First-principles Calculations of Nuclear Magnetic Resonance Chemical Shielding Tensors in Complex Ferroelectric Perovskites

Daniel Lawrence Pechkis
College of William & Mary - Arts & Sciences

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First-principles Calculations of Nuclear Magnetic Resonance Chemical Shielding Tensors in Complex Ferroelectric Perovskites

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A Dissertation presented to the Graduate Faculty of the College of William and Mary in Candidacy for the Degree of Doctor of Philosophy

Department of Physics

The College of William and Mary
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Nuclear magnetic resonance (NMR) spectroscopy is one of the most important experimental probes of local atomistic structure, chemical ordering, and dynamics. Recently, NMR has increasingly been used to study complex ferroelectric perovskite alloys, where spectra can be difficult to interpret. First-principles calculations of NMR spectra can greatly assist in this task. In this work, oxygen, titanium, and niobium NMR chemical shielding tensors, \( \hat{\sigma} \), were calculated with first-principles methods for ferroelectric transition metal prototypical ABO\(_3\) perovskites [SrTiO\(_3\), BaTiO\(_3\), PbTiO\(_3\) and PbZrO\(_3\)] and A(B,B')O\(_3\) perovskite alloys Pb(Zr\(_{1/2}\)Ti\(_{1/2}\))O\(_3\) (PZT) and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (PMN). The principal findings are 1) a large anisotropy between deshielded \( \sigma_{xx}(O) \approx \sigma_{yy}(O) \) and shielded \( \sigma_{zz}(O) \) components; 2) a nearly linear dependence on nearest-distance transition-metal/oxygen bond length, \( r_s \), was found for both isotropic \( \delta_{iso}(O) \) and axial \( \delta_{ax}(O) \) chemical shifts \( \hat{\delta} = \hat{\sigma}_{\text{reference}} - \hat{\sigma} \), across all the systems studied, with \( \delta_{iso}(O) \) varying by \( \approx 400 \) ppm; 3) the demonstration that the anisotropy and linear variation arise from large paramagnetic contributions to \( \sigma_{xx}(O) \) and \( \sigma_{yy}(O) \), due to virtual transitions between O(2p) and unoccupied B(nd) states. Using these results, an argument against Ti clustering in PZT, as conjectured from recent \(^{17}\)O NMR magic-angle-spinning measurements, is made. The linear dependence of the chemical shifts on \( r_s \) provides a scale for determining transition-metal/oxygen bond lengths from experimental \(^{17}\)O NMR spectra. As such, it can be used to assess the degree of local tetragonality in perovskite solid solutions for piezoelectric applications. Results for transition metal atoms show less structural sensitivity, compared to \(^{17}\)O NMR, in homovalent B-site materials, but could be more useful in heterovalent B-site perovskite alloys. This work shows that both \(^{17}\)O and B-site NMR spectroscopy, coupled with first principles calculations, can be an especially useful probe of local structure in complex perovskite alloys.
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CHAPTER 1

Introduction

Due to their reversible electronic polarization (ferroelectricity) and ability to convert mechanical energy into and from electrical energy (piezoelectricity) ferroelectric perovskites have become key components in many electronic and mechanical devices such as sensors, actuators, and random access memory [1, 2]. Studies have indicated that these technologically important macroscopic properties are directly related to the material's local atomic geometric structure [3]. The goal of my research was to relate local atomic structure to the nuclear magnetic resonance (NMR) spectra of complex ferroelectric perovskites. The ability of NMR to identify distinct crystallographic sites and their symmetries, makes it an excellent tool for investigating the local structure of solid-state systems. The chemical shielding tensor, \( \sigma \), determines the local magnetic field (\( B_{loc} = [1 - \sigma]B_{ext} \)) at a nucleus, where the induced field (\( B_{ind} = -\sigma B_{ext} \)) arises from electronic screening currents around the nucleus. The spectra for complex ABO\(_3\) perovskites can be challenging to interpret without theoretical modeling. For example, while the \( ^{17}\text{O} \) NMR spectrum of crystalline tetragonal PbTiO\(_3\) consists of two well resolved narrow peaks, each corresponding to a unique oxygen environment. spectra for disordered perovskites, such as Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) (PZT), show partially resolved peaks and broad spectral features [4]. In this dissertation, I will show how theoretical modeling and first-principles quantum mechanical calculations of the chem-
ical shielding can provide insight into the local atomic arrangements and chemical interactions in these materials.

Oxygen, titanium, and niobium NMR chemical shielding tensors were calculated for prototypical perovskites [SrTiO$_3$, BaTiO$_3$, PbTiO$_3$ and PbZrO$_3$] and the disordered solid solutions [Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_3$ (PZT) and Pb(Mg$_{1/3}$,Nb$_{2/3}$)$_3$O$_3$ (PMN)]. The embedded cluster approach was used, and the chemical shielding tensor was calculated with first-principles quantum chemistry methods. These calculations were cross-checked with results from gauge including projector augmented waves [5] (GIPAW) periodic boundary conditions (PBC) calculations. The disordered environments of PZT and PMN were simulated by a variety of atomistic models with different arrangements of the B-site cations (Ti and Zr for PZT: Mg and Nb for PMN). The calculations revealed a strong correlation between the oxygen chemical shielding tensor and the covalent O(2p)-cation(nd) interaction. A nearly linear dependence on nearest-distance transition-metal/oxygen bond length, $r_s$, was found for both isotropic $\delta_{iso}$ and axial $\delta_{ax}$ chemical shifts, across all the systems studied, with $\delta_{iso}$ varying by $\approx 400$ ppm. Using these results, we argue against Ti clustering in PZT, as conjectured from recent $^{17}$O NMR magic-angle-spinning measurements. The linear dependence of the chemical shifts on $r_s$ provides a scale for determining transition-metal/oxygen bond lengths from experimental $^{17}$O NMR spectra. As such, it can be used to assess the degree of local tetragonality in perovskite solid solutions for piezoelectric applications.

B-site NMR chemical shielding tensors provide additional information about the local structure. First-principles quantum calculations of SrTiO$_3$, BaTiO$_3$, PbTiO$_3$, and PZT showed that the titanium chemical shift has a nearly linear dependence on the BO$_6$ volume. Interestingly, this volume dependence is relatively insensitive to A-site species, unit cell structural parameters, and B-site ordering. This means that titanium NMR is less sensitive than $^{17}$O NMR to structural details in isovalent B-site perovskites. However, preliminary niobium chemical shielding results for heterovalent PMN indicate that the B-site is strongly effected by the configuration Mg$^{2+}$ and Nb$^{5+}$ cations. It has been proposed that specific B-site ionic charge distribution, i.e. unique arrangements Mg$^{2+}$ and Nb$^{5+}$ cations, are responsible for the ferroelectric behavior in PMN [6].
This indicates that B-site NMR can be more useful in mixed heterovalent B-site perovskites.

This work demonstrates that oxygen and B-site NMR spectroscopy, coupled with first-principles quantum mechanical calculations, can be an especially useful tool to study the local structure in complex ferroelectric perovskites.

The remainder of this dissertation is organized as follows. Chapters 2 and 3 provide a theoretical overview of first-principles quantum mechanical electronic structure methods and the NMR chemical shielding tensor. Chapter 4 will also introduce the embedded cluster and PBC-GIPAW methodologies. Illustrative calculations of the embedded cluster approach and the shortcomings of commonly used DFT exchange-correlation functionals in the predicting oxygen chemical shielding will be examined by studying in the rocksalt alkaline earth oxide series MgO through BaO in Chapter 5. Chapter 6 will discuss the high sensitivity of $^{17}$O NMR to p-d hybridization in transition metal perovskites. Chapter 7 connects $^{17}$O NMR spectroscopy to the local structure of the PZT and PMN solid solution series with first-principles calculations and it emphasizes the $^{17}$O NMR linear scale for determining transition metal-oxygen bond lengths. It should be noted that Chapters 6 and 7 have been published [7] and submitted, respectively, word for word to the Journal of Chemical Physics. Chapter 8 discusses the Ti NMR chemical shielding calculations for the prototypical perovskites and the isovalent B-site PZT solid solutions. Finally, the prospects and benefits of Nb NMR chemical shielding calculations in the heterovalent B-site PMN are considered in Chapter 9.
CHAPTER 2

First-Principles Methodologies

2.1 Introduction

The non-relativistic time-independent Schrödinger equation can be expressed by

\[ \hat{H} | \Psi \rangle = E | \Psi \rangle, \]  

(2.1)

where \( \hat{H} \) is the Hamiltonian operator and \( \Psi \) is a wave function that describes the full quantum state of a system containing \( n \) electron and \( M \) nuclei. The Hamiltonian in Hartree atomic units for a system with the electrons at position \( r_i \) and the nuclei locate at \( R_N \) is

\[ \hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \frac{1}{2M_N} \sum_{i=1}^{N} \nabla_{R_i}^2 - \sum_{i=1}^{n} \sum_{N=1}^{M} \frac{Z_N}{|R_{iN}|} + \frac{1}{2} \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{1}{|r_{ij}|} + \sum_{N=1}^{M} \sum_{L \neq N}^{M} \frac{Z_N Z_L}{|R_{NL}|}, \]  

(2.2)

where \( M_N \) and \( Z_N \) is the mass and atomic number of the nuclei. While \( r_{ij} = r_i - r_j \), \( r_{in} = r_i - R_N \), and \( R_{NL} = R_N - R_L \) are the vector difference between electron-electron, electron-nucleus, and nucleus-nucleus positions, respectively. The first and second term on the right side of Eq. 2.2 are the electron and nucleus kinetic energy operators, respectively; while the third, fourth, and fifth terms represent the electron-nucleus, electron-electron, and nucleus-nucleus Coulomb
interactions, respectively.

An essential part of solving the Schrödinger equation in current first-principles electronic structure methods is the Born-Oppenheimer approximation [8], which considers the electrons in a molecule or solid to be moving in a field generated by fixed nuclei. This approximation is based on nuclei being much more massive than the electrons. Application of this approximation results in an simplified electronic-only Hamiltonian,

$$\tilde{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=0}^{n} \nabla_{i}^{2} - \sum_{i=0}^{n} \sum_{N=0}^{M} \frac{Z_{N}}{|r_{iN}|} - \frac{1}{2} \sum_{i=0}^{n} \sum_{j \neq i}^{n} \frac{1}{|r_{ij}|} + \sum_{N=0}^{M} \sum_{L \neq N}^{M} \frac{Z_{N}Z_{L}}{|R_{NL}|}. \tag{2.3}$$

Eq. 2.1 with Eq. 2.3 used for the Hamiltonian can only be solved exactly for systems with one electron, due to the presence of the electron-electron Coulomb interaction term in Eq. 2.3. In Mean-field theories, the full-many body electron-electron interaction is replaced by an average one-body interaction, in which a mean field generated by the other \((n - 1)\) electrons in the system. The Hartree-Fock (HF) approximation [8] is an example. Density Functional Theory (DFT) [9] operationally resembles a mean-field theory, but it is exact, in principle. In practice, approximate exchange-correlation functionals are used. Hybrid-DFT approximations like B3LYP [10], combine HF theory with DFT, and are widely used. Because of their relative simplicity, these approaches can be used to study systems with large numbers of electrons. In contrast to these "one-electron" methods, many-body techniques, such as Møller-Plesset (MP) Perturbation Theory [8], Configuration Interaction (CI) [8], and Coupled Cluster (CC) Theory [11] incorporate the full electron-electron interaction. These methods are much more computationally intensive and can only be used for relatively small systems. As will be discussed in Chapter 4, widely available quantum chemistry electronic structure codes allow for the chemical shielding tensor to be calculated with the various levels of approximation. The remainder of this chapter will introduce the fundamental concepts of each theory.
2.2 Mean-field Type Methods

2.2.1 Hartree-Fock Theory

Hartree-Fock (HF) Theory [8] restricts the ground state wave function to a single \( n \times n \) Slater determinant,

\[
\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix}
\phi_1(r_1s_1) & \phi_2(r_1s_1) & \cdots & \phi_n(r_1s_1) \\
\phi_1(r_2s_2) & \phi_2(r_2s_2) & \cdots & \phi_n(r_2s_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(r_Ns_n) & \phi_2(r_Ns_n) & \cdots & \phi_n(r_Ns_n)
\end{vmatrix},
\]

(2.4)

where \( n \) is the number of electrons. It is composed of a set of single particle wave functions \( \phi_i(r_j,s_j) \) (a.k.a. spin-orbitals), each of which is a product of spacial \( \chi_i(r_j) \) and spin \( \eta_i(s_j) \) functions, i.e. \( \phi_i(r_j,s_j) = \chi_i(r_j)\eta_i(s_j) \). The rows of the \( n \)-electron Slater determinant are labeled by the electrons and the columns are labeled by the single particle wave functions. By construction, a Slater determinant satisfies fermion statistics, since the permutation of any two rows in the determinant is equivalent to interchanging the coordinates of any two electrons, which results in \( \Psi \) changing sign. The set of of wave functions \( \{\phi_j\} \) are chosen to minimize the total energy

\[
E_{o}^{HF} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}
\]

(2.5)

according to the variational principle. The minimization resultes in \( n \) coupled second order differential equations, which have the form

\[
-\frac{1}{2} \nabla^2 \phi_i(x_1) + V_{ion}(r)\phi_i(x_1) + \sum_{j \neq i}^{n} \left[ J_j(x_1) - K_j(x_1) \right] \phi_j(x_1) = \epsilon_i \phi_i(x_1)
\]

(2.6)

\[
V_{ion} = -\sum_{N=0}^{M} \frac{Z_N}{|r_{1N}|},
\]

(2.7)

\[
J_j(x_1)\phi_i(x_1) = \int dx_2 \frac{\phi_j(x_2)^2}{|r_{12}|} \phi_i(x_1),
\]

(2.8)
(2.9)

where \( x_i \) indicates both the space \( r_i \) and spin \( s_i \) coordinates. The Hartree term \( J_f(x_1) \) is the classical Coulomb repulsion between electron densities and the summation of it over all \( i \neq j \) is the total average potential acting on the electron in \( \phi_i \), arising from the \( n-1 \) electrons in the other wave functions. The quantum mechanical exchange term \( K_f(x_1) \) captures the correlation that arise between same-spin electrons, due purely to fermion anti-symmetry. However, HF theory does not include correlation between opposite spin electrons. By definition, the correlation energy is given by \( E_{corr} = E_o - E_{HF} \), where \( E_o \) is the exact ground state energy.

### 2.2.2 Density Functional Theory

Density Functional Theory (DFT) [9] frames the solution of \( E_o \) as a function of the one-electron charge density \( n_0(\mathbf{r}) \). It can be shown that any property of a system of many interacting particles can be represented as a functional (unknown in general), \( F[n_0(\mathbf{r})] \) of the ground state electronic density \( n_0(\mathbf{r}) \). This formal result is a single consequence of the fact that \( n_0(\mathbf{r}) \) determines the external potential (e.g. \( V_{\text{ext-ion}} \)). Kohn and Sham [12] wrote the electron density of the interacting system in terms of a set of one-electron wave functions (Kohn-Sham orbitals) of a noninteracting system. In DFT, the ground state energy is expressed as functional of \( n(\mathbf{r}) \)

\[
E[n(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^{n} \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) + \int d\mathbf{r} n(\mathbf{r}) V_{\text{ion}}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\]

\[
+ \sum_{N=0}^{M} \sum_{L \neq N} \frac{Z_N Z_L}{|\mathbf{R}_{NL}|} + E_{xc}[n(\mathbf{r})]
\]

(2.10)

where, \( n(\mathbf{r}) = \sum_{i=1}^{n} |\psi_i(\mathbf{r})|^2 \). The first two terms on the right-hand side are the non-interacting kinetic energy and the electron-nuclear Coulomb potential. The following two terms are the Hartree energy and the exchange-correlation energy. Minimizing Eq.2.10 leads to a set of mean-field like
single particle equations for non-interacting electrons.

\[-\frac{1}{2} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{2.11}\]

where the last two terms are the Hartree potential and the exchange-correlation potential. The exact $E_{\text{xc}}[n(\mathbf{r})]$ is not known in general, but it would deliver the exact ground state energy. In practice, several successful approximations have been developed. The local density approximation [13] (LDA),

$$E_{\text{xc}}^{\text{LDA}}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}(n(\mathbf{r})) d\mathbf{r}$$

is based on a parameterization of the exchange-correlation energy per electron $\varepsilon_{\text{xc}}(n(\mathbf{r})) d\mathbf{r}$ of a uniform interacting electron gas of density $n$. LDA treats the non-uniform electron density at $\mathbf{r}$ in a molecule or solid as if it were part of an uniform electron gas of constant density. Although $n(\mathbf{r})$ in molecular and solid-state systems is far from homogeneous, LDA produces reliable results for many systems [9]. Many schemes have been formulated to improve upon the LDA. One of the most used is the generalized gradient approximation (GGA), which modifies LDA to include effects of the density gradient.

### 2.2.3 Hybrid-B3LYP

Hybrid functionals [14] are a group of approximations to the DFT $E_{\text{xc}}$ that include a fraction of HF exact exchange in order to improve agreement between calculated DFT properties and some experimental data. One of the most often used is B3LYP (Becke, three-parameter, Lee-Yang-Parr) [15, 16] which is expressed as

$$E_{\text{xc}}^{\text{B3LYP}} = 0.80 * E_X^{\text{Slater}} + 0.20 * E_X^{\text{HF}} + 0.72 * \Delta_{E_X}^{\text{Becke}} + E_C^{\text{VWN}} + 0.81 * \Delta E_C^{\text{non-local}}, \tag{2.13}$$

where $E_X^{\text{Slater}}$ and $E_C^{\text{VWN}}$ are exchange and correlation components from LDA functionals. $E_X^{\text{HF}}$ and $\Delta_{E_X}^{\text{Becke}}$ are HF and GGA exchange functionals. The non-local $\Delta E_C$ comes from the LYP
functional. The coefficients were empirically adjusted via fitting calculated properties to experimental measurement for the G1 molecule set [15].

2.3 Many-body methods

2.3.1 MP2

Møller-Plesset (MP) Perturbation Theory [8] uses the HF wave function as the unperturbed system. The nomenclature used to represent the degree (n) of the MP expansion is MPn, which indicates that the correction to HF energy is determined to the nth order in perturbation theory. Most MP expansions are carried out to second order (MP2) for the ground state (wave function corrected to first order). Higher order MP expansions exhibit oscillatory convergence and are usually avoided. Among the possible methods to explicitly treat electron correlation, MP2 requires a relatively reasonable amount of computational resources, such as storage, memory, number of processors, and time.

