparison to experiment.
By contrast, in this work we use fixed-node diffusion Monte Carlo (FN-DMC), a type of quantum Monte Carlo method, to assess the properties of the zincblende and the rock salt polymorphs of MnO. The reasons are twofold. First, in quantum Monte Carlo, statistical sampling is used to approximate the many-body wave function and evaluate total energies directly from the first-principles many-body Schrödinger equation, greatly reducing the extent of approximation necessary. Quantum Monte Carlo methods therefore offer a parameter-free, systematically improvable approach. Because of their direct treatment of electron correlation, they are amongst the most accurate electronic structure approaches available today [44, 45, 46]. Second, although the FN-DMC method is in principle exact when the nodal structure is exactly known, there remain outstanding questions as to the practical accuracy of the technique. It is important to test how well simple nodal surface do in practice. This material system offers a test of the capabilities, using “best practices” for DMC simulation of solids as they are currently understood, to obtain quantitative descriptions of challenging correlated oxide materials.

For MnO, our results show that the DMC method obtains accurate descriptions of the ground state of both the RS and ZB phase, including their relative energies and lattice constants. We find that the magnitude of the fixed node error for the ground state is small in comparison to the substantial improvement that comes from adopting an explicitly correlated approach. Because DMC samples the true many-body wave function, we analyze the properties of this highly accurate model to assess the physical reason for the failure of DFT methods. Thus, the use of FN-DMC helps to reveal aspects, such as charge fluctuation and localization, that may not be accurately captured by other methods. In agreement with other theoretical methods, we also find that the band gap of the ZB phase is substantially lower than that of RS phase according to FN-DMC. However, FN-DMC overestimates the band gaps of both polymorphs in comparison to experiment. We discuss possible reasons for the overestimate.

3.2 DFT and DMC Methodology

The QMC calculations reported here were carried out within the FN-DMC framework as implemented in the QWalk code [47], with single-determinant Slater-Jastrow trial wave functions constructed from DFT Kohn-Sham orbitals, with variance-minimized two-body Jastrow coefficients, and a time step of 0.004 au. We also assessed the sensitivity of the DMC energy to various forms of trial wave functions, such as two and three body Jastrow factors and both energy and variance minimization to optimize the Jastrow parameters. However in all cases we find the DMC energies to be statistically equivalent. This is similar to our observations for DMC simulations of the wide band gap material zinc oxide, also using small-core BFD pseudopotentials and a similar simulation strategy [48].

Ground state energies were determined by twist averaging the DMC energies
Figure 3.1: (Color online). The rock salt (left) and zincblende (right) polymorphs of manganese oxide; both exhibit an antiferromagnetic ordering of Mn atoms. The grey atoms are oxygen and the blue or red are opposing spin manganese atoms. In the rock salt structure each Mn atom possesses a neighboring octahedral field of O atoms; in the zincblende structure the neighboring field of O atoms surrounding each Mn atom is tetrahedral instead.

calculated at real-valued $k$-points, which corresponds to a $2 \times 2 \times 2$ grid in each supercell. Scalar-relativistic energy-consistent Hartree-Fock pseudopotentials ([Ne] core for Mn) as implemented by Burkatzki, Filippi, and Dolg (BFD) [49] were used to remove the core electrons. These pseudopotentials are designed for use within QMC and there are now several indications in the literature that they are well-suited for DMC simulations of solids[50, 51, 52, 53]. The rock salt structure of MnO has previously been studied within DMC[54]; to this analysis we now provide a comparison between the ZB and RS polymorphs, physical insights into the electronic structure of the two phases, and statistical analysis of the many body wave functions to reveal the reasons for the failure of conventional and hybrid DFT to obtain the correct energy ordering.

To obtain the trial wave functions for the DMC calculations, we carried out DFT simulations for the RS and ZB phases. For these simulations, we used the CRYSTAL code[55] and gaussian-type localized basis sets to expand the Kohn-Sham orbitals. The DFT results presented here implement the “PBE1$_x$” framework in which the degree of exact exchange mixing $\alpha$ is systematically varied. We do this to study the effect on both the DFT results themselves as well as the the final DMC results arising from different selections of trial wave functions.
3.3 Density Functional Theory Results and Construction of Trial Wave Functions

3.3.1 Effect of Exchange Mixing

![Graph showing the energy difference $E_{ZB} - E_{RS}$ as a function of exchange weight.](image)

Figure 3.2: (Color online). The energy difference $E_{ZB} - E_{RS}$ according to DFT-PBE1-x, obtained from all electron calculations (orange) and with Burkatski-Filippi-Dolg (Hartree-Fock) pseudopotentials (blue). According to all electron results, for $\alpha = 0$ the ZB phase is lower in energy but as $\alpha$ increases the RS phase becomes stable. The crossing occurs around $\alpha = 10\%$. When Burkatski-Filippi-Dolg pseudopotentials are used, the trends are very similar.