2.3.2 Configuration Interaction

The Configuration Interaction (CI) [8] method is based on representing the exact many-body wave function by a linear combination of Slater determinants

\[ | \Psi_{CI} \rangle = a_0 | \Psi_{HF} \rangle + \sum_{i=1} a_i | \Phi_i \rangle, \]

where \( | \Psi_{HF} \rangle \) is normally the HF determinant and \( | \Phi_i \rangle \) are determinants in which occupied HF single particle wave functions are swapped with virtual HF single particle wave functions. The \( | \Phi_i \rangle \) determinants resemble excited states in HF theory. If only one occupied spin orbital is exchanged with a virtual orbital, the determinant is referred to as a single excitation. While a determinant with \( m \) replaced spin-orbitals is called a \( m \)-tuple excitation. The expansion coefficients are determined by requiring the total energy to be minimum via the linear variational principle. In
practice, the summation in Eq. 2.14 most often is truncated.

2.3.3 Coupled Cluster

The Coupled cluster (CC) [11] method effectively generates a CI expansion for a reference HF solution. CC uses an exponential operator $\hat{T}$ to form the CC wave function

$$| \Psi_{CC} \rangle = e^{\hat{T}} | \Psi_{HF} \rangle. \quad (2.15)$$

In principle, CC can determine the exact wave function from a reference wave function if $\hat{T}$ generates all possible orbital groupings for a given $n$-electron system. In practice, the exponential operator in Eq. 2.15 is expanded in a power series, which is truncated at a specific excitation level. This truncation results in a hierarchy of CC techniques. For example, CCS and CCSD refer to series expansions that include single excitations and single excitations plus double excitations, respectively.
CHAPTER 3

Basic NMR chemical shielding theory
and gauge invariance issues

3.1 The NMR chemical shielding tensor

A bare nucleus with a non-zero nuclear spin quantum number, $I_N$, has a nuclear magnetic
dipole moment, $\mu_N$, associated with it. This magnetic moment can interact with a magnetic field
(a.k.a. magnetic flux density) $B$ and the interaction can be represented as

$$\hat{H}_N = -\mu_N \cdot B = -\gamma_N \hbar I_N \cdot B,$$

where $\gamma_N$ is the gyromagnetic ratio of the target nucleus, $\hbar$ is the reduced Plank constant, and $\hbar I_N$ is the nuclear spin angular momentum [17]. The reduced Plank constant is set equal to one since
Hartree atomic units ($\hbar = 1$, $m_e = 1$, $e = 1$) are used throughout this dissertation. The dot product
indicates that the magnetic energy depends on the relative direction of the vectors $B$ and $\mu_N$ and
the minus sign indicates that the magnetic energy is lowest if the $\mu_N$ is parallel to $B$. According to
quantum mechanics, the projection of $I_N$ along any directions is quantized. Therefore, if $B = B_z$
and the quantization direction is chosen in the \( z \)-direction. The interaction energy will be

\[
E = -\gamma_N m_I B_z,
\]  

(3.2)

where \( m_I \) is the nuclear magnetic spin quantum number, which may have any integer number between \(-I_N\) and \(I_N\). The energy difference, \( \Delta E \), between two neighboring states is equal to \( \gamma_N B_L \). This separation between the \( m_I \) energy levels is called the nuclear Zeeman splitting. A transition between two neighboring energy levels can be induced by the application of a second magnetic field, which is perpendicular to \( B_z \) and oscillating at the Larmor frequency [17]

\[
\nu_L = \frac{-\gamma_N B_L}{2\pi}.
\]  

(3.3)

The ability to transition between energy states of a nucleus by the application of a perpendicular magnetic field with frequency \( \nu_L \) is the fundamental concept behind NMR.

The magnetic interaction between a bare NMR active nucleus \((I_N \neq 0)\) and an applied magnetic field \( B_{\text{ext}} \) is augmented by the motion of neighboring electric charge. This electronic response induces a secondary magnetic field \( B_{\text{ind}} \) at the nuclear site and the total field \( B_{\text{loc}} \) at the nucleus can be expressed as follows

\[
B_{\text{loc}} = B_{\text{ext}} + B_{\text{ind}} = B_{\text{ext}} - \hat{\sigma} B_{\text{ext}} = (1 - \hat{\sigma}) B_{\text{ext}},
\]  

(3.4)

where \( \hat{\sigma} \) is the NMR chemical shielding tensor of the nucleus. Consequently, the nuclear spin Hamiltonian (Eq. 3.1) is modified to

\[
\hat{H}_N^B = -\mu_N \cdot (1 - \hat{\sigma}) B_{\text{ext}} = -\gamma_N \hat{I}_N \cdot (1 - \hat{\sigma}) B_{\text{ext}},
\]  

(3.5)
with a chemically shifted Larmor frequency of

$$v_L = -\gamma_N (1 - \sigma_{zz}) B_{\text{ext}, z}/2\pi. \quad (3.6)$$

Each component of $\hat{\sigma}$ is a mixed second derivative of the ground state energy with respect to the applied magnetic field and nuclear magnetic moment and is formally defined [18] as

$$\sigma_{\kappa, \lambda} = \frac{\partial E}{\partial \mu_N \partial B^\lambda_{\text{ext}}}; \quad \kappa, \lambda = x, y, z. \quad (3.7)$$

As such, it is an asymmetric second rank tensor with nine independent components in general, although its symmetry can be higher, depending on the site symmetry of the target nucleus. [19] The anti-symmetric part of $\hat{\sigma}$ contributes negligibly to the NMR resonance frequency shift, since it enters only in second order, [20, 21] although it can contribute to relaxation. [22] The symmetric part can always be diagonalized, and the NMR frequency is determined by the following combinations of its principal axis components [23]

$$\sigma_{\text{iso}} = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \frac{1}{3} \text{Tr} \hat{\sigma}$$
$$\sigma_{\text{ax}} = \frac{1}{6} (2\sigma_{zz} - \sigma_{xx} - \sigma_{yy}) = \frac{1}{2} (\sigma_{zz} - \sigma_{\text{iso}})$$
$$\sigma_{\text{aniso}} = \frac{1}{2} (\sigma_{yy} - \sigma_{xx}), \quad (3.8)$$

where $\sigma_{\text{iso}}$, $\sigma_{\text{ax}}$, and $\sigma_{\text{aniso}}$ are the isotropic, uniaxial, and anisotropic components, respectively.

Positive values of $\sigma$ are conventionally denoted as shielding the external field, while negative elements are referred to as deshielding [see Eq. (3.5)]. Measurements of $\hat{\sigma}$ are usually reported with respect to a reference compound, where the chemical shift tensor is defined as [24]

$$\hat{\delta} = - (\hat{\sigma} - \sigma_{\text{iso}}^{\text{ref}}). \quad (3.9)$$
3.2 Ramsey Equation

In the absence of an applied magnetic field, the behavior of electrons in molecules and solids is governed by the time-independent Schrödinger equation (Eq. 2.1) within the Born-Oppenheimer approximation (Eq. 2.3). The presence of an external magnetic field \( \mathbf{B}_{\text{ext}} \) and the nuclear magnetic moments \( \mu_N \) of the nuclei causes the electronic non-relativistic Hamiltonian to take the form

\[
\hat{H}_{\text{elcc}}^{\mu_B} = \frac{1}{2} \sum_{i=0}^{n} \left[-i \nabla_i - \mathbf{A}_i^{\text{tot}}(t)\right]^2 + V_{\text{Coul}}, \tag{3.10}
\]

where \( V_{\text{Coul}} \) is the Coulombic potentials described by Eq. 2.3 and \( \mathbf{A}_i^{\text{tot}} \) is the sum of vector potentials, which describe the externally applied magnetic field and the nuclear magnetic moments. The respective vector potentials are represented by

\[
\mathbf{A}_i^{\text{tot}} = \mathbf{A}_i^{\text{ext}} + \sum_{N=1}^{M} \mathbf{A}_{i,N}, \tag{3.11}
\]

\[
\mathbf{A}_i^{\text{ext}} = \frac{1}{2} \mathbf{B}_{\text{ext}} \times \mathbf{r}_i, \quad \mathbf{r}_{i,0} = \mathbf{r}_i - \mathbf{R}_0, \tag{3.12}
\]

\[
\mathbf{A}_{i,N} = \alpha \frac{\mu_N \times \mathbf{r}_{i,N}}{|\mathbf{r}_{i,N}|^3}, \quad \mathbf{r}_{i,N} = \mathbf{r}_i - \mathbf{R}_N, \tag{3.13}
\]

where \( \alpha \) is the fine structure constant, \( \mathbf{r}_i \) is the position of the \( i^{th} \) electron, \( \mathbf{R}_0 \) is the gauge origin, and \( \mathbf{R}_N \) is the position of the \( N^{th} \) nucleus. If the term in the square brackets of Eq. 3.10 is expanded out and we work within the Coulomb gauge \( (\nabla \cdot \mathbf{A}_i^{\text{tot}} = 0) \), Eq. 3.10 becomes

\[
\hat{H}_{\text{elcc}}^{\mu_B} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 + V_{\text{Coul}} + \sum_{i=1}^{n} \mathbf{A}_i^{\text{ext}} \cdot (-i \nabla_i) + \sum_{i=1}^{n} \sum_{N=1}^{M} \mathbf{A}_{i,N} \cdot (-i \nabla_i) + \sum_{i=1}^{n} |\mathbf{A}_i^{\text{ext}}| + \sum_{N=1}^{M} |\mathbf{A}_{i,N}|^2. \tag{3.14}
\]

The first two terms are just the electronic Hamiltonian in the absence of a magnetic field (Eq. 2.3). If the vector potentials are replaced by the definitions is Eq. 3.11 - Eq. 3.13 and the vector identities \((a \times b) \cdot c = a \cdot (b \times c)\) and \((a \times b)(c \times d) = (a \cdot c)(b \cdot d) - (b \cdot c)(a \cdot d)\) are used, \( \hat{H}_{\text{elcc}}^{\mu_B} \) can be
expressed as

$$
\hat{H}^\mu B_{\text{elec}} = \hat{H}^{0,0}_{\text{elec}} + B_{\text{ext}} \cdot \sum_{i=1}^{n} \frac{1}{2} \hat{L}_{iO} + \sum_{N=1}^{M} \frac{\mu_N}{|r_{iN}|^3} \hat{L}_{iN} 
+ \sum_{N=1}^{M} B_{\text{ext}} \cdot \frac{\alpha^2}{2} \sum_{i=1}^{n} \frac{r_{iO} \cdot r_{iN} - |r_{iO}| |r_{iN}|}{|r_{iN}|^3} \cdot \mu_N 
+ \frac{1}{8} \sum_{i=1}^{n} (|B_{\text{ext}}| r_{iO})^2 - [B_{\text{ext}} \cdot r_{iO}]^2) \sum_{N=1}^{M} \sum_{i=1}^{n} \frac{\alpha^4}{2} |r_{iN}|^6 ([\mu_N]^2 |r_{iN}|^2 - [\mu_{N} \cdot r_{iN}]^2),
$$

(3.15)

where $\hat{L}_{iO} = r_{iO} \times -i\nabla_i$ and $\hat{L}_{iN} = r_{iN} \times -i\nabla_i$. The terms quadratic in $B_{\text{ext}}$ and $\mu_N$ can be neglected for field strengths used in practice. This simplification results in the Hamiltonian taking the form

$$
\hat{H}^\mu B_{\text{elec}} = \hat{H}^{0,0}_{\text{elec}} + \sum_{\lambda} B_{\text{ext}}^\lambda \hat{H}^{0,1}_{\lambda} + \sum_{N=1}^{M} \sum_{\kappa} \mu_N^0 \hat{H}^{1,0}_{\kappa} + \sum_{N=1}^{M} \sum_{\kappa} B_{\text{ext}}^\lambda \hat{H}^{1,1}_{\lambda,\kappa} \mu_N^\kappa.
$$

(3.16)

where the vector dot products are now expressed in terms of their components ($x, y, z$), which are represented by $\kappa$ and $\lambda$. While the superscripts associated with the $\hat{H}$ terms signify their order in $\mu$ and $B$. Similar to Eq. 3.16, a series expansion of the total electronic energy $E$ in powers of and $B_{\text{ext}}^\lambda$ and $\mu_N^\kappa$ gives

$$
E = E^{0,0} + \sum_{\lambda} B_{\text{ext}}^\lambda E^{0,1}_{\lambda} + \sum_{N=1}^{M} \sum_{\kappa} \mu_N E^{1,0}_{\kappa} + \sum_{N=1}^{M} \sum_{\lambda} \mu_N E^{1,1}_{\lambda,\kappa} \mu_N^\kappa.
$$

(3.17)

A comparison Eq. 3.17 and Eq. 3.7 indicates that the $\lambda, \kappa$ component of the chemical shielding tensor, $\sigma_{\lambda,\kappa}$, of the $N$th nucleus is equal to $E^{1,1}_{\lambda,\kappa}$. $\sigma_{\lambda,\kappa}$ can be evaluated with perturbation theory [25]. Since each vector component of $\mu_N$ and $B_{\text{ext}}$ can be considered a separate perturbation, multiple perturbation theory must be used. However, the formalism of this approach and the basic form of the equation that determines the chemical shielding tensor can be understood and developed through double perturbation theory, which begins by expanding $\hat{H}^\mu B_{\text{elec}}, \Psi$ and $E$ in a
power series expansion around $\beta$ and $\epsilon$, each of which could represent two individual component of $\mu_N$ and $B_{\text{ext}}$, such as $\mu_{N,0}$ and $B_{\text{ext},\lambda}$. $\mathbf{H}_{\text{elec}}^{\mu B}$ and $E$ will have a form similar to Eq. 3.16 and Eq. 3.17 while $\Psi$ will be

$$\Psi = \Psi^{0,0} + \beta \Psi^{1,0} + \epsilon \Psi^{0,1} + \beta^2 \Psi^{2,0} + \beta \epsilon \Psi^{1,1} + \epsilon^2 \Psi^{0,2} + \ldots$$

(3.18)

The first superscript counts the orders of $\kappa$ and the second superscript counts orders of $\lambda$. The first order corrections to the ground state electronic wave function, $\Psi^{1,0}$ and $\Psi^{0,1}$, and the total electronic energy, $E^{1,0}$, $E^{0,1}$, and $E^{1,1}$, can be determined by plugging in the expanded representations of $H$, $\Psi$ and $E$ into Eq. 2.1 and sorting and equating by powers of $\beta$ and $\epsilon$. The Hermitian property of $\mathbf{H}_{\text{elec}}^{0,0}$ and the completeness relationship and orthonormality of $\Psi^{0,0}$ can be used to obtain

$$| \Psi^{1,0} \rangle = \sum_{i \neq 0} \frac{| \Psi_i^{0,0} \rangle \langle \Psi_i^{0,0} | H^{1,0} | \Psi_0^{0,0} \rangle}{E_0^{0,0} - E_i^{0,0}}$$

(3.19)

$$| \Psi^{0,1} \rangle = \sum_{j \neq 0} \frac{| \Psi_j^{0,0} \rangle \langle \Psi_j^{0,0} | H^{0,1} | \Psi_0^{0,0} \rangle}{E_0^{0,0} - E_j^{0,0}}$$

(3.20)

$$E^{1,0} = \langle \Psi_0^{0,0} | H^{1,0} | \Psi_0^{0,0} \rangle$$

(3.21)

$$E^{0,1} = \langle \Psi_0^{0,0} | H^{0,1} | \Psi_0^{0,0} \rangle$$

(3.22)

$$E^{1,1} = \sigma_{\lambda,\kappa} = \langle \Psi_0^{0,0} | H^{1,1} | \Psi_0^{0,0} \rangle = \sum_{i \neq 0} \frac{\langle \Psi_0^{0,0} | H^{1,0} | \Psi_1^{0,0} \rangle \langle \Psi_1^{0,0} | H^{0,1} | \Psi_0^{0,0} \rangle + \langle \Psi_0^{0,0} | H^{0,1} | \Psi_1^{0,0} \rangle \langle \Psi_1^{0,0} | H^{1,0} | \Psi_0^{0,0} \rangle}{E_0^{0,0} - E_i^{0,0}}$$

(3.23)
The generalization of Eq. 3.23 can compactly represented as

\[ \hat{\sigma}(N) = \langle \Psi_0 | \frac{\alpha^2}{2} \sum_{i=1}^{n} \frac{\mathbf{r}_{iO} \cdot \mathbf{r}_{iN}}{|r_{IN}|^3} \mathbf{1} - \mathbf{r}_{iN} \mathbf{r}_{iO} | \Psi_0 \rangle + \frac{\sum_{\ell \neq 0} \langle \Psi_0 | \mathbf{f}_{\ell i} | \Psi_i \rangle \langle \Psi_i | \sum_{i=1}^{n} \frac{\mathbf{L}_{iO}}{2} | \Psi_0 \rangle + \langle \Psi_0 | \sum_{i=1}^{n} \frac{\mathbf{L}_{iO}}{2} | \Psi_i \rangle \langle \Psi_i | \alpha^2 \sum_{i=1}^{n} \frac{\mathbf{f}_{\ell i}}{|r_{iN}|^3} | \Psi_0 \rangle}{E_0 - E_t} \]

(3.24)

where | \Psi_0 \rangle and | \Psi_i \rangle are the ground and excited eigenstates of the unperturbed Hamiltonian \( \hat{H}^{0,0} \) with the eigenvalues \( E_0 \) and \( E_t \) [17, 18]. This formulation of the chemical shielding is usually referred to as Ramsey’s Expression. Eq. 3.24 shows that the nuclear magnetic shielding tensor can be divided into two parts. The first term, diamagnetic shielding, corresponds to an expectation value of the unperturbed state | \Psi_0 \rangle, which conceptually originates from electric charges in a Larmor precession around the applied magnetic field \( \mathbf{B}_{\text{ext}} \) that produces the induced magnetic field \( \mathbf{B}_{\text{ind}}^{D\alpha} \) (opposing \( \mathbf{B}_{\text{exp}} \)) at the nucleus [26]. While the second term, paramagnetic shielding, depends on the excited states | \Psi_i \rangle and represents the relaxation of the wave function in response to the perturbations due to the couplings of the nuclear magnetic moments to the orbital motion of the electrons (\( \alpha^4 \) term) and the coupling of external field to the orbital motion of the electrons (orbital angular moment operator). The paramagnetic term is a consequence of \( \mathbf{B}_{\text{ext}} \) polarizing the electronic shells. The shells distort in a way that produces an induced magnetic field \( \mathbf{B}_{\text{ind}}^{\text{para}} \) (additive to \( \mathbf{B}_{\text{ext}} \)) at the nucleus [26]. The chemical shielding depends on the distribution of the electrons around the nucleus and naturally has different values in different electronic environments.