To begin, we construct a set of trial wave functions for the DMC calculations using the DFT-PBE1-x approach, in which the degree of exchange mixing $\alpha$ is varied between 0 and 60%. In Figure 3.2, we illustrate the ground state energy difference ($E_{ZB} - E_{RS}$) per formula unit MnO, as a function of the degree of exchange mixing used in the DFT-PBE1-x calculations. For comparison, we also show all electron results as well. It is encouraging that the two sets of results are quite similar, which suggests that the relativistic Hartree-Fock pseudopotentials are not affecting the analysis substantially. For these calculations, 4 atom unit cells were used for both RS and ZB in conjunction with an $8 \times 8 \times 8$ Monkhorst-Pack sampling of $k$-points in the Brillouin zone. The RS lattice constant was set to 4.43 Å, matching experiment[1], while the ZB lattice constant was set to the PBE0 lattice constant of 4.73 Å since the experimental value is not known. Positive values of ($E_{ZB} - E_{RS}$) in Fig. 3.2 denote more stable rock salt phase.

Consistent with previous results[3, 2], we find that without exchange mixing ($\alpha = 0\%$, PBE) the ZB phase is more stable (by $\approx 70$ meV/fu in our case, both for all electron and BFD pseudopotentials. As the degree of exchange mixing is increased, the RS phase becomes more favored. For instance, for $\alpha = 60\%$
Figure 3.3: (Color online). The partial density of states for O 2s,2p and Mn 3d orbitals, as obtained within DFT for different degrees of exchange mixing $\alpha$. As $\alpha$ increases, the band gap becomes larger as expected. Also below the valence band maximum, the $p-d$ hybridization increases as the relative Mn 3d orbital energies near the VBM drop.

RS has become more stable by $\approx 250$ (BFD) or 300 (all electron) meV/fu. The cross-over occurs around an exchange mixing of $\alpha \approx 10\%$. We note the wide variability of relative DFT energy differences predicted for different selections of $\alpha$ in Figure 3.2. For oxides and wide gap semiconductors, although the empirical choice $\alpha = 25\%$ in hybrid calculations is motivated from perturbation theory\[?] and appears to be quite reasonable in many instances, sometimes tuning of the parameter is required\[56]. This sensitivity to simulation parameters renders true quantitative predictions of energy ordering and phase stability challenging within the hybrid DFT framework.

Regarding the energy differences shown in Fig. 3.2, our results are consistent with previous results in which several DFT functionals including the Heyd-Scuseria-Ernzerhof screened exchange hybrid functional (incorrectly) find ZB to be more stable than RS \[2, 3\]. For instance, using HSE06, the energy difference $E_{ZB} - E_{RS}$ is reported to be -28 meV/fu\[3\]. There are some cautionary notes to be aware of when comparing our results in Fig. 3.2 to others, however. We are using BFD (Hartree-Fock) rather than DFT pseudopotentials since our primary interest is to generate the best possible QMC description, and not to carry out a DFT study per se. The more localized treatment of the core within Hartree-Fock influences DFT results reported here. Also, the lattice constants are fixed to generate the results of Fig. 3.2, rather than optimized separately for each value of $\alpha$ considered. This affects the precise energy differences as well as the...
Figure 3.4: (Color online). The total absolute spin on the manganese atoms increases with increasing exchange weight $\alpha$. The spin on the ZB phase is always lower than that of the RS phase.

“cross-over” value of $\alpha$. Qualitatively, however, Figure 3.2 shows the expected behavior that is consistent with previous results\cite{3, 2} for this system, and the BFD results appear to be a good starting point for DMC analysis.

### 3.3.2 Density of States

To better understand the DFT trends in Fig. 3.2, in Fig. 3.3 we show the density of states for both phases for different selections of $\alpha$. The black lines are the total DOS, while blue and red respectively indicate states with O 2s,2p and Mn 3d character. The first trend, as expected, is that increasing $\alpha$ widens the band gap in all cases. In addition, $\alpha$ also has an effect on the relative position of the O 2p and Mn 3d orbitals below the valence band maximum (VBM). For both phases, for $\alpha = 0\%$ there are two distinct groups of states: one near the VBM dominated by Mn 3d orbitals, and another lower in energy dominated by O 2p orbitals. As $\alpha$ increases, the mixing between these sets of orbitals below the VBM increases and the two groups begin to merge; $\alpha$ is essentially a tuning parameter that governs the degree of p-d hybridization in the materials. \textit{A priori} it is not possible to know which degree of hybridization best captures reality (nor do we expect that sweeping through $\alpha$ will span all possibilities). However, to first order increasing $\alpha$ has the effect of canceling the self-interaction error that is present within DFT. Given the trends in Fig. 3.2, it appears that RS benefits more from this cancellation than ZB (i.e., its energy decreases faster as
Crystal field theory provides a plausible explanation for why this may be the case. In RS the octahedral field of O surrounding each Mn splits the five degenerate 3d orbitals into three lower energy $t_{2g}$ and two higher energy $e_g$ orbitals. The $t_{2g}$ orbitals are non-bonding, but the $e_g$ orbitals directly overlap and hybridize with the O ligands to form bonding $e_g$ and antibonding $e_g^*$ states (see Fig. 3.3 for RS for $\alpha = 25\%$). For RS the direct orbital overlap results in a large hybridization and large crystal field splitting between the $t_{2g}$, $e_g$ levels. By contrast, in the ZB phase the tetrahedral coordination of the Mn 3d orbitals results in a splitting of the Mn 3d orbitals into two lower energy $e$ orbitals and three higher energy $t_2$ orbitals. This time the $e$ orbitals are non-bonding while the $t_2$ orbitals interact with the O ligands (see Fig. 3.3 for ZB for $\alpha = 25\%$). The difference is that the $t_2$ orbitals are oriented in between the O orbitals, so the spatial overlap now is less direct. Although the interaction creates bonding and antibonding $t_2$ states, the resulting crystal field splitting is smaller for ZB.

We speculate that the direct overlap of orbitals for the RS phase, in contrast to the indirect overlap for ZB, contributes to the difficulty of accurately modeling the RS phase. Greater overlap implies more electrons will occupy the same region in space, which can only be captured by a very good description of electron correlation and exchange. The approximate description of electron correlation in DFT may therefore more adversely affect RS MnO than ZB MnO, causing its energy to be higher than it should be and resulting in the wrong energy ordering.

### 3.3.3 Total Magnetic Moment

Before proceeding to the DMC results, we also show in Fig. 3.4 the total absolute spin on each of the Mn as a function of the exchange weight $\alpha$. For both phases, as expected the total spin increases with increasing $\alpha$ as the electrons become more localized.\(^1\) The effect of increasing $\alpha$ diminishes over the domain as the spin approaches 5, the total spin in the ionic limit of the high spin $d^5$ oxide. Furthermore, the total spin on the manganese atoms of ZB is consistently less than those of RS, which is again related to its smaller crystal field splitting.

### 3.4 Results from DMC Description

#### 3.4.1 Effect of Trial Wave Function

For the DMC calculations, our first goal is to determine the trial wave function that gives the best description of each phase. Figure 3.5 shows the total DMC

\(^1\)Note that the increased localization as the exchange mixing grows is not inconsistent with the increased hybridization discussed in Section III.B. In particular, in our terminology hybridization and localization are not equivalent. Hybridization indicates the degree of mixing of isolated atomic states, but the resulting state (even after hybridization) can still be localized.
energies for both the RS (red) and ZB (blue) phase as a function of the α used to generate the trial wave function for a 4 atom unit cell. As DMC is a variational technique, the α that results in the lowest DMC energy gives the best representation of the true nodal surface. Thus, we can use α to vary the nodes of the trial wave function. Although the exact nodal structure is not known, it is expected to sample a wide range since this parameter tunes an important physical quantity: the hybridization between oxygen and manganese.

For both RS and ZB, a minimum in the DMC energy is observed around α ≈ 25%. It is interesting to note that this is similar to several other transition metal oxides for which minima in DMC energy tend to occur in a range 15% < α < 35% including VO₂ [50], FeO[53], CaCuO₂[?], LaCuO₄[?], and ZnO[48]. We speculate that α = 25% may tend to offer the best description of hybridization between the transition metal d and the O 2p orbitals, although we emphasize that this may not always be the case. For both phases the overall variation of the total DMC energy is less than 0.15 eV/fu across the full range sampled here, indicating that variations in nodal structure can give rise to total energy differences of roughly this magnitude. Nevertheless, the exchange weight that offered the lowest ground state DMC energy within the 4 atom system was used for both polymorphs for all subsequent calculations. This exchange weight was calculated by applying a Bayesian quadratic fit[57] to the data of Fig. 3.5 from

Figure 3.5: (Color online). The effect of varying the trial wave function in DMC using different DFT-PBE1ₓ exchange weights α on the DMC total energies for RS and ZB (error bars are smaller than the marker size). Both phases demonstrate a minimum energy around α = 25%, and maintain similar relative energies over the domain.
Figure 3.6: (Color online). The effect of varying the trial wave function in DMC using different DFT-PBE$_1$ exchange weights $\alpha$ on the DMC total energies for RS and ZB (error bars are smaller than the marker size). Both phases demonstrate a minimum energy around $\alpha = 25\%$, and maintain similar relative energies over the domain.
which a minimum was determined: \( \alpha_{\text{min}} \approx 25.0 \pm 0.7\% \) for rock salt, and
\( \alpha_{\text{min}} \approx 28.1 \pm 0.4\% \) for zincblende.