The Ramsey Expression is theoretically important for interpreting calculated results. In this work, the Ramsey Expression was a key component in the qualitative explanation of the strong correlation between the oxygen chemical shielding tensor and the covalent O(2p)-cation(nd) interaction, which is observed as a linear relationship between the oxygen NMR chemical shift and the O-cation bond length in perovskite oxides (Chapter 6, Section 6.4.1).
Eq. 3.24 and Eq. 3.7 are separate formulations of the chemical shielding tensor. A third formulation was introduced by Jameneson and Buckingham [27], who showed that \( \hat{\sigma} \) can be determined from a calculation of the first-order electronic current density \( j^{(1)}(r_i) \) induced in a system of \( n \) electrons by \( B_{\text{ext}} \),

\[
\hat{\sigma}(N)B_{\text{ext}} = \alpha^2 \int \frac{d^3r}{|r_i|^3} \times j^{(1)}(r_i), \tag{3.25}
\]

where \( j^{(1)}(r_i) \) is expressed in terms of the ground state wave function \( \Psi^0 \) and its corresponding first-order correction \( \Psi_i^1 \) to \( B_{\text{ext}} \cdot 2\sum_{i=1}^{n} \frac{1}{2}J_i^{\text{ext}} \) as

\[
j^{(1)}(r_i) = i \sum_{i=1}^{n} (\Psi_i^0 \nabla \Psi_i^1 - \Psi_i^1 \nabla \Psi^0) - A_i^{\text{ext}} n(r). \tag{3.26}
\]

The terms associated with the vector potential of the magnetic moment enter the calculation during the integration of the current density.

In practice, the chemical shielding tensor is usually solved with either Eq.3.7 (GIAO method), which is implement via analytical derivative techniques [16] or Eq.3.25 (CSGT and GIPAW methods) using standard computational perturbative methods (e.g. couple-Hartree Fock or Density Functional perturbation theory).

### 3.3 The Gauge Origin Problem

The vector potential representing the external magnetic field (Eq. 3.12) and therefore the Hamiltonian (3.15) and the chemical shielding tensor (Eq. 3.24) are not uniquely defined since the position of the the gauge origin, \( R_O \), can be arbitrarily chosen and still satisfy the requirement \( B_{\text{ext}} = \nabla \times A_i^{\text{ext}} \). In principle, an observable property should not depend on the choice of \( R_O \). More generally, the gradient of an arbitrary scalar function \( \nabla f(r) \) can be added to \( A_i^{\text{ext}} \), since the curl of a gradient is zero. Quantum mechanically, this fundamental principle is maintained because
a transformation of $\nabla f(r)$ in the Hamiltonian, $H \rightarrow H'$, results in the *exact* wave function of $H$ being transform as $\Psi \rightarrow \Psi' = e^{i\phi} | -i f(r)| \Psi$. This gauge transformation corresponds to both the Hamiltonian and wave functions undergoing an unitary transformation. Therefore, a change in $\mathbf{R}_N$ will result in a transformation of the wave function, but observable properties will remain unaltered:

$$\langle \Psi' | H' | \Psi' \rangle = \langle \Psi | H | \Psi \rangle.$$  

(3.27)

In practice, the wave function is never exactly solved and usually represented by an incomplete basis set. The finite size of the basis set results in Eqs. 3.19 and 3.2 becoming approximations and Eq. 3.27 is not strictly satisfied. Therefore, the value of the chemical shielding tensor will be dependent on the choice of gauge origin.

A variety of complimentary approaches for overcoming the gauge problem have been develop. One such approach is the gauge-invariant (a.k.a including) atomic orbitals (GIAO) method. GIAO eliminates the gauge dependence of properties and ensures a uniform description of the electronic system by making the basis functions explicitly dependent on the magnetic field with the inclusion of a complex phase factor that refers to the position of the basis function, which is centered on the nucleus. The wave function is expressed as

$$\phi(r_j - R_N) = \exp\left[\frac{-i}{2} (B_{\text{exp}} \times (R_N - R_O)) \cdot r_j\right] \Psi(r_j - R_N)$$  

(3.28)

Making the electronic wave function gauge dependent results in quantum mechanical inner products only containing differences in vector potentials, thereby removing the reference to an absolute gauge origin. For example, the wave function overlap integrals take the form,

$$\langle \phi(r_j - R_A) | \phi(r_j - R_B) \rangle = \langle \Psi(r_j - R_A) | \exp\left[\frac{-i}{2} (B_{\text{exp}} \times (R_A - R_B)) \cdot r_j\right] \Psi(r_j - R_B) \rangle$$  

(3.29)
CHAPTER 4

First-principles NMR chemical shielding methodologies

First-principles chemical shielding calculations have traditionally been done within the embedded cluster approach, using standard quantum chemistry methods (e.g., GAUSSIAN, [28–30], NWChem, [31] and ACES-II [32]) with gaussian type orbitals (GTO) [33]. More recently, the planewave based GIPAW [5] method with periodic boundary conditions (PBC) has provided an alternative approach.

4.1 Embedded clusters

An embedded cluster model is depicted in Fig. 4.1. Its core consists of atoms, which are fully treated quantum mechanically (Eq.2.3), with the target atom at its center. These atoms are referred to as “quantum” (QM) atoms. The total number of electrons is determined by satisfying the nominal formal valence of all the QM atoms. For example, the $A_1B_2O_{15}$ QM cluster in the figure thus has a net charge of 14−. So the QM cluster is written as $A_4B_2O_{15}^{14−}$. The QM cluster is embedded in the classical potential due to point charges, pseudopotentials, and, in some
FIG. 4.1: Illustration of cluster embedding for the O-centered $A_4B_2O_{15}$ quantum atom (QM) cluster (Sec. 4.1.1), shown for a [110] plane of the ideal perovskite structure. The QM A, B, and O atoms are depicted by filled black, blue and red circles, respectively. In the left panel, the QM atoms are embedded in point charges, "+" or "−" signs colored coded according to the QM atom they replace in the crystalline lattice. In the right panel, the boundary O QM atoms have had their nearest and next-nearest neighbor point charges replaced by "empty" pseudopotentials (Sec. 4.1.3), indicated by thick large circles, with corresponding color coding.

cases, an external electric field to cancel surface depolarization effects, as described in following subsections. The atomic site designations nn and nnn, used below, denote nearest-neighbor and next-nearest-neighbor sites, respectively, and are based on the ideal structures. Thus, for example, the Ti atom in tetragonal P4mm PbTiO₃ would be regarded as having six nn O atoms, despite the distortion of the TiO₆ octahedron. In the actual calculations, the tetragonal distortion results in two chemically inequivalent O_{eq} and O_{ax} atoms (O_{ax} lying on the polar axis), which require two separate embedded cluster calculations.

4.1.1 Quantum cluster

Perovskites

In all the perovskite QM clusters considered in this dissertation that give meaningful results, the target atom is at least fully coordinated with QM atoms located at its nn and nnn sites. Secondly, the target atom's nn QM atoms are themselves fully coordinated with nn QM atoms. Finally additional QM atoms are added, as required by ideal crystal symmetry. For example, this procedure results in a perovskite 21 oxygen center QM-atom cluster: $(A_4B_2O_{15})^{14−}$, depicted in
Fig. 4.1, where \( A = \text{Sr}, \text{Ba}, \text{or Pb}; \) \( B = \text{Ti} \) or \( \text{Zr} \). This includes two corner-shared \( \text{BO}_6 \) octahedra. centered on the targeted \( O \) atom (11 \( O \) and 2 \( B \) atoms), the target atom’s 4 nnn \( A \) cations, and 4 additional \( O \) atoms, which are also one lattice constant away from the center atom. 65 QM-atom cluster, \((A_4B_{10}O_{51})^{51-}\), is the \((A_4B_2O_{15})^{14-}\) cluster with the QM cation atoms fully coordinated with \( O \) QM atoms.

Embedded clusters with titanium target atoms consisted of either 75 QM atoms, \((A_8\text{Ti}_7\text{O}_{60})^{76-}\), or 111 QM atoms, \((A_8\text{Ti}_{19}\text{O}_{84})^{76-}\), where the target Ti atom is fully coordinated with its nn A-site and B-site (based on ideal perovskite symmetry) cations. These cations are fully coordinated with their nn \( O \) QM atoms. The 111-QM atom cluster is just the 65-QM atom cluster plus the target Ti atom’s nnn B-site cations, which are fully coordinated with nn \( O \) QM atoms.

Converging the electronic total energy for the larger clusters considered here was challenging due to the large number of electrons and GTO basis functions used in the calculations. Efficient DFT convergence was achieved by starting with smaller basis sets, gradually incrementing it in successive calculations. Wave functions from a converged calculation were used as the initial guess for the electronic state of the following calculation. For example, the DFT total energy convergence in the 111-QM atom ST cluster was achieved by (1) performing a restricted Hartree-Fock (RHF) calculation with \( O \), Ti, and Sr having smaller 6-311G, 6-311G, and Stuttgart RSC 1997 DZ GTO basis sets, respectively; (2) the converged wave functions were then input into a RHF calculation with the \( O \) atoms having the IGLO-III basis set; (3) these converged functions were inputted into a DFT calculation with the same basis sets; (4) The target Ti atom and the remaining Ti atoms were then given the cc-pwCVTZ-NR and 6-311G(2d,p) basis functions. Finally, the cc-pwCVQZ-NR was used for the target Ti atom and the chemical shielding was determined. A total energy convergence tolerance of \( 10^{-6} \) Hartree (Ha) can be used for all calculations. Upon completion of the final step, the tolerance can be increased to \( 10^{-8} \) Ha (program default) for the chemical shielding calculation.

It should be noted that 21 QM atom clusters were initially considered while they yielded isotropic chemical shifts that were found to be somewhat fortuitous. Inspection of the eigenval-
ues associated with the outer Ti cations, showed that their core eigenvalues differed substantially from the target Ti atom indicating large residual electrostatic shifts that were surmounted by fully coordinating all cations with QM oxygen anions, as described above.

**Rocksals**

The alkaline earth oxides considered here have a rocksalt-sodium chloride structure. Figure 4.2 presents a schematic of an embedded cluster for these crystals. This figure is for a charged (OX$_6$)$_{10}^{+}$ QM cluster, where $X = \text{Mg, Ca, Sr, Ba}$. The cluster consists of one O$^{2-}$ QM atom surrounded by its six $X^{2+}$ nearest neighbors. Larger QM clusters were built by fully coordinating the outer QM atoms of the smaller cluster. For example, the second XO cluster, (O$_{19}$X$_6$)$_{26}^{-}$ was formed by fully coordinating the six $X^{2+}$ cations of the (OX$_6$)$_{10}^{+}$ cluster with their nearest neighbor O$^{2-}$ anions. This 25 QM atom cluster was extended by fully coordinating the outer eighteen O$^{2-}$ anions with their nearest neighbor $X^{2+}$ cations to form the (O$_{19}$X$_{44}$)$_{50}^{-}$ QM cluster.
4.1.2 Madelung potential: point charges

Next, the QM cluster is embedded in the crystal environment by surrounding it with a large array of point charges. The purpose of the point charges is to better simulate the crystal environment by generating the correct crystalline electrostatic Madelung potential in the QM region. The correct Madelung potential also plays a key role in stabilizing the $O^{2-}$ ion, as has been shown in Gordon-Kim [34] type models, [35, 36] where the internal energy of ionic systems is determined from the energy of overlapping ionic charge densities. The finite point charge distribution is determined using the EWALD program, [37] as follows. In a first step, EWALD calculates the Madelung potential with the Ewald method for periodic boundary conditions (PBC), using nominal ionic values (e.g., $\tilde{Q}_c = -2$ and $\tilde{Q}_c = +2$ for $O^{2-}$ and $Pb^{2+}$, respectively) for the atoms placed at crystallographic positions of the targeted system. In a second step, EWALD retains the nearest $O(10^4) \tilde{Q}_c$ centered on the target atom, adjusting the values of the outermost $\tilde{Q}_c$ to reproduce the Madelung electrostatic potential on and in the vicinity of the QM atoms. In this second step, the nearest $\simeq 500 - 750 \tilde{Q}_c$ are fixed at their nominal values, and, in addition, the net monopole and dipole moments of the point charge distribution are constrained to vanish.

4.1.3 Boundary compensation via empty pseudopotentials

To accelerate the convergence of $\tilde{\sigma}$ with respect to the size of the QM cluster, it is advantageous to control the artificial polarization of boundary O(2p) states. This arises from the strongly attractive electrostatic potential of neighboring cation point charges for QM oxygen atoms on the periphery of the cluster. To alleviate this, the nn and nnn cation point charges of boundary O atoms are replaced by “empty” pseudopotentials (ePSP), [38] as illustrated in Fig. 4.1. The ePSP is defined as follows: i) it is a large core pseudopotential for the most loosely bound valence electrons of the corresponding cation (e.g., a Ti$^{4+}$ PSP); ii) there are no GTO basis functions associated with this site. The resulting modified cation classical potential simulates the Pauli cation core repulsion, thereby reducing the artificial polarization of boundary O(2p) states. [38] In the embedded
atom QM cluster discussed above, for example, 26 boundary point charges are replaced by ePSPs (labeled as $A^*$ or $B^*$), yielding a $(A_4B_2O_{15})^{14-} - A_{16}B_{10}$ cluster, which is surrounded by the remaining $\simeq O(10^4)$ point charges.

4.1.4 Cancellation of electric depolarization fields

Due to the spontaneous electric polarization found in some materials, such as tetragonal PbTiO$_3$, a macroscopic depolarizing electric field is present in finite samples, in the absence of surface compensating charges. Calculations using PBC are implicitly done in zero total macroscopic electric field, which automatically excludes surface depolarization effects. In the present finite size clusters, a depolarizing electric field can arise from a possible net dipole moment, due to polarization of the quantum mechanical charge density, *i.e.*, from the wave functions of the QM cluster. The net dipole moment due to the point charges and ePSPs is zero by construction, as discussed above. The resulting depolarizing electric field is removed in the calculation, by applying an external electric field in the opposite direction. The magnitude of the external field is chosen so that the force on the central target atom matches that of an all-electron PBC linearized augmented planewave (LAPW) [39] calculation. In normal equilibrium conditions, using experimentally determined structures, the LAPW forces are usually small, since the theoretical structure is usually close to that of experiment.

4.2 PBC-GIPAW (pseudo/ all-electron wave functions)

Historically, determining the chemical shielding tensor, $\sigma$, in a periodic system was problematic. The calculation of $\sigma$ using perturbation theory (linear response) requires the evaluation of the position operator expectation value, which is not defined when periodic boundary conditions (PBC) are used to represent an extended system. Moreover, PBC often employ a plane-wave basis, which in turn, requires the use of pseudopotentials. This is troublesome since chemical shielding is largely dependent on the character of the wave function at the nucleus. The pseudopotentials
remove the core electrons from the atomic potential there by destroying the behavior of the wave functions at the nucleus. Additionally, modern pseudopotentials are non-local and, until recently, it was unclear how to deal with a non-local Hamiltonian in a magnetic field.

To overcome these shortcomings, Pickard and Mauri adapted Van de Walle and Blöchl’s projector augmented wave (PAW) reconstruction method [40] to restore translation invariance in the presence of a uniform magnetic field. The PAW method can extract all-electron properties from a pseudopotential calculation by deriving an all-electron wave function from the pseudowavefunction. In the presence of a magnetic field the PAW approach is not invariant upon a spatial translation. However, by introducing a magnetic field-dependent phase factor, similar to what is used in the GIAO method, translational invariance is restored. This method is referred to as the gauge including projector augmented wave (GIPAW) [5].

The PBC chemical shielding values reported in this dissertation were performed with the GIPAW functionality of the QuantumESPRESSO (QE) code [41]. These calculations are done in two steps. A ground state calculation is first performed. This is followed by a perturbative calculation, which produces the first order correction to the ground state wave function (Eq.3.2) in the presence of an external magnetic field. This calculation uses all-electron like valence wave functions, which are represented using a PAW basis. The PAW basis is constructed from the all-electron and pseudowavefunctions during the pseudopotential generation and kept for later use.

It should be noted that the QE calculations reported here were performed in collaboration with Dr. Eric J. Walter and since this method is not the focus of this dissertation no detailed discussion will be presented. However, in the chapters where these results are presented, enough calculations details will be presented to reproduced the results. The reader is referred to reference [5] and the doctoral dissertation of Dr. Jonathan Yates [42] for an extensive discussion on the GIPAW method.
CHAPTER 5

Alkaline earth oxides and the role of electronic correlation

5.1 Introduction

First-principles techniques have become very successful in predicting nuclear magnetic resonance (NMR) chemical shift tensors in solid-state systems. When solid-state NMR spectra are difficult to interpret, theoretical modeling has been able to extract local structural information [7]. Recently, Profeta et al. [43] reported that density functional theory (DFT) within the generalized gradient approximation (GGA) produces inaccurate oxygen isotropic chemical shifts for a group of compounds containing both oxygen and calcium. Their largest error of 124 ppm was for CaO. The errors were attributed to GGA inaccurately capturing the O(2p)-Ca(3d) hybridization. To test this hypothesis, the d-channel inside the calcium pseudopotential was modified in order to raise the Ca(3d) energy level with respect to the O(2p) state. The energy difference was increased until the calculated oxygen isotropic chemical shift for CaO exactly matched the experimental value. When this tuned pseudopotential was transferred to other calcium and oxygen containing compounds, the calculated oxygen isotropic chemical shifts agreed with experiment. However, calculations with
the tuned pseudopotential produce incorrect results for other material properties. For instance, the larger O(2p)-Ca(3d) energy level difference inaccurately increases the phonon frequencies due to a smaller dielectric screening, which depends on the electronic 3d transitions [43]. Postemak et al. showed that a similar alteration of the O(2p)-cation(nd) energy levels in CaO, SrO and BaO artificially suppresses the bonding between the O(2p) and cation(nd) states. Such a modification produces inaccurate dynamical (Born) effective charge tensors $Z^*$ [44].