From the parabolas in Fig. 3.5, it appears that when comparing energy differences between two structures, variations in the nodal structure benefit from a cancellation of errors. The DMC energy differences (space between the parabolas for a given \( \alpha \)) are even less sensitive to changes in the nodal surface that arise from varying \( \alpha \) in the trial wave function. The total variation in \( (E_{\text{ZB}} - E_{\text{RS}}) \) per \( \text{fu} \) across the full range of \( \alpha \) spanned is now only \( 0.053 \pm 0.010 \) eV (in spite of the 0.3 eV/fu variation exhibited by the DFT starting point calculations). We caution that since these DMC results are for 4 atom cells, they suffer from finite size effects and therefore the precise value \( (E_{\text{ZB}} - E_{\text{RS}}) \) is not meaningful (we later carry out a full extrapolation of \( (E_{\text{ZB}} - E_{\text{RS}}) \) for increasing supercell size). Our focus here instead is on the sensitivity of \( (E_{\text{ZB}} - E_{\text{RS}}) \) to the trial wave function, which is quite small. It is encouraging that DMC gives consistent results in spite of the large variability of the starting point.

### 3.4.2 Effect of DMC Timestep

In diffusion Monte Carlo, a Green’s function approach is used to propagate a set of walkers in a \( 3N_e \)-dimensional space \( (N_e \) is the number of electrons), to statistically sample the many-body wave function. The Green’s function projector is exact only in the limit of vanishingly small time step, but in practice implementation of DMC requires a finite time step, which introduces an error in the projected energy\[^{[58, 59]}\]. Therefore, it is important to show that errors in the projected energy due to the finite time step are small, in comparison to the energies of interest. In Fig. 3.6, we show the DMC energy for RS and ZB (4-atom supercells, twist averaged) as a function of the DMC time step, and the extrapolation of the energy to infinitesimal time step. For both phases the dependence of the energy on the time step shows a linear or near-linear dependence, which is expected for sufficiently small time steps. For time steps smaller than 0.01 au, for each phase the energy varies within \( \approx 0.1 \) eV/fu of the extrapolated value.

Most importantly, the inset of Fig. 3.6 shows the energy difference \( E_{\text{ZB}} - E_{\text{RS}} \) (eV/fu) vs. the DMC time step, which is the quantity which we are ultimately interested in resolving. This figure shows that energy differences somewhat benefit from a cancellation of time step errors. For instance, in the limit of zero time step the energy difference is \( 0.05(1) \) eV/fu. For a time step of 0.01 au, the computed energy difference instead is around \( 0.06(1) \) eV/fu, which indicates a time step error in the energy difference of \( \approx 0.01(1) \) eV/fu. For a time step of 0.004 au, the computed energy difference is within error bars of the extrapolated energy difference. For the remainder of this work, we use a DMC time step of 0.004 a.u. The uncertainty in \( E_{\text{ZB}} - E_{\text{RS}} \) arising from the time step error here is then less than 0.01 eV/fu, which (as we will demonstrate later) is smaller
than the energy difference that we are trying to resolve.

### 3.4.3 Lattice Constants

![Graph showing lattice constants](image)

Figure 3.7: (Color online). Extrapolated values of lattice constants according to DMC for ZB and RS MnO are $4.73 \pm 0.004$ Å and $4.47 \pm 0.005$ Å respectively. The RS value is within 1% of experiment $4.43$ Å\[^{[1]}\]. The experimental value for ZB is unknown, but the DMC value matches the PBE0 value of $4.73$ Å.

Since energy differences due to using the wrong lattice constant can be significant when resolving small differences in total energies, it is necessary to find the optimal lattice constants for both phases within DMC itself. Finding lattice constants in DMC is complicated by the fact that DMC simulations of bulk solids themselves suffer from both one-body and many-body finite size effects. The former are accommodated by twist-averaging, but the latter arise from a spurious correlation between image electrons in the computational domain which typically reduces the total energy\[^{[60]}\]. For large enough supercells, the energy variations scale as $1/V$, where $V$ is the volume of the cell\[^{[60]}\] (or $1/N$, where $N$ is the number of atoms in the supercell, since $N$ is proportional to $V$).

Using the optimal $\alpha$ for each phase, we evaluated the total DMC energy of the RS and the ZB phase as a function of the lattice constant $\alpha$, for supercells of size 4, 8, and 16 atoms. Fig. 3.7 shows the minimum $\alpha$ obtained for each phase and supercell size. We find that the optimal lattice constant is not the same for different sized supercells but that they increase with increasing supercell size. To our knowledge, there are no studies of finite size effects on lattice constants within DMC, which would be an interesting avenue for further analysis. From the results in Fig. 3.7, we speculate that many-body finite size
effects bias towards smaller lattice constants. For small supercells, the calculated total energies are artificially low, dominated by the finite size effect. The lattice constant is drawn towards smaller values, which further enhances the stabilizing influence of the spurious image electron correlation. As the supercell size increases, the finite size effect is reduced and the lattice constants better reflect the true values.