Recently we found that B3LYP yields accurate chemical shift tensors for the ferroelectric perovskite oxides, which have a strong O(2p)-cation(nd) interaction [7]. Here we examine how B3LYP performs on the alkaline earth oxide series MgO through BaO. Tossell calculated the B3LYP and Hartree Fock (HF) isotropic chemical shifts for MgO, CaO and SrO [45]. The materials were modeled with $[\text{OX}_6(\text{OH})_{12}]^{2-}$ finite clusters ($X = \text{Mg, Ca, Sr}$). The CaO and SrO chemical shifts were reported with respect to the MgO isotropic value. These relative differences were in fair agreement with experiment. Tossell also emphasized the importance of the cation(nd) orbitals in the CaO and SrO isotropic chemical shift calculations. Yet, the non-inclusion of the bulk electrostatic potential and lack of basis set convergence creates some uncertainty in the results. Calculated values can vary as much as 100 ppm with the choice basis set, and the largest basis set was only of double zeta quality.

Here GGA, B3LYP, and HF oxygen isotropic chemical shifts are presented for the alkaline earth oxide series MgO through BaO using sized converged embedded clusters and converged site-centered Gaussian type orbitals (GTO). Results will illustrate the accuracy of the embedding as well as the accuracy of available GTO basis functions. The importance of exact HF exchange is examined by performing oxygen chemical shift calculations with a tuned GGA-Hybrid functional. A limited study of correlation effects was undertaken with second order Moller-Plesset (MP2) perturbation theory and coupled cluster singles and doubles (CCSD) methods [18, 24, 46] on small 7 atom clusters. Results are discussed in terms of increasing covalency and increasing cation(nd) orbital diffuseness in the XO crystals with heavier cations.
5.2 Methodology

5.2.1 QM Cluster Size and Basis Set Convergence

TABLE 5.1: Forces, EFGs, and isotropic chemical shielding $\sigma_{\text{iso}}$ results for distorted rocksalt MgO with various MgO embedded clusters. The EFGs, $V_{zz}$ (in units of $10^{-21}$ V/m$^2$) and the force (in units of eV/Å) are given for the cluster center. Results for Mg- and O-centered clusters are shown. An asterisk (*) refers to a pPSP atom (see Section 4.1.3). Cluster forces and EFGs are at the LDA level of theory and the $\sigma_{\text{iso}}$ is at the PW91-GGA level. The Oxygen basis set is IGLO-III and all Mg atoms have cc-pCVTZ basis sets except the outer 38 Mg atoms in the 63 atom cluster. Those outer 38 Mg atoms have the STO-3G basis set. GGA-GIPAW (QE and CASTEP) PBE results are shown for comparison. LAPW results are LDA.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>$V_{zz}$</th>
<th>Force</th>
<th>$V_{zz}$</th>
<th>Force</th>
<th>$\sigma_{\text{iso}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO$<em>6$-Mg$</em>{18}$</td>
<td>-3.32</td>
<td>-1.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg$_{19}$O$_6$</td>
<td>-2.92</td>
<td>-1.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OMg$_6$</td>
<td>-0.80</td>
<td>1.42</td>
<td></td>
<td>357.5</td>
<td></td>
</tr>
<tr>
<td>O$_{19}$Mg$<em>5$-Mg$</em>{35}$</td>
<td>-0.75</td>
<td>0.85</td>
<td></td>
<td>180.0</td>
<td></td>
</tr>
<tr>
<td>O$<em>{10}$Mg$</em>{44}$</td>
<td>-0.72</td>
<td>1.31</td>
<td></td>
<td>189.0</td>
<td></td>
</tr>
<tr>
<td>QE</td>
<td></td>
<td></td>
<td></td>
<td>190.2</td>
<td></td>
</tr>
<tr>
<td>CASTEP</td>
<td></td>
<td></td>
<td></td>
<td>198.0$^a$ / 204.5$^b$</td>
<td></td>
</tr>
<tr>
<td>LAPW</td>
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<td>-1.28</td>
<td>-0.79</td>
<td>1.28</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ PBC-GIPAW results Ref. [47]
$^b$ PBC-GIPAW results Ref. [43]

Successful implementation of the embedded cluster method (Chapter 4) relies on the properties of interest being converged with respect to atomic basis (Unless explicitly stated, all basis sets and pseudopotentials were taken from the EMSL website (see references within) [33],) as well as QM atom cluster size. The convergence of the chemical shielding, electric field gradients (EFGs) [48], and forces were studied on the distorted MgO rocksalt structure (Table 5.1). MgO was distorted by displacing the Mg atom 0.5 Å from its ideal position along the body diagonal of its unit cell. MgO, being purely ionic, is ideal for testing the accuracy of the embedding, and the distorted MgO verifies that the embedding removes any point charge polarization effects. The all-electron (AE) embedded cluster calculations were performed with the computational package GAUSSIAN [29]. The EFGs and forces were computed using the local density approximation.
(LDA) method [13]. The chemical shielding tensor was determined by the continuous set of gauge transformation (CSGT) method [16, 49] using the PW91 functional form of GGA [50]. The accuracy of this approach was tested by comparing the embedded cluster EFG and force results to calculations made with the PBC-LAPW approach [39]. Chemical shielding tensors were cross-checked to PBC-GIPAW [5] calculations performed with the QuantumESPRESSO (QE) [41] and CASTEP [43, 47] electronic structure packages, which used the PBE GGA functional [51]. Convergence of basis set size was tested for both atoms with OMg₆ and MgO₆ clusters. Convergence was achieved with Mg and O having the AE cc-pCVTZ and IGLO-III basis sets respectively. Both the forces and EFGs calculated with embedded clusters compare favorably with LAPW (Table 5.1). Even the 7 QM atom Mg center cluster is in good agreement. The EFGs and isotropic chemical shielding σ₁₄₀ values are converged with the 25 QM atom O centered cluster.

Subsequently, convergence of the O isotropic chemical shift (with respect to liquid water) with respect to basis set size was examined for MgO, CaO, SrO, and BaO with O-centered, 25 QM atom clusters at the GGA level of theory (Table 5.2). Chemical shifts between the PW91 and PBE functions are small and differed by no more than 3 ppm (not shown in table). The AE IGLO-III and cc-pwCVxZ, where x = D, T, Q, were used for the oxygen QM atoms. Mg and Ca QM atoms had the AE cc-pCVxZ basis sets, while both Sr and Ba were represented with small core pseudopotentials and associated basis sets: Stuttgart RSC 1997 and def2-xZVP. Also, shown is a BaO calculation with the Ba CRENBL pseudopotential and basis set, where the most diffuse d function exponent was tuned (see below). Table 5.2 shows that the cations with triple zeta and oxygen with IGLO-III basis sets produce reasonable chemical shift values compared to the calculations performed with the high quality quadrupole zeta basis. However, in the case of BaO, the cluster chemical shifts with Ba DZ and TZ basis sets differed substantially from the GIPAW results. These differences are attributed to these DZ and TZ basis sets insufficiently treating Ba. For example, the CRENBL basis set, which adds an additional d-function, produced a comparable chemical shift to PBC-GIPAW. This is further discussed below.

Chemical shift convergence with respect to cluster size is shown in Table 5.2. A comparison
TABLE 5.2: GGA-PW91 oxygen chemical shifts calculations for 25 quantum atom oxygen centered $XO$ clusters surrounded by 38 ePSPs, where $X = \text{Mg, Ca, Sr, and Ba}$. Mg and Ca use the all electron cc-pCVxZ basis sets while Sr and Ba use the Stuttgart RSC ECP with DZ basis set and the def2 ECP with TZVP basis sets. Oxygen basis sets are cc-pwCVDZ, cc-pwCVTZ, cc-pwCVQZ and IGLO-III basis sets. Calculated values are compared to 63 QM atom clusters and PBC-GIPAW results. QE and CASTEP refers to GGA-PBE calculation performed with PBC-GIPAW.

<table>
<thead>
<tr>
<th>O Basis</th>
<th>X Basis</th>
<th>MgO</th>
<th>CaO</th>
<th>SrO</th>
<th>BaO</th>
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<td></td>
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</tr>
<tr>
<td>IGLO-III</td>
<td>DZ</td>
<td>79</td>
<td>466</td>
<td>522</td>
<td>658</td>
</tr>
<tr>
<td></td>
<td>TZ</td>
<td>84</td>
<td>453</td>
<td>517</td>
<td>664</td>
</tr>
<tr>
<td></td>
<td>QZ</td>
<td>81</td>
<td>448(^a)</td>
<td>502</td>
<td>674</td>
</tr>
<tr>
<td>CRENB(^b)</td>
<td>DZ</td>
<td>69</td>
<td>463</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>TZ(^c)</td>
<td>75</td>
<td>461</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$O_{19}X_{6-X_{38}}^{26-}$ 25 quantum atom cluster

$O_{19}X_{44}^{+30}$ 63 quantum atom cluster

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>QE(^d)</td>
<td>97</td>
</tr>
<tr>
<td>CASTEP</td>
<td>89(^d) / 83(^e)</td>
</tr>
<tr>
<td></td>
<td>444(^e)</td>
</tr>
<tr>
<td></td>
<td>493(^d)</td>
</tr>
<tr>
<td></td>
<td>732(^d)</td>
</tr>
<tr>
<td>Exp(^f)</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>629</td>
</tr>
</tbody>
</table>

\(^a\) Ca basis: cc-pVQZ and total energy converged to $10^{-6}$ Ha

\(^b\) GTO d exponent of 0.0527 was changed to 0.1342 (see text)

\(^c\) 38 ePSPs were replaced by AE QM atoms. The 14 cations that make up the oxygen centered conventional cube have the cc-pVxZ basis set while the remainder have the STO-3G basis set.

\(^d\) PBC-GIPAW results Ref. [47]. Experiment [52] $\sigma_{1/2}^{77/66}(O)=287.5$ ppm was used instead of the theoretically derived value in Ref. [47]

\(^e\) PBC-GIPAW results Ref. [43]. Experiment [52] $\sigma_{1/2}^{77/66}(O)=287.5$ ppm was used as the reference instead of 261.5 ppm in Ref. [43]

\(^f\) Powder results Ref. [53]
of the 25 and 63 MgO and CaO QM atom clusters with oxygen IGLO-III and cation TZ basis sets shows that the oxygen isotropic chemical shift differs by \( \approx 9 \) ppm.

To further confirm that QM atom cluster size and basis set convergence has been achieved, GGA calculations on MgO, CaO, SrO, and BaO on the 25 QM atom embedded clusters with oxygen IGLO-III, Mg, Ca, and Sr TZ, and Ba CRENBL basis sets are compared to PBC-GIPAW results. Table 5.2 reveals that the embedded cluster calculated oxygen isotropic chemical shift values of 84.453, 517, 737 ppm for MgO, CaO, SrO, and BaO are in good agreement with the mean isotropic PBC-GIPAW values of 90, 440, 497, and 742 ppm.

In light of the Ba basis set difficulties, additional studies were undertaken. CSGT results were compared to oxygen chemical shifts computed with the GIAO method. In the infinite basis set limit, the CSGT and GIAO values should agree. GTO p, d and f functions were added and removed from the CRENBL basis set. The additional p, d, and f functions had a tendency to produce basis set linear dependence. The calculations suggest that the inclusion/removal of the diffuse Ba(d) functions mostly affects the GIAO result, while the inclusion/removal of the Ba(f) function mostly affects the CSGT results. However, the CSGT method consistently produced chemical shifts closer in agreement to PBC-GIPAW. Agreement between GIAO and CSGT was achieved by adjusting the most diffuse d exponent \((0.0527 \rightarrow 0.1343)\) of the published CRENBL basis set so that it produced the lowest electronic energy without yielding linear dependent wave functions. The CSGT value for this basis set (Table 5.2) was within 7 ppm of GIAO. SrO chemical shifts revealed a similar, yet less dramatic behavior. It should be noted that the perovskite oxygen chemical shifts did not show such sensitivity to either the Ba or Sr GTO basis sets.

### 5.2.2 Computational Details

For the remainder of this chapter, all comparisons between experiment and calculated isotropic chemical shifts are made with the \( \text{O}_{19}\text{X}_{6}^{26-}\text{-X}_{58}^{58} \) embedded cluster (Chapter 4) and all GGA calculation will be PW91. All oxygen QM atoms have the IGLO-III basis set. Mg and Ca have
the cc-pCVTZ basis set, while Sr and Ba have the def2-TZVP and CRENBL (tuned-d) basis set / pseudopotential, respectively. The Ca, Sr, and Ba ePSPs are represented by the Stuttgart RLC pseudopotential and Mg ePSPs are represented by the Mg pseudopotential found in Ref [54]. GGA, B3LYP, tuned-Hybrid (see section 5.2.3) and HF calculations were performed with GAUSSIAN, and the chemical shift tensor was computed with the CSGT method.

Due to the computational demands of MP2 and CCSD, two simpler QM atom clusters and somewhat smaller basis sets were employed. The first was a \((\text{O}X_6)_1^{10+}\) embedded cluster. The O and Mg QM atoms used the AE cc-pVDZ basis, while Ca, Sr and Ba all used the Stuttgart RSC pseudopotential and associated DZ basis set. GGA, B3LYP, HF and MP2 calculations were performed with GAUSSIAN and the chemical shift tensors were computed with GIAO. All CCSD calculations were performed on a \((\text{O}X_6)_1^{10+}\) without point charge embedding using ACES-II and the GIAO method. O, Mg and Ca all had the AE cc-pVTZ basis set while Sr and Ba used the AE Sadlej pVTZ basis set. The Ba basis set is labeled Ba I in Ref [55]. That article states that Ba basis set is the same quality as the Sr Sadlej pVTZ. It should be noted that relativity was not incorporated in these calculations. GGA, B3LYP and HF GIAO chemical shift tensors were computed for this cluster by GAUSSIAN.

5.2.3 Tuned Hybrid

It is well documented for both molecular and solid-state systems that calculations of the magnetic shielding tensor is strongly dependent on the type of DFT functional, and especially on the amount of HF exchange incorporated within the functional [56]. In Table 5.3 we examine the effects of electronic exchange on the CaO oxygen isotropic chemical shift value by modifying the PW91 exchange-correlation functional via substituting a percentage of HF exchange for PW91 exchange:

$$E_{xc}^{\text{Hybrid}} = a\% E_{x}^{\text{HF}} + (1 - a)\% E_{c}^{\text{PW91}} + E_{xc}^{\text{PW91}}.$$ (5.1)
As the exchange is added, the oxygen isotropic chemical shift decreases and the HOMO-LUMO gap increases (Table 5.3). As more and more HF exchange is added, the HOMO-LUMO gap becomes larger than the experimental band gap 7.1 eV [57]. The tuned Hybrid with a = 78.5% reproduces the experimental chemical shift value of 294 ppm. In the remainder of this Chapter, "Hybrid" refers to a a = 78.5%. B3LYP refers to its standard definition (Chapter 2 Section 2.2.3).

<table>
<thead>
<tr>
<th>Method</th>
<th>( \delta_{iso} ) (ppm)</th>
<th>Homo-Lumo (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>453</td>
<td>4.22</td>
</tr>
<tr>
<td>50.0%HF</td>
<td>358</td>
<td>8.58</td>
</tr>
<tr>
<td>78.0%HF</td>
<td>295</td>
<td>10.64</td>
</tr>
<tr>
<td>78.5%HF</td>
<td>294</td>
<td>10.67</td>
</tr>
<tr>
<td>80.0%HF</td>
<td>290</td>
<td>10.90</td>
</tr>
<tr>
<td>83.0%HF</td>
<td>283</td>
<td>10.97</td>
</tr>
<tr>
<td>HF</td>
<td>232</td>
<td>11.01</td>
</tr>
<tr>
<td>B3LYP</td>
<td>395</td>
<td>5.70</td>
</tr>
<tr>
<td>Expt.</td>
<td>294</td>
<td>7.1 eV</td>
</tr>
</tbody>
</table>

**5.3 Results**

The GGA, B3LYP, tuned Hybrid, HF, and experiment oxygen isotropic chemical shift values for the alkaline earth oxide series MgO through BaO are presented in Table 5.4. The computed MgO values for all four theories all fall within 37 ppm of experiment. In the cases of CaO, SrO and BaO, GGA produces chemical shift errors of 159, 127, and 108 ppm respectively. While B3LYP's CaO and SrO deviations from experiment are smaller than GGA, the 101 and 76 ppm differences are still substantial. MgO, CaO and SrO isotropic chemical shifts calculated with the tuned Hybrid have no greater than 8 ppm error with experiment. For both systems, HF produces
TABLE 5.4 Calculations of $^{17}$O isotropic chemical shifts in ppm (relative to liquid water, $\sigma_{iso}^{rel}(O)=287$ ppm). $O_{19}X_{6}-X_{7}$, where $X = Mg, Ca, Sr, Ba$ were used for these calculations. $O$, Mg, Ca, Sr, and Ba basis sets are IGLO-III (AE), cc-pCVTZ (AE), cc-pCTZ (AE), def2-TZVP (pseudopotential) and CRENBL-AD (pseudopotential) respectively. The numbers in parentheses are the theory-exp differences.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>B3LYP</th>
<th>Hybrid</th>
<th>HF</th>
<th>Exp$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>84</td>
<td>63</td>
<td>39</td>
<td>14</td>
<td>47</td>
</tr>
<tr>
<td>CaO</td>
<td>453</td>
<td>395</td>
<td>294</td>
<td>232</td>
<td>294</td>
</tr>
<tr>
<td>SrO</td>
<td>517</td>
<td>466</td>
<td>396</td>
<td>327</td>
<td>390</td>
</tr>
<tr>
<td>BaO</td>
<td>737</td>
<td>670</td>
<td>584</td>
<td>495</td>
<td>629</td>
</tr>
</tbody>
</table>

$^a$ Powder results Ref [53]

TABLE 5.5 $O^{10-}$ embedded cluster, various levels of theory, Gaussian98-03 calculations of $^{17}$O isotropic chemical shifts in ppm (relative to liquid water). $O^{10+}_x$, where $X = Mg, Ca, Sr, Ba$ were used for these calculations. $O$ and Mg have the cc-pVDZ (AE) basis set, while Ca, Sr, and Ba have the Stuttgart RSC pseudopotential with DZ basis set. The numbers in parentheses are the theory-MP2 differences.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>B3LYP</th>
<th>HF</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>-104</td>
<td>-104</td>
<td>-101</td>
<td>-115</td>
</tr>
<tr>
<td>CaO</td>
<td>279</td>
<td>247</td>
<td>135</td>
<td>95</td>
</tr>
<tr>
<td>SrO</td>
<td>292</td>
<td>282</td>
<td>203</td>
<td>158</td>
</tr>
<tr>
<td>BaO</td>
<td>414</td>
<td>425</td>
<td>337</td>
<td>313</td>
</tr>
</tbody>
</table>

chemical shift values that are within 63 ppm of experiment. However in BaO, HF does well for MgO and CaO, but shows increasingly larger discrepancies for SrO and BaO.

The HF chemical shifts of CaO and SrO relative to MgO in Table 5.4 are 9 and 8 ppm greater than those reported by Tossell. The corresponding B3LYP values for CaO and SrO are 31 and 37 ppm larger than Tossell's values. We attribute discrepancies between the two studies to differences in basis size sets, cluster size, and embedding.

MP2 oxygen isotropic chemical shifts are compared to values computed with GGA, B3LYP, and HF on 7 QM atom embedded clusters in Table 5.5. The GGA, B3LYP, and HF calculated chemical shifts for MgO all differ from MP2 by no more than 14 ppm. The GGA and B3LYP results for CaO, SrO, and BaO deviate from MP2 by more than 100 ppm. HF produces chemical shift differences with MP2 of 40, 45, and 24 ppm respectively. We note that correlated calculations
TABLE 5.6: OX\textsuperscript{10+} NO embedding, various levels of theory, Gaussian98 for HF, B3LYP, and GGA. ACES-II: MP2 and CCSD: calculations of \textsuperscript{17}O isotropic chemical shifts in ppm (relative to liquid water). OX\textsuperscript{10+}, where X = Mg, Ca, Sr, Ba were used for these calculations. O, Mg, and Ca having the cc-pVTZ (AE) basis set, while Sr and Ba have the Sadlej pVTZ (AE) basis sets. The numbers in parentheses are the theory-CCSD differences.

<table>
<thead>
<tr>
<th></th>
<th>GGA</th>
<th>B3LYP</th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>-89  (4)</td>
<td>-88   (5)</td>
<td>-87  (7)</td>
<td>-96  (-2)</td>
<td>-94</td>
</tr>
<tr>
<td>CaO</td>
<td>263 (133)</td>
<td>242   (112)</td>
<td>159 (29)</td>
<td>125 (-5)</td>
<td>130</td>
</tr>
<tr>
<td>SrO</td>
<td>294 (132)</td>
<td>277   (115)</td>
<td>208 (46)</td>
<td>152 (-10)</td>
<td>162</td>
</tr>
<tr>
<td>BaO</td>
<td>535 (185)</td>
<td>519   (169)</td>
<td>403 (53)</td>
<td>350 (0)</td>
<td>350</td>
</tr>
</tbody>
</table>

converge more slowly with basis set quality than do DFT, HF, or hybrid calculations. We did not systematically study this.

CCSD oxygen isotropic chemical shifts are compared to values computed with GGA, B3LYP, HF, and MP2 on 7 atom QM clusters without any point charge embedding in Table 5.6. CCSD and MP2 differ by at most 10 ppm for all four crystals. GGA, B3LYP, and HF produce chemical shifts for MgO that deviate from CCSD by at most 7 ppm. CaO and SrO both have GGA-CCSD and B3LYP-CCSD difference of \( \approx 132 \) ppm and \( \approx 113 \) ppm respectively. Both crystals have HF chemical shifts that are separated from CCSD by \( \approx 29 \) ppm and \( \approx 46 \) ppm respectively. In the case of BaO, GGA and B3LYP deviations from CCSD are much larger than in any of the other crystals. HF is closer to CCSD, but produces a difference of 53 ppm that is much larger than in the other crystals. Since the calculations performed on these clusters have no inclusion of relativity, the BaO results cannot be given much weighting.

### 5.4 Discussion

Posternak et al. [44] stressed the importance of the cation(nd) orbital in the alkaline earth oxide bonding. Interactions between the O(2p) and cation(nd) orbitals are responsible for the anomalous BECs [44]. Table 5.7 contains \( Z^* \) computed by Posternak and coworkers. MgO, which as no O(2p)-cation(nd) interaction is ionic, as indicated by \( Z^* \) being very close to the nom-
TABLE 5.7: LDA and measured Born Effective Charges. Both calculated and experimental values are taken from Ref [44]

<table>
<thead>
<tr>
<th></th>
<th>Theory</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>1.98</td>
<td>1.96/2.02</td>
</tr>
<tr>
<td>CaO</td>
<td>2.35</td>
<td>2.26/2.30</td>
</tr>
<tr>
<td>SrO</td>
<td>2.44</td>
<td>2.34/2.47</td>
</tr>
<tr>
<td>BaO</td>
<td>2.72</td>
<td>2.69/2.97</td>
</tr>
</tbody>
</table>

In this case, the chemical shifts computed by GGA, B3LYP and HF are all in similar agreement with experiment. For the heavier atoms in Table 5.7, the cation(nd) orbitals (Ca(3d), Sr(4d), Ba(5d)) become more diffuse and $Z^*$ increases, indicating more covalency. The increase in the BEC indicates a stronger covalency in the bonding. In the weakly covalent bonded systems of CaO and SrO the chemical shifts computed by GGA and B3LYP are in poor agreement. HF, which has only exact exchange and no electronic correlation, produces oxygen chemical shifts that are more accurate than GGA or B3LYP. This implies that electronic correlation has a small effect on the CaO and SrO oxygen chemical shift calculations and GGA overestimates the correlation effects. The importance of exact exchange is supported by the fact that B3LYP, which incorporates 20% HF exchange in its functional, produces chemical shifts that are closer to experiment than GGA for all materials. In BaO, the HF failure, slight GGA improvement, and drastic B3LYP improvement indicate that correlation plays a larger role. GGA’s improvement and B3LYP success in BaO is not totally surprising because the Ba(5d) orbital is more delocalized and GGA exchange-correlation functional is determined from the free electron gas, where the electron density is homogeneous. This is consistent with oxygen chemical shifts in ferroelectric perovskites [7]. In these systems, the oxygen chemical shift depends strongly on the oxygen interaction with its nearest neighboring titanium or zirconium cation. Ti, Zr, and other transition metal ions and O have large anomalous $Z^{**}$’s, and DFT does better than in the more ionic X0 systems than BaO.

The effects of adding electron correlation to HF were examined by performing explicitly cor-
related MP2 calculations. Due to the computational intensiveness of MP2, the embedded cluster model had to be simplified to a system of 7 QM atoms embedded in point charges. The (GGA-MP2) difference trends are similar to the converge cluster (GGA-Expt.) differences for MgO, CaO, and SrO. But the addition of electronic correlation (HF-MP2) to HF has a small effect on the chemical shift. These results are consistent with what is observed in the sized converged clusters. However, in BaO, the addition of electronic correlation to HF does not yield a result closer to B3LYP. This could be due to inadequate treatment of the Ba basis set (Section 5.2.1). It is also conceivable that accurate MP2 chemical shift calculations require larger correlation consistent GTO basis sets for all the QM atoms, as mentioned. Unfortunately, a systemic basis set study is currently infeasible because of the computational demands TZ and QZ basis sets and the unavailability of such basis sets for both Sr and Ba atoms.

We also carried out similar CCSD calculations. Due to computational limitations, non-relativistic all electron calculations were performed on 7 QM clusters without point charge embedding. When comparing these results to the 7 QM atom embedded cluster results, it must be kept in mind that the QM atoms not only experience different electrostatic potentials, but different basis sets were employed. Even with these two changes, the two systems produce similar chemical shifts for MgO, CaO and SrO with the GGA, B3LYP, and HF theories. The MP2 values differ by at most 30 ppm. For MgO, CCSD oxygen isotropic chemical shifts are quite similar to the other theoretical values. For CaO and SrO, the differences with GGA, B3LYP, and HF are consistent with the 7 QM atom embedded cluster results. The CCSD results for BaO were inconclusive due to competing errors due to relativistic and electronic correlation effects.

Due to the success in accurately calculating a large number of molecular properties with CCSD, it would be interesting to see what oxygen isotropic chemical shifts CCSD would produce for the (O_{19}X_6)^{26-} embedded clusters with correlation consistent TZ basis sets on all of the QM atoms and relativistic pseudopotentials for Sr and Ba. If the O(2p)-cation(nd) interaction is the reason for the inconsistent results though the series, it would be sufficient to perform a frozen core calculation with all occupied orbitals frozen except the O(2p). Unfortunately, to the best of our
knowledge, no current electric structure package incorporates all the necessary features.

5.5 Summary

We presented GGA, B3LYP, and HF oxygen isotropic chemical shifts for the alkaline earth oxide series MgO through BaO using sized converged embedded clusters and converged site-centered Gaussian basis sets. This investigation studied why GGA does poorly in CaO, as well as in SrO. We found that B3LYP does well in MgO where there are no d-orbitals and in BaO where the Ba(5d) is more diffuse than the Ca(3d) or Sr(4d). It is also interesting to note that B3LYP is accurate in perovskites where there exists a large p-d covalency. However, in CaO and SrO, B3LYP does better than GGA, but it still has large errors. The effects of exact exchange and electron correlation were investigated with the tuned Hybrid functional, MP2 and CCSD. The tuned (CaO) exact exchange Hybrid improves the SrO result, but over corrects BaO. MP2 calculations for MgO, CaO and SrO suggest that electronic correlation is less important than exact exchange. CCSD results support this finding. However, the BaO results are inconclusive. The large BaO cluster B3LYP agreement with experiment suggest that exact exchange is less important than electronic correlation. However, the minimal cluster MP2 suggests the opposite.
6.1 Introduction

Due to their reversible polarization and strong electro-mechanical coupling, ferroelectric perovskite oxides are key components in many electronic and mechanical devices such as sensors, actuators, and random access memory [1]. The largest piezoelectric response occurs when competing structural instabilities are present [3], so that the local structure depends sensitively on strain, external fields, and chemical composition, as for example, near the morphotropic phase.
boundary near $\alpha = 1/2$ in Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT). Nuclear magnetic resonance (NMR) can be an important probe of local structure, and NMR has increasingly been used to study complex ferroelectric alloys [6, 58, 59]. First-principles calculations of NMR properties are likely to play an important role in helping to interpret complex measured spectra.

A material's characteristic NMR spectra is determined by the coupling of the nuclear magnetic dipole and electric quadrupole moments with the local magnetic field and with the electric field gradients (EFG), respectively [48]. The chemical shielding tensor, $\delta$, determines the local magnetic field at a nucleus

$$B = (1 - \delta)B_{\text{ext}},$$

(6.1)

where the induced field $B_{\text{ind}} = -\delta B_{\text{ext}}$ arises from electronic screening currents. Theoretical determination of the chemical shielding tensor, $\delta$, is more subtle than the EFGs, since the latter depend only on the ground state charge density. Linear response methods have long been used to calculate $\delta$ for isolated molecules and clusters [18, 60–65]. In extended systems complications arise due to the use of periodic boundary conditions (PBC), [5, 66, 67] and implementations have been limited to planewave-based methods. Recently, an alternative to the linear response method has been proposed based on calculations of the orbital magnetization [68–71]. If this approach proves successful, calculations of $\delta$ could be implemented in other standard band structure codes, including all-electron methods [70].

Calculations of $\delta$ in crystals and extended systems have largely used finite-size clusters, due to the lack of generally available PBC computer codes with NMR functionality. Accurate results can be obtained with this approach if the screening currents are sufficiently localized near the target nucleus, and if its local environment is adequately modeled by the cluster. Embedded cluster techniques have been successfully used in crystals and macromolecules to obtain nuclear quadrupole resonance spectrum, ligand to metal charge transfer excitations, photoemission, electric field gradients, and hyperfine coupling in high $T_c$ superconductors [72–75].

Such calculations have generally used standard all-electron quantum (QM) chemistry meth-
ods, which are widely available in many QM chemistry computer programs, such as GAUSSIAN [28, 29]. These methods are very mature and can calculate \( \sigma \) with a range of approximations, using well tested Gaussian type orbital (GTO) basis sets [33]. In increasing order of computational cost, these methods range from mean-field type [density functional theory (DFT), Hartree Fock (HF), and hybrid methods] to correlated approximations [such as second-order Moller-Plesset (MP2) perturbation and coupled cluster (CC) methods] [18, 24, 46]. The present cluster calculations exploit this flexibility to calculate chemical shieldings, comparing DFT/GGA, restricted HF (RHF), and hybrid-DFT/B3LYP calculations. Currently, only LDA and GGA DFT approximations are available for NMR calculations in PBC methods.

For covalently bonded systems, cluster calculations typically use hydrogen atoms to terminate dangling bonds at the cluster surface [60]. Instead, we use point charge embedding [37] to model the long range Coulomb interactions in the ABO₃ materials studied here. Additional techniques are also used to better handle the polarizable character of the large O³⁻ anion and also to control surface depolarization effects.

In this chapter, we show that the embedded cluster approach can yield accurate oxygen \( \sigma \) for transition metal perovskites. The focus is on four prototypical materials: BaTiO₃, SrTiO₃, PbTiO₃ and PbZrO₃. Strong covalency between the O and transition metal B atoms (and between the A and O atoms in Pb based materials) delicately balance ionic electrostatic interactions in these materials and related alloys, resulting in a wide variety of interesting and technologically important properties. The classic ferroelectric material BaTiO₃ exhibits three reversible temperature dependent ferroelectric phases. SrTiO₃ is a key constituent in superlattice structures with novel material properties [3]. PbTiO₃ is the prototypical Pb based ferroelectric. The strong covalency of Pb on the A-site is responsible for the large \( c/a = 1.065 \) ratio in PbTiO₃, and it plays a similar role in large electromechanical response of relaxor ferroelectrics such as PMN [76]. PbZrO₃ adopts a complicated non-polar antiferrodistortive structure with five chemically inequivalent O sites, which our calculations reproduce. PbZrO₃ is also of the end-point compounds, together with PbTiO₃, of the PZT solid solution series.
The chapter is organized as follows. The theoretical approach is described in Sec. 6.2. Calculated results for ABO₃ systems are presented in Sec. 6.3, and an analysis of the results is presented in Sec. 6.4. Finally, we summarize and conclude in Sec. 6.5.

6.2 Theoretical Approach

After briefly reviewing conventions, the construction of embedded clusters for ionic materials is described. Finally, we describe the QM chemistry methods and GTO basis sets used in the calculations.

6.2.1 Chemical shielding tensor

The chemical shielding tensor \( \sigma \) [Eq. (6.1)] is a mixed second derivative of the ground state energy with respect to the applied magnetic field and nuclear magnetic moment [18]. As such, it is an asymmetric second rank tensor with nine independent components in general, although its symmetry can be higher, depending on the site symmetry of the target nucleus [19]. The antisymmetric part of \( \sigma \) contributes negligibly to the NMR resonance frequency shift, since it enters only in second order, [20, 21] although it can contribute to relaxation [22]. The symmetric part can always be diagonalized, and the NMR frequency is determined by the following combinations of its principal axis components [23]

\[
\begin{align*}
\sigma_{\text{iso}} &= \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \frac{1}{3} \text{Tr} \sigma \\
\sigma_{\text{ax}} &= \frac{1}{6} (2\sigma_{zz} - \sigma_{xx} + \sigma_{yz}) = \frac{1}{2} (\sigma_{zz} - \sigma_{\text{iso}}) \\
\sigma_{\text{aniso}} &= \frac{1}{2} (\sigma_{yy} - \sigma_{xx}),
\end{align*}
\]

(6.2)

where \( \sigma_{\text{iso}}, \sigma_{\text{ax}}, \) and \( \sigma_{\text{aniso}} \) are the isotropic, uniaxial, and anisotropic components, respectively. In this chapter, \( \sigma_{zz} \) is chosen to correspond to the principal axis that is most nearly along the B-O-B bond direction.

Positive values of \( \sigma \) are conventionally denoted as shielding the external field, while negative
elements are referred to as deshielding [see Eq. (7.1)]. Measurements of $\delta$ are usually reported with respect to a reference compound, where the chemical shift tensor is defined as [24]

$$\delta = -(\hat{\sigma} - \sigma_{\text{ref}}). \quad (6.3)$$

### 6.2.2 Embedded clusters

An embedded cluster model is depicted in Fig. 6.1. Its core consists of real, or "QM" atoms, with the target O atom at its center. The total number of electrons is determined by satisfying the nominal formal valence of all the QM atoms. The $A_4B_2O_{15}$ QM cluster in the figure thus has a net charge of -14. The QM cluster is embedded in the classical potential due to point charges, pseudopotentials, and, in some cases, an external electric field to cancel surface depolarization effects, as described in following subsections. The atomic site designations nn and nnn. used below, denote nearest-neighbor and next-nearest-neighbor sites, respectively, and are based on the ideal structures. Thus, for example, the Ti atom in tetragonal $P4mm$ PbTiO$_3$ would be regarded as having six nn O atoms, despite the distortion of the TiO$_6$ octahedron. In the actual calculations, the tetragonal distortion results in two chemically inequivalent $O_{eq}$ and $O_{ax}$ atoms ($O_{ax}$ lying on the polar axis), which require two separate embedded cluster calculations.

**Quantum cluster**

In all the QM clusters considered in this chapter, the target oxygen atom is fully coordinated with QM atoms located at its nn and nnn sites. Secondly, the target atom’s nn QM atoms are themselves fully coordinated with nn QM atoms. Finally, additional QM atoms are added, as required by ideal perovskite symmetry. This procedure results in a 21 QM-atom cluster: $(A_4B_2O_{15})^{14-}$, depicted in Fig. 6.1, where $A = $ Sr, Ba, or Pb; $B = $ Ti or Zr. This includes two corner-shared BO$_6$ octahedra, centered on the targeted O atom (11 O and 2 B atoms), the target atom’s 4 nnn A cations, and 4 additional O atoms, which are also one lattice constant away from the center atom. Tests with larger QM clusters were used to estimate convergence of the chemical shielding tensor...
Madelung potential: point charges

Next, the QM cluster is embedded in the crystal environment by surrounding it with a large array of point charges. The purpose of the point charges is to better simulate the crystal environment by generating the correct crystalline electrostatic Madelung potential in the QM region. The correct Madelung potential also plays a key role in stabilizing the $O^{2-}$ ion, as has been shown in Gordon-Kim [34] type models, [35, 36] where the internal energy of ionic systems is determined from the energy of overlapping ionic charge densities. The finite point charge distribution is determined using the EWALD program, [37] as follows. In a first step, EWALD calculates the Madelung potential with the Ewald method for PBC, using nominal ionic values (e.g., $\bar{Q}_i = -2$ and $\bar{Q}_i = +2$ for $O^{2-}$ and $Pb^{2+}$, respectively) for the atoms placed at crystallographic positions of the targeted system. In a second step, EWALD retains the nearest $O(10^4) \bar{Q}_i$ centered on the target atom, adjusting the values of the outermost $\bar{Q}_i$ to reproduce the Madelung electrostatic potential on and in the vicinity of the QM atoms. In this second step, the nearest $\simeq 500 - 750 \bar{Q}_i$ are fixed.