In any case, extrapolating our results to the thermodynamic limit $N \to \infty$, the lattice constants for the ZB and RS polymorphs of MnO were determined to be $4.730 \pm 0.004 \, \text{Å}$ and $4.470 \pm 0.005 \, \text{Å}$. While there is no experimental measurement for the ZB structure, the lattice constant for the RS structure has been previously measured to be $4.43 \, \text{Å}$\cite{1}, demonstrating that in this case our DMC approach can estimate lattice constants to within $\sim 1\%$ of experiment. For the ZB phase the estimated lattice constant matches well the PBE0 value of $4.73 \, \text{Å}$.

### 3.4.4 Total Energies and Phase Stability

Finally, using the optimal values of $\alpha$ and the DMC-optimized lattice constants for each phase, we are able to estimate the energy difference for the two phases in the thermodynamic limit. We extrapolated the DMC total energies to the thermodynamic limit using supercells of size $N = 8, 16, \text{and} 32$ atoms. Our extrapolated DMC results, shown in Fig. 3.8a, find that the RS phase is more stable than ZB by $132 \pm 6.5 \, \text{meV/fu}$. A summary of our DMC results, in comparison to results obtained using other theories, is presented in Fig. 3.8b. It is interesting to note the excellent agreement with the estimate of $131 \, \text{meV/fu}$ obtained using the random phase approximation to the correlation energy, in conjunction with the application of a Hubbard $U$ as well as a nonlocal external potential $V$ (which are carefully chosen to obtain the correct $p\text{-}d$ coupling between unoccupied and occupied states, respectively) \cite{3}. It is encouraging that fixed-node DMC with single determinant wave functions leads to a good description of the basic properties of this highly correlated, antiferromagnetic system. This suggests that this technique can be used for other, similarly complicated materials.

### 3.4.5 Charge Fluctuations

Since they predict different relative energy ordering, a natural question is “what changed between the description of the materials in DFT and in DMC?” To provide some insights, in Fig. 3.9 we present the site-resolved charge fluctuations, also known as the compressibility, according to both DFT (a Slater determinant composed of the Kohn-Sham orbitals) and DMC. The compressibility is the expectation value $e^{\langle \hat{n}_i - \langle \hat{n}_i \rangle \rangle^2} \Psi$, where $\hat{n}_i$ is the number operator on the Voronoi polyhedron surrounding atomic site $i$. The expectation value is evaluated for a given site by sampling over the DMC configurations of the wave function. The
compressibility represents the degree to which the number of electrons around a given site fluctuate about the average when the many body wave function is properly sampled. Larger compressibility indicates more fluid charges and delocalized states, while smaller compressibility indicates larger barriers to charge fluctuations and localized states. The charge fluctuations, resolved into majority and minority spins on Mn atoms, are compared for a Slater determinant of DFT (PBE, HSE06, and PBE0) orbitals and our DMC results. We have included the site fluctuations according to Hartree Fock as well for comparison.

According to Figure 3.9, the charge fluctuations vary substantially amongst the different theories. As expected, across the board the fluctuations are largest for PBE (green markers) and smallest for Hartree Fock (brown markers). The DMC results (red markers), presumably the closest to reality, lie somewhere in between. Both PBE0 and HSE06 are observed to improve the description in comparison to PBE, decreasing the charge fluctuations towards the DMC values. It is remarkable that HSE06 and PBE0 both recover the correct qualitative ordering of the fluctuations on the different atomic species. By contrast, PBE does not get the qualitative ordering correct. For example for ZB the Mn fluctuations are all larger than the O fluctuations, different from the DMC result. Further, Mn in the high spin $d^5$ configuration should have the compressibility of the majority spin higher than that of the minority. This is properly captured by FN-DMC, HF, and the hybrids. By contrast, PBE misses this physics entirely both in RS and ZB: majority and minority spin Mn have similar compressibility. As Fig. 3.9 shows, PBE does not describe the localization properly. Ultimately, obtaining the correct energy ordering depends on obtaining a good description of the localization of the states in both phases. Given the inability to properly describe the localization, PBE cannot be expected to give quantitative information about the relative stability of the materials in question.

## 3.4.6 Optical Excitation Energies

Lastly we turn to the DMC calculation of the optical excitation energies for both polymorphs. Interest in the polymorphs of MnO has grown recently thanks to computational suggestions that for $d^5$ oxides the zincblende polymorph, although metastable, should have a smaller band gap and a favorable band like hole transport mechanism [34]. Subsequent non-equilibrium growth of Mn$_{1-x}$Zn$_x$O alloys in the wurtzite structure and photo-electrocatalytic device measurements have recently confirmed the predictions [39]. A summary of previously reported band gaps, both from experiment and computation, is given in Table 3.1.

To these results, we now add the the band gaps of the two phases as obtained from DMC using a procedure that has previously been used successfully [45, 7, 68]. For both phases, we calculate both the quasiparticle gap (QP) and the optical gap (OG). We obtain the quasiparticle gap by calculating the difference
### Method – Rock salt

<table>
<thead>
<tr>
<th>Method</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity [61]</td>
<td>3.8 – 4.2</td>
</tr>
<tr>
<td>Optical Absorption [62]</td>
<td>3.6 – 3.8</td>
</tr>
<tr>
<td>Photoemission spectroscopy [63]</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>Photocurrent measurements [64]</td>
<td>3.4</td>
</tr>
<tr>
<td>LDA [65]</td>
<td>0.78</td>
</tr>
<tr>
<td>GGA [66]</td>
<td>2.6</td>
</tr>
<tr>
<td>LDA + GW [65]</td>
<td>3.5</td>
</tr>
<tr>
<td>(GGA+U) + GW [34], [65]</td>
<td>3.36</td>
</tr>
<tr>
<td>GGA + GW [66]</td>
<td>1.7</td>
</tr>
<tr>
<td>HSE03 + GW [66]</td>
<td>3.4</td>
</tr>
<tr>
<td>DMC [67]</td>
<td>4.8 ± 0.2</td>
</tr>
<tr>
<td>DMC (QP) (this work)</td>
<td>4.55 ± 0.26</td>
</tr>
<tr>
<td>DMC (OG) (this work)</td>
<td>4.47 ± 0.16</td>
</tr>
</tbody>
</table>

### Method – Zincblende

<table>
<thead>
<tr>
<th>Method</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(GGA+U) + GW (Mn$_{1-x}$Zn$_x$O, $x = 0.5$) [39]</td>
<td>2.30</td>
</tr>
<tr>
<td>(GGA+U) + GW [34], [39]</td>
<td>2.13, 2.38</td>
</tr>
<tr>
<td>DMC (QP) (this work)</td>
<td>3.55 ± 0.17</td>
</tr>
<tr>
<td>DMC (OP) (this work)</td>
<td>3.84 ± 0.14</td>
</tr>
</tbody>
</table>

Table 3.1: Compiled existing data and current DMC results on the band gaps of MnO ZB and RS polymorphs.

The optical gap is obtained as

$$OP = E_{\Gamma \rightarrow \Gamma} - E_o .$$  \hspace{1cm} (3.2)
In this expression $E_o$ denotes the ground state energy and $E_{\Gamma \rightarrow \Gamma}$ denotes the energy of the first optically excited state. We estimate the energy difference by evaluating $E_o$ and $E_{\Gamma \rightarrow \Gamma}$ at $\Gamma$, and $E_{\Gamma \rightarrow \Gamma}$ is calculated by promoting an electron from the highest occupied Kohn-Sham orbital at $\Gamma$ to the lowest unoccupied orbital in the construction of the Slater determinant. For the OG, once again 32 atom supercells are used. For both phases, the OP and the QP obtained in this manner are close, within error bars of each other.

According to Table 3.1, compared to previously reported DFT and GW values our DMC results are high (but our gap for the rock salt phase is similar to Kolorenc and Mitas’s previous DMC results[67]). While DMC also predicts that ZB has a lower gap by around 1 eV than RS, the DMC gaps themselves appear to overestimate the experimental values by 0.5 – 1 eV. We suggest several possible reasons for this. The first is that finite size effects affect the calculated values. A second possibility is that the trial wave functions generated for excited states may not be as good as those generated for the ground state. If the nodal structure of the excited state wave function is more complex, then nodal errors will result in an overestimated gap.

In fact, we note that the case of MnO is particularly challenging for DMC. According to the picture from Zaanen, Sawatsky, and Allen [69], the 3d transition metal oxides can be classified as either Mott-Hubbard insulators or charge transfer insulators, based on the degree of 3d orbital filling. The early 3d elements form Mott-Hubbard insulators, for which the gap appears across states of d orbital character (upper and lower Hubbard bands). The late 3d elements form charge transfer insulators, for which the gap appears across O 2p and TM 3d states. The case of $d^5$ MnO lies just at the transition, suggesting that the VBM has mixed $p - d$ character. Since the excited state calculation requires removing an electron from the VBM, the sensitivity to the trial wave function is expected to be particularly strong. We suspect that obtaining a better description of the gap depends strongly on generating trial wave functions which more accurately capture the nature of the VBM.
Figure 3.8: (Color online). (a) The extrapolated DMC total energies of the RS and ZB phase; the RS phase is found to be lower in energy by $E_{ZB} - E_{RS} = 132 \pm 6.5$ meV/formula unit. (b) Compiled existing results and current DMC results on the energy ordering of MnO ZB and RS polymorphs.
Figure 3.9: (Color online). The charge fluctuations $\langle \Psi | (\hat{n}_i - \langle \hat{n}_i \rangle)^2 | \Psi \rangle$ site-resolved onto Mn and O atoms from Slater determinants of PBE, PSE0, HSE06 orbitals, in comparison to DMC and Hartree-Fock for rock salt (top) and zincblende (bottom). The trends demonstrate that both PBE0 and HSE06 improve the description of the materials, bringing the fluctuations closer to that of the DMC values.
4 Materials Discovery in the Barium-Ruthenium-Sulfur Phase Space