FIG. 6.1: Illustration of cluster embedding for the O-centered $A_4B_2O_{15}$ quantum atom (QM) cluster (Sec. 6.2.2), shown for a $[110]$ plane of the ideal perovskite structure. The QM A, B, and O atoms are depicted by filled black, blue and red circles, respectively. In the left panel, the QM atoms are embedded in point charges, "+" or "−" signs colored coded according to the QM atom they replace in the crystalline lattice. In the right panel, the boundary O QM atoms have had their nearest and next-nearest neighbor cation point charges replaced by "empty" pseudopotentials (Sec. 6.2.2), indicated by thick large circles, with corresponding color coding.
at their nominal values. and, in addition, the net monopole and dipole moments of the point charge
distribution are constrained to vanish.

**Boundary compensation via empty pseudopotentials**

To accelerate the convergence of $\sigma$ with respect to the size of the QM cluster, it is advan-
tageous to control the artificial polarization of boundary O(2p) states. This arises from the strongly
attractive electrostatic potential of neighboring cation point charges for QM oxygen atoms on the
periphery of the cluster. To alleviate this, the nn and nnn cation point charges of boundary O atoms
are replaced by “empty” pseudopotentials (ePSP) [38], as illustrated in Fig. 6.1. The ePSP is de-
fined as follows: i) it is a large core pseudopotential for the most loosely bound valence electrons
of the corresponding cation (e.g., a Ti$^{4+}$ PSP); ii) there are no GTO basis functions associated
with this site. The resulting modified cation classical potential simulates the Pauli cation core repul-
sion, thereby reducing the artificial polarization of boundary O(2p) states [38]. In the embedded
21 atom QM cluster discussed above, for example, 26 boundary point charges are replaced by
ePSPs (labeled as A* or B*), yielding a $(A_4B_2O_{15})^{14-} \cdot A_{16}B_{30}$ cluster, which is surrounded by
the remaining $\simeq O(10^3)$ point charges.

**Cancellation of electric depolarization fields**

Due to the spontaneous electric polarization found in some materials, such as tetragonal
PbTiO$_3$, a macroscopic depolarizing electric field is present in finite samples, in the absence of
surface compensating charges. Calculations using PBC are implicitly done in zero total macro-
scopic electric field, which automatically excludes surface depolarization effects. In the present
finite size clusters, a depolarizing electric field can arise from a possible net dipole moment, due
to polarization of the QM charge density, *i.e.*, from the wave functions of the QM cluster. The net
dipole moment due to the point charges and ePSPs is zero by construction, as discussed above.
The resulting depolarizing electric field is removed in the calculation, by applying an external elec-
tric field in the opposite direction. The magnitude of the external field is chosen so that the force
on the central target atom matches that of an all-electron PBC linearized augmented planewave (LAPW) [39] calculation. In normal equilibrium conditions, using experimentally determined structures, the LAPW forces are usually small, since the theoretical structure is usually close to that of experiment.

### 6.2.3 Calculational details

The embedded cluster calculations were performed with the GAUSSIAN computational package [28, 29]. The chemical shielding tensor was determined using the continuous set of gauge transformations (CSGT) method [16, 49]. The gauge-independent atomic orbital (GIAO) method [77] was also used for comparison in some cases. The gauge origin in GIAO is at the target atom, yielding a useful decomposition into diamagnetic and paramagnetic components, as discussed further below and in the next Section. We did not include a surface dependent magnetic depolarization contribution to $\delta_{\text{iso}}$, which depends on the magnetic susceptibility [78, 79].

Calculations were done using the DFT hybrid B3LYP [10], as well as the generalized gradient approximation (GGA), using the PW91 form [50]. The B3LYP calculations were found to yield generally better agreement with experiment (Sec. 6.3) than GGA. Site-centered GTO basis functions were associated with all the QM atoms. All-electron treatments were used for the O and Ti atoms, while the other QM atoms were represented using scalar-relativistic small core (RSC) pseudopotentials [also called effective core potentials (ECPs)]. All basis sets and ECPs listed below were taken from the EMSL website [33]. O-centered ($A_4B_2O_{15}$)$^{14-}$ QM clusters were used in the calculations, suitably embedded with point charges and ePSPs, as discussed in Sec. 6.2.2). Test calculations for larger clusters were used to check size convergence, as discussed at the end of this section.

The RSC ECPs for the QM atoms were Sr(28), Zr(28), Ba(46), Pb (60), where the number of core electrons is shown in parenthesis. These pseudopotentials are generally specified by the same label as their associated basis sets listed below, except where otherwise indicated. For ePSPs
(Sec. 6.2.2), which have no associated GTOs, scalar-relativistic large core (RLC) ECPs were used as follows: CRENBS RLC for Ti(18) and Zr(36); Stuttgart RLC for Sr(36) and Ba(54). [The Ba ePSP was also used for the Pb ePSP atoms, because we could not find a large core Pb\(^{2+}\) quantum chemistry type pseudopotential in the standard databases.] The following GTO basis sets were found to give well-converged results: O(IGLO-III), Ti(cc-pwCVTZ-NR), Zr(cc-pwCVTZ-PP), and Pb(cc-pVTZ-PP). For the Sr and Ba atoms, the associated Stuttgart RSC 1997 basis sets were used. The correlation consistent basis sets were employed in this study, because this basis function series facilitates a systematic study of chemical shift convergence with respect to basis set size. (We could not find correlation consistent basis sets for Sr and Ba.) The O(IGLO-III) basis set was used, because it was specifically designed for magnetic property calculations. In convergence tests, we found that it had quadruple-\(\zeta\) (QZ) accuracy even though it has fewer basis functions.

In SrTiO\(_3\), for example, B3LYP CSGT principle value components calculated with the aforementioned basis sets differed by no more than 10 ppm from results calculated with the O(cc-pwCVQZ), Ti (cc-pwCVQZ-NR), and Sr (def2-QZVP) basis sets, while \(\delta_{\text{iso}}\) differed by only \(\approx 8\) ppm. In PbTiO\(_3\), changing the Pb basis set from DZ to TZ changed \(\delta_{\text{iso}}\) by less than 10 ppm, while the difference between inequivalent O sites changed by less than 4 ppm. These results are consistent with calculations for SrTiO\(_3\), using two different gauge methods. shown in Table 6.1, where, in the infinite basis set limit, the CSGT and GIAO values should agree. The individual B3LYP components, \(\sigma_{xx} = \sigma_{yy}\) and \(\sigma_{zz}\), are seen to differ by 3 and 26 ppm, respectively, while \(\sigma_{\text{iso}}\) differs by only 6 ppm.

Size convergence errors of about 30 ppm in the absolute value of the chemical shieldings were estimated from calculations on larger clusters, using the above basis sets. In SrTiO\(_3\), for example, increasing the O-centered cluster size from the Sr\(_4\)Ti\(_2\)O\(_{15}\) (21 atoms) to Sr\(_4\)Ti\(_{10}\)O\(_{47}\) (61 atoms) changed the RHF, B3LYP, and PW91 \(\sigma_{\text{iso}}\) by -13, -27, and -25 ppm, respectively, while individual principal values changed by less than 16, 30, and 37 ppm. These test calculations used large core Ti pseudopotentials for the additional Ti atoms.
6.3 Results

Calculated chemical shielding results for the prototypical perovskites SrTiO$_3$, BaTiO$_3$, PbTiO$_3$ and PbZrO$_3$ are presented and compared to $^{17}$O NMR single crystal and powder spectra chemical shift measurements in this section. Calculations were performed for embedded clusters corresponding to the following structural parameters. For cubic SrTiO$_3$, the lattice parameter of Ref. [80] was used. BaTiO$_3$ cubic and tetragonal P4mm structures were taken from Ref. [81]; rhombohedral R3m from Ref. [82]. The PbTiO$_3$ tetragonal P4mm structure was taken from Ref. [83]. For PbZrO$_3$, which has a complicated Pbam unit cell containing eight formula units, experimental lattice parameters from neutron scattering measurements were used together with internal coordinates determined from first principles calculations [84]. All calculations were carried out using the embedded cluster approach described in Sec. 6.2, using the hybrid B3LYP exchange-correlation functional. In some cases RHF and GGA/PW91 results are reported for comparison.

Table 6.1 presents our calculated results for the principal values of the symmetrized chemical shielding tensor $\sigma$. (The asymmetry in the chemical shielding tensors was less than 0.5 ppm; see Sec. 6.2.1.) The principal axis frame of the target O atom is indicated by $x$, $y$, $z$, where the $z$-axis is always identified with the local B-O-B direction. This is exact in the cubic and tetragonal crystals. For lower O-site symmetry, the $z$-axis well approximates the quasilinear B-O-B bond in all the structures considered here.

A striking feature in Table 6.1 is the large $\sigma_{xx} \simeq \sigma_{yy}$ vs. $\sigma_{zz}$ anisotropy of the principal values for each case, with two large negative (deshielded) principal values and one considerably smaller positive (shielded) $\sigma_{zz}$ principal value. The O atoms have their highest site-symmetry in the cubic crystals, resulting in an exact two-fold $\sigma_{xx} = \sigma_{yy}$ degeneracy. For lower symmetry cases, the degeneracy is lifted, but the splitting remains small in most cases; the largest splitting is 65 ppm for the O1-4g site in PbZrO$_3$. As shown by the GIAO calculations for SrTiO$_3$, the anisotropy arises from the paramagnetic components. We note that the GIAO diamagnetic components in SrTiO$_3$ differ by only $\simeq$ 50 ppm from that of the the isolated, purely diamagnetic, O$^{2-}$.
TABLE 6.1: Calculated oxygen chemical shielding principal values (in ppm) for SrTiO$_3$, BaTiO$_3$, PbTiO$_3$, and PbZrO$_3$. In all cases, "z" denotes the principal axis that is most closely along the B-O bond direction. Unless otherwise indicated, the CSGT gauge method was used, with B3LYP for exchange and correlation. For some cases, GGA results are given in parenthesis. RHF and GIAO gauge method B3LYP results are given for SrTiO$_3$. GIAO results for the isolated diamagnetic O$^{2-}$ atom are also shown. See the text for a discussion of the fake SrTiO$_3$ calculation. For PbZrO$_3$, we adopt the site labeling convention of Ref. [84]; the O(i) site notation of Ref. [4] is also given in brackets.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{xx}$</th>
<th>$\sigma_{yy}$</th>
<th>$\sigma_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SrTiO$_3$(cubic)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GIAO diamag.</td>
<td>-343 (-353)</td>
<td>-343 (-353)</td>
<td>90 (46)</td>
</tr>
<tr>
<td>GIAO paramag.</td>
<td>347</td>
<td>347</td>
<td>371</td>
</tr>
<tr>
<td>GIAO total</td>
<td>-694</td>
<td>-694</td>
<td>-255</td>
</tr>
<tr>
<td>RHF</td>
<td>-134</td>
<td>-134</td>
<td>201</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>410</td>
<td>410</td>
<td>410</td>
</tr>
<tr>
<td><strong>fake calculation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GIAO diamag.</td>
<td>397</td>
<td>397</td>
<td>448</td>
</tr>
<tr>
<td>GIAO paramag.</td>
<td>-228</td>
<td>-228</td>
<td>-262</td>
</tr>
<tr>
<td>GIAO total</td>
<td>169</td>
<td>169</td>
<td>186</td>
</tr>
<tr>
<td><strong>BaTiO$_3$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cubic</td>
<td>-413 (-414)</td>
<td>-413 (-414)</td>
<td>97 (49)</td>
</tr>
<tr>
<td>P4mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{ax}$</td>
<td>-505 (-480)</td>
<td>-505 (-480)</td>
<td>116 (70)</td>
</tr>
<tr>
<td>$O_{eq}$</td>
<td>-401 (-407)</td>
<td>-353 (-355)</td>
<td>87 (40)</td>
</tr>
<tr>
<td>R3m</td>
<td>-423 (-416)</td>
<td>-412 (-406)</td>
<td>97 (51)</td>
</tr>
<tr>
<td><strong>PbTiO$_3$(P4mm)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{ax}$</td>
<td>-608 (-562)</td>
<td>-608 (-562)</td>
<td>163 (123)</td>
</tr>
<tr>
<td>$O_{eq}$</td>
<td>-263 (-286)</td>
<td>-219 (-228)</td>
<td>13 (-32)</td>
</tr>
<tr>
<td><strong>PbZrO$_3$(Pbam)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1-4g [O(1)]</td>
<td>-172 (-197)</td>
<td>-107 (-130)</td>
<td>85 (48)</td>
</tr>
<tr>
<td>O1'-4g [O(2)]</td>
<td>-132 (-158)</td>
<td>-104 (-126)</td>
<td>77 (40)</td>
</tr>
<tr>
<td>O2-8i [O(3)]</td>
<td>-147 (-171)</td>
<td>-139 (-162)</td>
<td>100 (64)</td>
</tr>
<tr>
<td>O3-4f [O(4)]$^a$</td>
<td>-93 (-118)</td>
<td>-64 (-90)</td>
<td>62 (26)</td>
</tr>
<tr>
<td>O4-4e [O(5)]</td>
<td>-251 (-269)</td>
<td>-223 (-239)</td>
<td>175 (136)</td>
</tr>
</tbody>
</table>

$^a$ Note: our calculations suggest that the assignment of the O3-4f[O(4)] and O4-4e[O(5)] peaks should be reversed in Ref. [4], as done here.
TABLE 6.2: Comparison between calculated and measured single crystal and powder spectra $^{17}$O chemical shifts (in ppm) for BaTiO$_3$ and SrTiO$_3$. Calculated isotropic shifts $\delta_{\text{iso}}$ and uniaxial components $\delta_{\text{ax}}$ are derived from Table 6.1, referenced to liquid water. $\sigma_{\text{water}} = 287.5$ ppm (Ref. [52]). Calculated values are from B3LYP (GGA values are in parenthesis), and RHF results are also shown for SrTiO$_3$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SrTiO$_3$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cubic</td>
<td>486 (507)</td>
<td>467 ± 5$^a$, 465$^b$</td>
<td>-144 (-132)</td>
<td>-135.3 ± 5$^a$</td>
</tr>
<tr>
<td>cubic RHF</td>
<td>310</td>
<td></td>
<td>-112</td>
<td></td>
</tr>
<tr>
<td><strong>BaTiO$_3$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cubic</td>
<td>530 (547)</td>
<td>546 ± 5$^a$</td>
<td>-170 (-154)</td>
<td>-150 ± 1$^a$</td>
</tr>
<tr>
<td>P4mm</td>
<td>O$_{\text{ax}}$ 585 (584)</td>
<td>570 ± 5$^a$, 553$^c$, 564$^d$</td>
<td>-207 (-183)</td>
<td>-171 ± 1$^a$</td>
</tr>
<tr>
<td></td>
<td>O$_{\text{eq}}$ 510 (528)</td>
<td>520 ± 5$^a$, 530$^c$, 523$^d$</td>
<td>-155 (-140)</td>
<td>-142 ± 1$^a$</td>
</tr>
</tbody>
</table>

$^a$ Single crystal experimental values are from Ref. [85]
$^b$ Powder results Ref. [86]
$^c$ Powder results Ref. [87]
$^d$ Powder results Ref. [88]

In the fake SrTiO$_3$ calculation, where d-like ($\ell = 2$) Ti-centered GTO basis functions were deliberately excluded from the calculation, the large $x, y$ vs. $z$ anisotropy is absent. The fake diamagnetic values are closer to the atomic O$^{2-}$ shielding, and the paramagnetic contributions are close to isotropic. The $x, y$ vs. $z$ anisotropy of the calculated principal values and its relation to O(2p) hybridization with the B-atom d-states is analyzed in Sec. 6.4.1.

Table 6.2 compares the results for SrTiO$_3$ and BaTiO$_3$ in Table 6.1 with recent single crystal measurements [85] and with earlier powder spectrum measurements of the isotropic shifts. Isotropic and uniaxial components of the chemical shift tensors are given, where $\delta_{\text{ax}} = (\delta_{zz} - \delta_{\text{iso}})/2$, using Eq. (7.2). In SrTiO$_3$, the calculated $\delta_{\text{iso}}$ and $\delta_{\text{ax}}$ differ from experiment by $\approx 20$ ppm and $\approx 9$ ppm respectively. In BaTiO$_3$, $\delta_{\text{iso}}$ calculated and experiment values differ by at most...
Table 6.3 compares the results for PbTiO$_3$ and PbZrO$_3$ isotropic shifts $\delta_{\text{iso}}$ (derived from Table 6.1) with well resolved measured powder spectra [4]. For both systems, the calculated results differ from experiment by no more than 21 ppm, with an average discrepancy of approximately 10 ppm. Differences of relative shifts between chemical sites are smaller in most cases. For example, in tetragonal PbTiO$_3$ the calculated B3LYP splitting between the two inequivalent O sites is $\simeq 200$ ppm, in good agreement with measured powder spectra [4].