4.1 Variable Composition Search with USPEX

In describing existing studies using the USPEX code, it is helpful to categorize prior work based on the type of restrictions placed on the phase space search. With this in mind, there are a few potential approaches to classification. When looking for new compounds with USPEX, the focus of the code can be primarily restricted by specifying starting symmetries, number of atoms or composition. There are other attributes, such as mutation and heredity parameters, but these do not affect the scope of potential structures. The starting symmetries determine the randomly generated structures USPEX generates in the process of the search. Typically these symmetries are either lost or transformed into other symmetry groups after "breeding" with other compounds. Consequently, categorization based on symmetry restriction loses its ability to distinguish various searches as the code loses memory of the initial symmetry restrictions given enough time. The maximum number of atoms used in the simulation, while important, should not be a primary factor in the search if it is large enough to cover the domain of interest. The last restriction, composition, therefore seems most apt for categorization.

When using USPEX, one must identify the compositional phase space within which the evolutionary search will operate. When the stoichiometry of the material is known in these systems but little is known of the geometry, USPEX can be restricted to the particular composition with the number of atoms specified by some multiple of formula units per cell. However, this creates a dilemma whereby there is a tradeoff between computational time and predictive accuracy. A system composed of a smaller number of formula units is faster for computing energies and has a smaller phase space to sample but may not encompass a domain containing the global minimum. On the other hand, a larger number of atoms will be much slower to compute energies and sample phase space but is more likely to encompass a domain containing the optimal structure. To cope with this conundrum, one can run USPEX with an increasing number of formula units per cell\[22, 23, 24\]. By progressively widening the phase space like this, the structure search can sometimes be made quicker, while improving sampling of the structural domain.

There are some instances where USPEX is used to explore a phase space
composed of two or more constituent compounds[25]. In this case the variable composition functionality of USPEX is implemented. Each compound’s stoichiometry is inputted as building blocks and the code generates structures with compositions that are linear combinations of these building blocks. The total number of atoms within the cell can still be controlled as an additional constraint. This building block functionality has also been modified by some in search of novel polymers[26]. Instead of using compositional building blocks, the code was modified to accept repeating units as building blocks in determining optimal polymeric structure.

USPEX has also been implemented in systems where there is no information regarding the composition of the crystal[27]. This type of structure search represents the most difficult of the ones mentioned as the compositional phase space is entirely unrestricted. One must consider all combinations of constituent elements with a given number of atoms in the crystal. In this case, a variable composition is used with building blocks consisting of singular elements. Within this type of search it is difficult to predict, and thus restrain, both the number of atoms per unit cell and its composition. The search for new compounds within the Barium-Ruthenium-Sulfur phase space encompasses this last type of phase space search.

In the course of the research, three phase space searches were conducted using USPEX: a Barium-Sulfur search, a Ruthenium-Sulfur search and the full Barium-Ruthenium-Sulfur search.

4.2 Binary Search of Barium-Sulfur and Ruthenium Sulfur Phase Space

4.2.1 Computational Details

Both the ruthenium-sulfur and barium-sulfur searches were restricted to between 8 and 30 atoms per unit cell. The variation operators (parameters controlling the mutation and heredity) were set to the “autofrac” function of USPEX, which automatically adjusts these factors over the course of the structure search. The initial population consisted of no less than 100 structures including seeds derived from the Materials Project structure predictor [70, 71]. Subsequent generations were restricted to 75 structures. Local relaxations for structures were conducted using Vienna ab-initio simulation packaged (VASP)[72, 73, 74] utilizing the projector augmented wave (PAW) pseudopotentials [75]. Relaxations were performed for both the geometry of the unit cell as well as the ionic positions. Final energies were calculated at a k-resolution of $2\pi \times 0.08\AA^{-1}$ at an energy cutoff of 500 eV.
Figure 4.1: The formation enthalpies of the barium-sulfur search (a) and ruthenium-sulfur search (b) are plotted along with their convex hulls. Known formation enthalpies of barium-sulfur and ruthenium-sulfur compounds have been added to the figure. In barium-sulfur search, the known BaS (space group 225) compound appears to be located at the global minimum formation enthalpy for this phase space search. Other known compounds have formation enthalpies equal or near the minimum of their respective compositions. In the ruthenium-sulfur search, the known compound RuS2 (space group 205) appears at the global minimum.
4.2.2 Binary Search Results

The formation enthalpies of USPEX-generated structures, along with those of known barium-sulfur compounds are plotted in Figure 4.1(a). It is clear that the BaS compound with space group 225 is the most stable crystal in this phase space search. Moreover, the other known compounds appear to be at the energy minimum for their respective composition. The exception is the compound Ba2S3 with space group 109. It is particularly noteworthy that the known compounds do not necessarily appear on the edges of the convex hull. The compounds that are located on the edges of the convex hull happen to have primitive symmetries.

For the ruthenium-sulfur compounds, the formation enthalpies and energies of known compounds are plotted in Figure 4.1(b). In this USPEX run, there appears to be less variance in the compositions, with most of the structures confined to one composition. This could be due to a combination of the materials project seeds favoring this particular composition and too few generated structures. The global minimum for this run again appears to be a known compound. In this case, it is the compound RuS2 with space group 205.

The appearance of compounds significantly above the convex hull and the general lack of local minima in both calculations suggests that metastable states may be difficult to parse out from structures generated by a USPEX calculation. They generally appear at the minima of their respective compositions, but it is difficult to determine by inspection when the compositional minimum is thermodynamically stable as there are many such compounds that were generated that have this quality. Therefore, choosing compounds to further explore can be very challenging.

4.3 Barium-Ruthenium-Sulfur Phase Space

4.3.1 Computational Details

For the full barium-ruthenium-sulfur search, cell sizes were restricted to between 8 and 30 atoms per unit cell. Like the binary calculations, the variation operators (parameters controlling the mutation and heredity) were also set to the “autofrac” function of USPEX with local relaxations for structures conducted using VASP and PAW pseudopotentials. Again, relaxations were performed for both the geometry of the unit cell as well as the ionic positions. Final energies were calculated at a k-resolution of $2\pi \times 0.08\AA^{-1}$ at an energy cutoff of 300 eV. Unlike the binary searches, though, the ternary search represents a combination of different searches. The population size for these searches varied between 15 and 50 for all runs. Due to the lack of sampling of the compositional phase space, further fixed compositional searches were taken to “push down” the convex hull. The results of this search can be seen in Figure 4.2.
Figure 4.2: The formation enthalpies of structures generated by USPEX for the barium-ruthenium-sulfur phase space are plotted in on a (a) three-dimensional ternary scatter plot with a convex hull and on a (b) two-dimensional ternary heat map. Compositions are represented as stoichiometric fractions with axes parallel to the tick marks indicated on the edges of the plot.
4.3.2 Ternary Search Results

It is difficult to assess the effectiveness of the ternary search for the barium-ruthenium-sulfur phase space as there are no known preexisting compounds to which one can compare. However, Figure 4.2 suggests that binary ruthenium-sulfur compounds are significantly more stable than any of the generated ternary compounds. The preference of the USPEX search for these binary compounds does not preclude the possibility of there existing ternary compounds as it is demonstrated in Figure 4.1(a) that stable compounds can form even when their formation enthalpies are significantly greater than the global minimum. After analysis of the results, it was found that the most stable symmetric ternary compound in the search was one with formula BaRu2S2 and space group 139. This compound is illustrated in Figure 4.3. There is still more work that needs to be done to determine whether this compound is indeed stable. With more insight into its thermodynamic stability, it may be possible to predict whether BaRu2S2 can be synthesized.
In this work, we have utilized FN-DMC to elucidate the electronic properties and stability of the RS and ZB polymorphs of MnO. We find that DMC predicts a ground state energy ordering of these two phases in agreement with experiment without the use of any parameters. The energy ordering is insensitive to the choice of the trial wave function, even though different DFT trial wave functions predict very different phase stabilities. DMC lattice constants are also in good agreement with experiment. Analysis of the site resolved charge fluctuations illustrate some of the primary problems with conventional DFT and show that hybrid functionals make improvements. Finally, we find that the DMC calculated band gaps indicate that the tetrahedrally coordinated phase has a lower gap, but that (within our approach) DMC overestimates the gap according to experiment. We attribute this to the challenge of capturing proper description of $p - d$ hybridization in the trial wave functions used in the DMC calculations.

We also have found that there is difficulty in predicting new materials in the Ba-Ru-S phase space. Within both binary Ba-S and Ru-S, the most stable known compounds are heavily favored, without the presence of local minima dependent on composition. It is therefore difficult to discern which structures are in fact thermodynamically stable and which are simply an artifact of the USPEX algorithm. Despite this challenge, we have identified the structure BaRu$_2$S$_2$ with space group 139 as a potential new ternary compound. Further calculations are needed to test the viability of this structure.
References


31] Yoichi Kamihara, Takumi Watanabe, Masahiro Hirano, and Hideo Hosono. Iron-based layered superconductor La[(1-x)F(x)]FeAs (x = 0.05-0.12) with T(c) = 26 K. *Journal of the American Chemical Society*, 130(11):3296–7, March 2008.