<table>
<thead>
<tr>
<th>Theory</th>
<th>Expt.$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO$_3$</td>
<td></td>
</tr>
<tr>
<td>$O_{ax}$</td>
<td>639 (621)</td>
</tr>
<tr>
<td>$O_{eq}$</td>
<td>444 (469)</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td></td>
</tr>
<tr>
<td>$O1-4g$ [O(1)]</td>
<td>352 (380)</td>
</tr>
<tr>
<td>$O1'-4g$ [O(2)]</td>
<td>340 (369)</td>
</tr>
<tr>
<td>$O2-8i$ [O(3)]</td>
<td>349 (377)</td>
</tr>
<tr>
<td>$O3-4f$ [O(4)]$^b$</td>
<td>319 (348)</td>
</tr>
<tr>
<td>$O4-4e$ [O(5)]</td>
<td>387 (412)</td>
</tr>
</tbody>
</table>

$^a$ Experimental values are from Ref. [4]

$^b$ Note: our calculations suggest that the assignment of the O3-4f[O(4)] and O4-4e[O(5)] peaks should be reversed in Ref. [4], as done here.
6.4 Discussion

A key feature in the electronic structure of transition metal perovskites are the covalent interactions between the O(2p) and the (formally) unoccupied transition metal-d states. Indeed, the delicate balance between covalent and electrostatic ionic interactions is responsible for the wide variety of interesting properties exhibited by these materials and related alloys. In this section, we analyze the calculated chemical shieldings in Sec. 6.3 in relation to p-d hybridization.

The measured NMR $^{17}$O spectra show narrow well separated peaks in these materials, indicating that second-order quadrupolar broadening, and thus the EFGs, are small [4], consistent with first principles calculations of O EFGs [84, 89]. For the systems studied here, all the O sites are clearly resolved in the measurements, and the chemical shielding tensor largely determines the second order quadrupolar peak positions [4].

6.4.1 p-d hybridization and anisotropy of oxygen chemical shielding

As mentioned, a striking feature in Table 6.1 is the large anisotropy of the chemical shielding principal values. This is due to hybridization between the O(2p) and virtual B-site d-states. The qualitative features can be understood from a simplified picture, which focuses on the B-O-B quasilinear structural unit (Fig. 6.1). In a linear molecule, the dependence of $\tilde{\sigma}$ on the direction of the applied field $B_{ext}$ is particularly simple, if we choose to locate the vector potential gauge origin at the target nucleus [90, 91]. In this case, when $B_{ext}$ is parallel to the molecular axis, only the diamagnetic (shielding) component contributes to $\tilde{\sigma}$; when $B_{ext}$ is perpendicular to the axis, both diamagnetic and paramagnetic (deshielding) components contribute. (Note that the calculated $\tilde{\sigma}$ are invariant under a change of the gauge origin. Consequently, we are free to interpret the $\tilde{\sigma}$ values as if they had been calculated with any particular choice of origin.) The diamagnetic component depends only on ground state wave functions, while the paramagnetic component depends on virtual transitions to unoccupied states, i.e., occupation of virtual states in the first order perturbed wave functions. In a DFT or HF calculation, this implies that large paramagnetic contributions
could be expected, if there are low lying unoccupied one particle eigenstates that are strongly
coupled to occupied states. This is the case in these materials, where there is strong coupling
between O(2p) and virtual B-site d-states.

In cubic SrTiO3, for example, when B_{ext} is applied along the Ti-O bond direction (z-
direction), the O nucleus is shielded by the applied field (i.e., the principal value \( \sigma_{zz} = 90 \) is
positive [Eq. (7.1)]. By contrast, when B_{ext} is perpendicular to the Ti-O bond, the O nucleus
is strongly deshielded (\( \sigma_{xx} = \sigma_{yy} = -343 \)) as shown in Table 6.1. According to this B-O-B
picture, we would infer that only diamagnetic contributions should contribute to \( \sigma_{zz} = 90 \), and
the positive \( \sigma_{zz} = 90 \) value is consistent with this. Similarly, we would attribute the deshielded
\( \sigma_{xx} = \sigma_{yy} = -343 \) value to paramagnetic contributions arising from the O(2p)-Ti(3d) hybridiza-
tion mechanism. This interpretation is supported by the fake SrTiO3 calculations, where removal
of Ti d basis functions quenches O(2p)-Ti(3d) hybridization and results in nearly isotropic prin-
cipal value components. \( \sigma_{xx} = \sigma_{yy} \approx \sigma_{zz} \).

While qualitatively correct, the simple B-O-B model leaves out important crystalline effects.
Thus the SrTiO3 GIAO total shielding value \( \sigma_{zz} = 116 \) arises from cancellation of large dia-
magnetic \( \sigma_{d,z} = 371 \) and smaller paramagnetic \( \sigma_{p,z} = -255 \) components. Note that the fake
\( \sigma_{p,z} = -262 \) value is similar to the normal \( \sigma_{p,z} = -255 \) value; in addition \( \sigma_{p,x,y} \approx \sigma_{p,z} \) in the
fake calculation. We therefore attribute the presence of a non-zero \( \sigma_{p,z} \) to interactions with other
atoms in the crystal, which are neglected in the simple B-O-B picture.

Variations in B-O-B bond distances will affect O(2p)-B(nd) hybridization, and this should
be reflected by corresponding changes in the calculated oxygen chemical shieldings. This is the
case, as seen in Figure 6.2, which shows that the isotropic \( \delta_{iso} \) and uniaxial \( \delta_{ax} \) chemical shifts
[Eq. (7.2)] exhibit a remarkably linear variation as a function of \( r_s \), the shortest B-O bond length
of the targeted O atom [92]. Indeed, \( \delta_{iso} \) changes by more than a factor of two over the plotted
range.

The linear behavior is largely due to the deshielding \( \sigma_{xx} \) and \( \sigma_{yy} \) components in Table 6.1.
To frame the discussion in terms of the paramagnetic components of the shielding tensors, we
FIG. 6.2: Calculated oxygen isotropic $\delta_{\text{iso}}$ and uniaxial $\delta_{\text{ax}}$ chemical shifts in SrTiO$_3$ (ST), BaTiO$_3$ (BT), PbTiO$_3$ (PT), PbZrO$_3$ (PZ), as a function of $r_s$, the shortest B-O bond length of the targeted O atom. The notation B - O - B indicates O atoms with two equidistant nn B atoms, and B - O - B indicates an O atom with one short and one long nn B bond (e.g., along the polar c-axis in P4mm PbTiO$_3$). The straight lines are linear fits.
FIG. 6.3: Calculated paramagnetic $\sigma_{p,z}$ and $\sigma_{p,xy}$ components (see text), as a function of $r_s$, the shortest B-O bond length of the targeted O atom. The straight lines are linear regressions of the points. Symbols as in Fig. 6.2.
first subtract the diamagnetic component of the isolated \(O^{2-}\) atom, \(\sigma(O^{2-}) = 410\) ppm, defining \(\sigma_{p,z} = \sigma_{zz} - \sigma(O^{2-})\) and \(\sigma_{p,xy} = (\sigma_{xx} + \sigma_{yy})/2 - \sigma(O^{2-})\). These are plotted in Fig. 6.3.

An alternative choice would be to plot the GIAO paramagnetic component. Even had we done GIAO calculations for all the different O-sites, this choice is not necessarily better, since both the diamagnetic and paramagnetic GIAO components include contributions from neighboring atoms [77]. Moreover, the separation into diamagnetic and paramagnetic components is, at best, only qualitatively useful, since the separate components depend on the choice of gauge method. The present choice is physically motivated, using a well defined diamagnetic reference system. As indicated by the SrTiO\(_3\) GIAO diamagnetic components, which differ by only \(\approx 50\) ppm from the \(O^{2-}\) value (Table 6.1), this subtraction largely removes the closed shell diamagnetic response. In any case, our definition of \(\sigma_p\) simply shifts all \(\sigma\) principal values by a constant. As seen in Fig. 6.3, both \(\sigma_{p,z}\) and \(\sigma_{p,xy}\) vary linearly with \(r_s\). The average slope of \(\sigma_{p,xy}\) is \(\approx 5\) times larger in magnitude than that of \(\sigma_{p,z}\). This shows that the linear behavior in Fig. 6.2 is largely due to the variations of the deshielding \(\sigma_{xx}\) and \(\sigma_{yy}\) components, which arise from the p-d hybridization mechanism.

The p-d hybridization mechanism also plays a key role in producing the anomalously large dynamical (Born) effective charge tensors \(Z^*\), which are universally seen in perovskite ferroelectrics for the O, transition metal B, and Pb atoms [93-97]. In cubic BaTiO\(_3\), SrTiO\(_3\), PbTiO\(_3\) and PbZrO\(_3\), \(Z^*_{zz}(O)\) (the component along the Ti-O bond) takes on the values \(-5.59, -5.66, -5.83,\) and \(-4.81\) [93], respectively, which is much larger than the nominal -2 value for \(O^{2-}\). By contrast, the perpendicular components \(Z^*_{xz}(O)=Z^*_{yz}(O)\) are given by \(-2.11, -2.00, -2.56, -2.48\), respectively, which are much closer to the nominal value, since these stretch the B-O bond only in second order. Similarly, all \(Z^*(B^{1+}) \approx 6 - 7\) are anomalously large, since these involve the flow of dynamic charge as the B-O bond is stretched or compressed. [In PbTiO\(_3\) and PbZrO\(_3\), \(Z^*(Pb) \approx 4\) is anomalously large compared to \(Z^*(Ba) \approx Z^*(Sr) \approx 2.6\), due to strong Pb-O covalency, and this is reflected in the somewhat more anomalous \(Z^*_{xx}(O)\) and \(Z^*_{yy}(O)\) in the Pb based crystals.] Artificially decreasing the p-d hybridization, as in Ref. [98], resulted in nominal
values of all the $Z^*$. Similarly, the fake SrTiO$_3$ calculation eliminates B(d)-O(2p) paramagnetic contributions to $\hat{\sigma}$ and largely removes the anisotropy between $\sigma_{xx} \simeq \sigma_{yy}$ and $\sigma_{zz}$ components. B(d)-O(2p) covalency is essential for ferroelectricity in transition metal perovskites, mitigating the repulsion between otherwise rigid ion-cores, which tends to suppress ferroelectric distortion; under pressure, this mechanism eventually fails and ferroelectricity disappears [99]. Figure 6.3 shows that the anisotropy between $\sigma_{p,xy}$ and $\sigma_{p,z}$ increases linearly with decreasing $r_s$, consistent with this picture, and indicating a strengthening of the p-d hybridization mechanism as $r_s$ is reduced.

### 6.4.2 Exchange and correlation effects

Despite the fact that the B3LYP band gap is nearly a factor of two larger than that of GGA, the results in Tables 6.1 and 6.2 are fairly similar, with the exception of PbTiO$_3$, where the B3LYP results are in better agreement with experiment (Table 6.3: Sec. 6.4.3). Although larger band gaps result in larger energy denominators in the paramagnetic perturbative equations, [90, 91] there is little difference in the shieldings between the two methods. Similarly, a significant deshielded SrTiO$_3$ RHF paramagnetic component is evident in Table 6.1, despite the much larger RHF highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of 8.8 eV, compared to the B3LYP 3.6 eV gap. The apparent dependence of the chemical shielding on the band gap can be somewhat misleading, however, since the transverse paramagnetic component of the first order current density could be made to vanish under suitable gauge transformations within the CSGT gauge method [49, 100]. The entire shielding would then be given by the diamagnetic component, which depends only on the occupied single particle states. Similar observations were made regarding calculations of the spontaneous polarization $P$ and $Z^*$ in ferroelectric perovskites, where RHF results for these quantities were found to be in good numerical agreement with both experiment and with DFT calculations [101, 102], both methods yielding anomalously large $Z^*$. 
6.4.3 Comparison of chemical shifts with experiment

The calculated results in Table 6.2 for SrTiO$_3$ and BaTiO$_3$ are in very good agreement with single crystal measurements. Overall, both B3LYP and GGA yield similar agreement with experiment, while RHF is significantly worse. When comparing cubic and ferroelectric P4mm tetragonal BT results with experiment, one should keep in mind the evidence for static and/or motional disorder of local structures suggested by experiment [85, 103, 104] and theory [105, 106], since the present calculations were performed for ordered crystalline structures.

In PbTiO$_3$, the O$_{ax}$ atom has two nn Ti atoms along the polar direction, with one short 1.77 Å and one long 2.39 Å bond length, while the O$_{eq}$ has two equal bonds of 1.98 Å. The experimental assignment of the two measured peaks is simplified by the fact that the relative integrated intensities of the two O spectral peaks corresponds to the 1:2 ratio of the O$_{eq}$ to O$_{ax}$ atoms in the simple 5-atom primitive unit cell [4]. The large $\approx 200$ ppm experimentally observed [4] splitting between the O$_{ax}$ and O$_{eq}$ reflects their very different Ti-O bond lengths. The B3LYP calculated chemical shifts in Table 6.3 reproduce the $\approx 200$ ppm splitting, while GGA underestimates it by $\approx 50$ ppm. Basis set and cluster size convergence errors (Section 6.2.3) can be expected to largely cancel in these calculated splittings, reducing the residual uncertainty to less than about 10 ppm. We are not aware of any measurements of the $^{17}$O uniaxial asymmetry in PbTiO$_3$.

In PbZrO$_3$ the peak assignments are more difficult, because four of the five inequivalent oxygen sites have the same ratio of occurrence in the unit cell. In Ref. [4] the peak assignment in the NMR spectrum was made based on the assumptions that (1) the proximity of the Zr cation plays the most important shielding role and (2) that the largest chemical shift corresponds to the largest bond length. The present calculations indicate that the first assumption is correct, but not the second. Instead, as seen in Fig. 6.2, the largest chemical shift corresponds to shortest bond distance between the targeted O atom and its nearest B atom. Indeed, the figure shows that this holds true, not only for PbZrO$_3$, but across several compounds, over a wide range of chemical shifts. Our calculations indicate that chemical shift site assignments for the O(4) and O(5) atoms
in Ref. [4] (their Table I) should be reversed. Finally, we note that differences between theory and experiment in the relative splittings are smaller than those of the absolute splittings, i.e., a rigid shift of the calculated B3LYP (GGA) values in Table 6.3 by \( \approx 10 \) ppm (\( \approx -15 \) ppm) removes most of the discrepancies.

### 6.5 Summary

We have shown that first-principles embedded cluster calculations, using the DFT hybrid B3LYP method, can accurately calculate O chemical shifts for prototypical perovskite structure transition metal oxides. Calculated isotropic and uniaxial chemical shifts were found to be in good agreement with recent single crystal NMR \(^{17}\)O measurements for SrTiO\(_3\) and BaTiO\(_3\). For ferroelectric P4mm BaTiO\(_3\) and PbTiO\(_3\), the calculations accurately reproduced measured power spectra NMR isotropic chemical shifts \( \delta_{\text{iso}} \) for the two inequivalent O sites. The large \( \approx 200 \) ppm experimental splitting in P4mm PbTiO\(_3\) is well reproduced by B3LYP, but DFT/GGA underestimates it by \( \approx 50 \) ppm. In PbZrO\(_3\), experimental and calculated \( \delta_{\text{iso}} \) are in very good agreement, but experimental peak assignments are more difficult, since four of the five inequivalent O sites appear in the same ratio. Our calculations, indicate a correction of the experimental assignments in Ref. [4].

Our most notable findings are 1) a large anisotropy in the chemical shielding tensor, between deshielded \( \sigma_{zx} \approx \sigma_{yy} \) and shielded \( \sigma_{zz} \) components, the latter principal axis being along the Ti-O bond, and 2) a nearly linear variation, across all the systems studied, of \( \delta_{\text{iso}} \) and \( \delta_{\text{ax}} \) as a function of B-O-B bond asymmetry. We have shown that the anisotropy and linear variation arise from large paramagnetic contributions to \( \sigma_{zx} \) and \( \sigma_{yy} \) due to virtual transitions between O(2p) and unoccupied B(nd) states. A qualitative explanation of the anisotropy was given and then confirmed by calculations for a fake material with no d-states.

We have shown that O NMR chemical shifts are a sensitive indicator of the local structure in perovskites with transition metal B-site atoms, due to covalent O(2p)-B(nd) interactions. This in-
icates that $^{17}$O NMR spectroscopy, coupled with first principles calculations, can be an especially useful tool to study the local structure in complex perovskite alloys.
CHAPTER 7

First-principles calculations of $^{17}\text{O}$ NMR chemical shielding

in Pb(Zr$_{1/2}$Ti$_{1/2}$)O$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$: linear dependence on transition-metal/oxygen bond lengths

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7.1 Introduction

High performance solid solution ferroelectrics, based on the ideal ABO$_3$ perovskite structure, are widely used in technological applications such as ultrasonic transducers, sensors, actuators,
and thin film applications [1, 107]. The strong electromechanical coupling in these materials is related to a balance of competing instabilities, such as cation off-centerings and oxygen octahedral rotations. The perovskite structure offers many ways to fine tune these interactions through chemical substitutions, such as alloying on the A and/or B sites, and through epitaxial control in layered and thin film geometries [107].

Solid state nuclear magnetic resonance (NMR) has increasingly been used to study the local structure and dynamics of these complex perovskites [4, 6, 58, 85]. NMR spectra of a target nucleus are largely determined by the coupling of its magnetic dipole and electric quadrupole moments with the local magnetic field and electric field gradient, respectively. The interpretation of NMR spectra in complex solid solution perovskites is complicated by the presence of broad spectral features due to disorder. First-principles calculations of electric field gradient [89] and chemical shielding (Chapter 6) tensors can play an important role interpreting NMR spectra in these materials.

Previously we demonstrated a near linear dependence of the chemical shielding tensor $\sigma$ on the oxygen nearest neighbor B-O bond distance $r_s$ for the prototypical perovskites BaTiO$_3$ (BT), SrTiO$_3$ (ST), PbTiO$_3$ (PT), and PbZrO$_3$ (PZ) (Chapter 6). The linear dependence was shown to arise from large paramagnetic contributions to $\sigma_{xx}$ and $\sigma_{yy}$ principal values (our convention identifies the "zz" principal axis as that most nearly parallel to the B-O-B bond direction), due to virtual transitions between O(2p) and unoccupied B(nd) states. This linear variation is confirmed here for two complex perovskite solid solutions, PZT and PMN.

First-principles chemical shielding calculations have traditionally been done with the embedded cluster approach, using standard quantum chemistry methods [28–30] with gaussian type orbitals (GTO). More recently, the planewave based GIPAW method with periodic boundary conditions (PBC) has provided an alternative approach. Relatively few calculations for transition metal oxides have been reported using either technique. Here we use complementary calculations with both methods to cross validate convergence with respect to cluster size and termination effects, basis sets, and the accuracy of pseudopotentials (PSPs).
Quantum-chemistry methods can calculate chemical shielding tensors for embedded clusters, using a range of approximations, from Hartree Fock and density functional theory (DFT) with semilocal or hybrid exchange-correlation functionals, to explicitly correlated methods such Moller-Plesset perturbation theory and coupled cluster approaches [18, 24, 46]. The principal difficulties with the embedded cluster approach are controlling size and basis set convergence. Size effects can be monitored by studying increasingly larger clusters. Long-range electrostatic interactions can be handled by embedding the cluster in large arrays of point charges and eliminating depolarizing fields, as described in Chapter 6. Achieving the basis set limit can be problematic in some cases, because atom-centered GTO’s do not form a complete orthogonal basis. Nevertheless, basis set convergence is generally well controlled through the use of standardized GTO basis sets [33]. The cluster approach becomes inefficient, however, for complex systems, because separate cluster calculations are usually required for each inequivalent target atom.

GIPAW calculations are naturally adapted to ordered crystalline solids, since size convergence is effectively achieved by using primitive unit cells with well-converged $k$-point quadrature grids for Brillouin zone integrations. Disordered solids can be treated using supercells. Planewaves form a complete basis, so convergence to the basis set limit is straightforward. The method applies the projector-augmented-wave (PAW) reconstruction [40] to a conventional PSP calculation to obtain all-electron valence wave functions, which are required for accurate calculations of the chemical shielding. There are two principle issues with the GIPAW method. GIPAW PSPs are more difficult to construct than standard norm-conserving PSPs. To achieve good transferability, they may require multiple partial wave channels and large planewave cutoff energies for some target atoms. The construction of the PAW atomic-like augmentation basis also requires care. To date, GIPAW calculations have been carried out for only a limited number of transition metal oxide systems [47, 108].

PZT is a homovalent mixture of Ti$^{4+}$ and Zr$^{4+}$ transition metal cations, while PMN is a heterovalent 2:1 mixture of the Nb$^{5+}$ transition metal cation and the Mg$^{2+}$ alkaline earth cation. Both embedded cluster and GIPAW calculations were carried out for PZT, while PMN results were
obtained only with the GIPAW method, using PBC. First-principles relaxed structural models were used to simulate PZT and PMN structures.

The remainder of the paper is organized as follows. The theoretical approaches are described in Sec. 7.2. Results and discussion are presented in Secs. 7.3 and 7.4, respectively. We summarize and conclude in Sec. 8.4.

7.2 Theoretical Methods

The chemical shielding tensor \( \sigma \) determines the total magnetic field at an atomic nucleus,

\[
\mathbf{B} = (1 - \hat{\sigma}) \mathbf{B}_{\text{ext}},
\]

where \( \mathbf{B}_{\text{ext}} \) is the external field. For the systems considered here, \( \hat{\sigma} \) is calculated using embedded cluster and GIPAW-PBC methods. The symmetric [20, 21] \( \hat{\sigma} \) tensor is determined by its principal axis components, with isotropic and anisotropic parts, conventionally defined as [23]

\[
\begin{align*}
\sigma_{\text{iso}} &= \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \frac{1}{3} \text{Tr } \hat{\sigma} \\
\sigma_{\text{ax}} &= \frac{1}{6} (2\sigma_{zz} - \sigma_{xx} - \sigma_{yy}) = \frac{1}{2} (\sigma_{zz} - \sigma_{\text{iso}}) \\
\sigma_{\text{aniso}} &= \frac{1}{2} (\sigma_{yy} - \sigma_{xx})
\end{align*}
\]

As mentioned, our convention for the perovskite structure identifies the "zz" principal axis as that most nearly parallel to the B-O-B bond direction. NMR measurements of \( \sigma \) are usually reported with respect to a reference material, where the chemical shift tensor \( \delta \) is defined as [24]

\[
\delta = -(\hat{\sigma} - \sigma_{\text{ref}}),
\]

with corresponding definitions to those in Eq. 7.2. The experimental reference for oxygen is liquid H\(_2\)O.

The theoretical oxygen reference value \( \sigma_{\text{ref}}^{\text{th}} \) is determined from a linear regression of \( \delta_{\text{iso}}^{\text{exp}} \).
versus \( \sigma_{\text{iso}}^{\text{theory}} \) [47, 109]. This yields the relation

\[
\delta^\text{th} = -m(\sigma^\text{th} - \sigma_{\text{ref}}^\text{th}).
\]

(7.4)

Rather than regarding the slope \( m \) as an independent fitting parameter, we set \( m = 1 \), which leaves \( \sigma_{\text{ref}}^\text{th} \) as the only independent parameter. Allowing \( m \) to vary yields fits of similar overall quality, but somewhat distorts chemical shift differences between inequivalent oxygen sites within the same material. Constraining \( m = 1 \) allows better cancellation of errors, due to systematic effects such as the choice of methodological approach or DFT exchange-correlation functional.

### 7.2.1 Embedded cluster calculations

A detailed discussion of this approach is given in Chapters 4 & 6. We briefly summarize some of the key features of this method. With central O atoms, embedded clusters consisted of either 21 “quantum” (QM) atoms, \((A_4B_2O_{15})^{11-}\), or 65 QM atoms, \((A_4B_{10}O_{31})^{51-}\). In these clusters, all QM cation atoms are fully coordinated with QM O atoms. The QM clusters are further surrounded by a large array of point charges, which reproduce the Madelung potential in the QM region [37]. To alleviate artificial polarization of boundary O(2p) states, the nearest-neighbor (nn) and the next-nearest-neighbor cation point charges of boundary O atoms are replaced by “empty” PSPs (ePSPs) [7, 38]. Finally, in non-centrosymmetric clusters, depolarizing electric fields are removed by applying an external electric field (Chapter 4 & 6).

Calculations were performed with the GAUSSIAN computational package [28–30] and the chemical shielding tensor was determined using the continuous set of gauge transformations (CSGT) method [16, 49]. Calculations were done using the DFT hybrid B3LYP [10], as well as generalized gradient approximations (GGA), using the PW91 [50] and PBE [51] forms. Douglas-Kroll-Hess 2nd order scalar relativistic calculations were performed on selected systems. Atom-centered GTO basis functions were associated with all the QM atoms. All-electron treatments were used for the O and Ti atoms, while the other QM atoms were represented using scalar-
relativistic small core (scalar-RSC) PSPs [also called effective core potentials (ECPs)]. The well-converged GTO basis sets and ECPs used for these calculations are described in Chapter 6 and were taken from the EMSL website [33].

7.2.2 GIPAW calculations

<table>
<thead>
<tr>
<th>reference state</th>
<th>$r_c$(au)</th>
<th>reference energies (Ry)</th>
<th>core correction radius (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O $2s^2,2p^4,3d,3s,3p$</td>
<td>1.2,1.2,1.5</td>
<td>*,-0.10,0.10,0.10</td>
<td>0.34</td>
</tr>
<tr>
<td>Ti $3s^2,3p^6,3d^0,4s,4p,4d$</td>
<td>0.9,0.9,0.9</td>
<td>*,-2.73,0.50,0.10</td>
<td>0.53</td>
</tr>
<tr>
<td>Pb $6s^2,6p^0,5d^{10},7s,7p,6d$</td>
<td>2.0,2.4,1.0</td>
<td>*,-1.00,-0.20,-1.80</td>
<td>0.89</td>
</tr>
<tr>
<td>Zr $4s^2,4p^6,4d^0,5s,5p,5d$</td>
<td>1.0,1.2,1.4</td>
<td>*,-2.45,-2.00,-1.37</td>
<td>0.80</td>
</tr>
<tr>
<td>Sr $4s^2,4p^6,4d^0,5s,5p$</td>
<td>1.2,1.3,1.7</td>
<td>*,-1.00,-0.72</td>
<td>0.88</td>
</tr>
<tr>
<td>Ba $5s^2,5p^6,5d,6s,6p$</td>
<td>1.5,1.7,2.0</td>
<td>*,-0.95,-0.90,-1.50</td>
<td>1.19</td>
</tr>
<tr>
<td>Mg $2s^2,2p^6,3d,3s,3p$</td>
<td>0.6,0.6,1.5</td>
<td>*,-0.3,-1.3,0.1</td>
<td>0.30</td>
</tr>
<tr>
<td>Nb $4s^2,4p^6,4d^0,5s,5p,5d$</td>
<td>1.0,1.1,1.3</td>
<td>*,-3.30,-2.70,-1.27</td>
<td>0.80</td>
</tr>
<tr>
<td>K $3s^2,3p^6,4d^0,4s,4p$</td>
<td>1.4,1.5,1.5</td>
<td>*,-1.50,-0.80</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Calculations with PBC used the GIPAW functionality of the QuantumESPRESSO (QE) code [41]. These calculations are done in two steps. A standard ground state norm-conserving PSP calculation is first performed. This is followed by a linear response calculation in the presence of an external magnetic field. The linear response calculation uses all-electron like valence wave functions, which are represented by planewaves, modified near the nuclei by atomic-like PAW augmentation basis functions. The PAW basis functions are constructed when the PSP is generated, as further discussed below. Calculations reported below used well converged Monkhorst-Pack [110] Brillouin zone $k$-point sampling, e.g. $6\times6\times6$ for the prototypical perovskites ST, BT, and PT. Unless otherwise specified, the PBE GGA functional was used in all QE calculations.

All PSPs were constructed using the “ldl” PSP generation code (distributed with QE). All norm-conserving PSPs were scalar relativistic Troullier-Martins [111] type. Table 7.1 shows the construction parameters used for all PSPs employed in this chapter. The local channel is indicated by boldface type. States that are in italics were generated using a Hamann type [112] reference
state. The $r_c$'s correspond to the $s$, $p$, and $d$ channels respectively. The next column shows the PSP reference energies for the $s$, $p$, and $d$ channels. The symbol '*' indicates that the corresponding all-electron eigenvalue was used for this state. It should be noted that these parameters are for the PSP projectors used in the ground state self-consistent total-energy calculations. Parallel to the PSP construction, a second atomic calculation is performed to generate the required GIPAW augmentation basis functions, consisting of all-electron and pseudo partial wave radial functions. The number of GIPAW angular momentum channels was the same as for the PSPs. For all except Pb, O, and K, the augmentation basis functions were generated using the corresponding all-electron eigenvalues (n.b., the $\text{Ti}^{4+}$ 4$d$ state is bound, for example), rather than the values in Table 7.1. For Pb, O, and K, the values in Table 7.1 were used. except for the Pb 7$s$, which used the all-electron eigenvalue. The final column shows the non-linear core-correction radius for each potential. A conservative 350 Ry energy cutoff was used. This could have been reduced by using larger $r_c$'s for the metal PSPs. The 350 Ry energy cutoff, while high, was easily tractable for all systems studied in this chapter. This cutoff yields chemical shieldings to within about 1 ppm, as indicated by test calculations with other settings.

7.2.3 Comparison of methods

Table 7.2 shows the comparison between the GIPAW and cluster approach for the TiO$_2$ molecule, the rutile crystalline solid, as well as some results for prototypical perovskites. Where available, published GIPAW results from Ref. [47] are also given for comparison.

TiO$_2$ molecule calculations were for a Ti-O bond length of 1.651 Å and a O-Ti-O angle of 114.2°. With PBC-GIPAW, a $22\times24\times28$ Bohr supercell was used. The Gaussian calculation was for the isolated molecule and used a basis set of cc-pwCVQZ-DK and IGLO-III for Ti and O, respectively. The experimental rutile structure was used for solid TiO$_2$ [113]. The PBC-GIPAW calculation used a $k$-point sampling of $4\times4\times6$. The cluster method used a O$_{77}$Ti$_{22}$ QM cluster with cc-pwCVTZ-DK and 6-311G(2d,p) basis sets for the inner 3 and outer 19 Ti atoms,
TABLE 7.2: Comparison of chemical shielding results, using embedded clusters and GIPAW-PBC from QE and [47]. The principle values of the oxygen chemical shielding tensor are presented for the TiO$_2$ molecule and rutile, cubic ST, cubic BT, and tetragonal PT. All values are from GGA calculations. Embedded cluster results are labeled as C-$n$, where $n$ is the number of QM atoms in the cluster. The GIPAW-PBC and C-65 calculations were done with relativistic PBE, while the C-21 calculations were done with non-relativistic PW91.

<table>
<thead>
<tr>
<th>TiO$_2$ (molecule)</th>
<th>$\sigma_{xx}$</th>
<th>$\sigma_{yy}$</th>
<th>$\sigma_{zz}$</th>
<th>$\sigma_{x\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td>-1803</td>
<td>-801</td>
<td>148</td>
<td>-819</td>
</tr>
<tr>
<td>GIPAW</td>
<td>-1826</td>
<td>-811</td>
<td>146</td>
<td>-830</td>
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<tr>
<td>TiO$_2$ (rutile)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C-99</td>
<td>-499</td>
<td>-380</td>
<td>-306</td>
<td>-395</td>
</tr>
<tr>
<td>GIPAW</td>
<td>-483</td>
<td>-380</td>
<td>-296</td>
<td>-386</td>
</tr>
<tr>
<td>SrTiO$_3$ (cubic)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C-21</td>
<td>-353</td>
<td>-353</td>
<td>46</td>
<td>-220</td>
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<tr>
<td>C-65</td>
<td>-403</td>
<td>-403</td>
<td>27</td>
<td>-260</td>
</tr>
<tr>
<td>GIPAW</td>
<td>-429</td>
<td>-429</td>
<td>7</td>
<td>$-284 \pm -287$</td>
</tr>
<tr>
<td>BaTiO$_3$ (cubic)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-21</td>
<td>-414</td>
<td>-414</td>
<td>49</td>
<td>-260</td>
</tr>
<tr>
<td>C-65</td>
<td>-483</td>
<td>-483</td>
<td>22</td>
<td>-315</td>
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<tr>
<td>GIPAW</td>
<td>-529</td>
<td>-529</td>
<td>-31</td>
<td>$-363 \pm -379$</td>
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<tr>
<td>PbTiO$_3$, axial O (P4mm)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>C-21</td>
<td>-562</td>
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<td>123</td>
<td>-334</td>
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<td>PbTiO$_3$, equatorial O (P4mm)</td>
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<td>-228</td>
<td>-32</td>
<td>-182</td>
</tr>
<tr>
<td>C-65</td>
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<td>-277</td>
<td>-35</td>
<td>-226</td>
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<tr>
<td>GIPAW</td>
<td>-398</td>
<td>-284</td>
<td>-23</td>
<td>-235</td>
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</table>
TABLE 7.3: The derived theoretical oxygen reference value, $\sigma^{17}_\text{ref}$, is used to determine theoretical isotropic chemical shifts from the corresponding calculated isotropic chemical shielding values. Experimental chemical shifts are shown for comparison. The values of $\sigma^{17}_\text{ref}$ are shown in the third row from the bottom of this table. The RMS error and maximum deviation of the calculated shifts, compared to experiment, are also shown. Calculated cluster results (21 and 65 QM atoms) with B3LYP and PW91 exchange-correlation are shown together with GIPAW-PBC with PBE exchange-correlation. (PZ experimental chemical shift site assignments were corrected in Chapter 6 and are used here.)

<table>
<thead>
<tr>
<th></th>
<th>E$\text{exp}^a$</th>
<th>Cluster</th>
<th>PBC-GIPA</th>
<th>PBE-REL</th>
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<tr>
<td></td>
<td></td>
<td>B3LYP</td>
<td>PW91</td>
<td></td>
</tr>
<tr>
<td>ST (cubic)</td>
<td>467 ± 5</td>
<td>491</td>
<td>477</td>
<td>494</td>
</tr>
<tr>
<td>BT (cubic)</td>
<td>546 ± 5</td>
<td>536</td>
<td>537</td>
<td>534</td>
</tr>
<tr>
<td>BT (P4mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{ax}$</td>
<td>570 ± 5</td>
<td>591</td>
<td>571</td>
<td>579</td>
</tr>
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<td>$O_{eq}$</td>
<td>520 ± 5</td>
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<td>$\Delta(O_{ax} - O_{eq})$</td>
<td>50</td>
<td>76</td>
<td>56</td>
<td>44</td>
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<td>PT (P4mm)</td>
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<td></td>
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<tr>
<td>$O_{ax}$</td>
<td>647 ± 2</td>
<td>644</td>
<td>644</td>
<td>608</td>
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<td>$O_{eq}$</td>
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<td>152</td>
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<td>PZ (Pbam)</td>
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<td>O1-4g</td>
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<td>O2-8i</td>
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<td>O3-4f</td>
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<td>309</td>
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<td>O4-4e</td>
<td>408 ± 2</td>
<td>392</td>
<td>399</td>
<td>415</td>
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<td>$\Delta(O4 - O1)$</td>
<td>43</td>
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<td>31</td>
<td>60</td>
</tr>
<tr>
<td>$\Delta(O4 - O1')$</td>
<td>57</td>
<td>47</td>
<td>43</td>
<td>79</td>
</tr>
<tr>
<td>$\Delta(O4 - O2)$</td>
<td>52</td>
<td>38</td>
<td>35</td>
<td>66</td>
</tr>
<tr>
<td>$\Delta(O4 - O3)$</td>
<td>79</td>
<td>68</td>
<td>63</td>
<td>105</td>
</tr>
</tbody>
</table>

| $\sigma^{17}_\text{ref}$ | 287.5$^e$ | 292.82 | 238 | 274.71 | 217.25 | 206.75 | 211.91 | 215.83 |
| RMS error | 11.89 | 6.98 | 16.02 | 23.2 | 28.43 | 20.16 | 25.7 |
| Max Dev$^c$ | 24.48 | 9.73 | 38.62 | 37.75 | 45.83 | 40.67 |         |

|          | 21 | 65 | 21 | 65 |         |         |

---

*a* ST and BT experimental chemical shift values are from Ref. [85] and the PT and PZ experimental chemical shift values are from Ref. [4].

*b* Ref. [47] determined $\sigma_{\text{exp}}$ using the experimental structure.

*c* Ref. [47] determined $\sigma_{\text{exp}}$ using the relaxed structure.

*d* The $^{17}$O experimental chemical shielding reference is liquid water, $\sigma_{\text{water}}^{17}(O) = 287.5$ ppm [152].

*e* Max Dev = max(abs($\delta^{\text{theory}} - \delta^{\text{exp}}$))
respectively; IGLO-III and IGLO-II basis sets were used for the inner 15 and outer 52 O atoms, respectively. (Embedding with ePSPs and point charges was done as described above.)

Calculations for the prototypical perovskites in Table 7.2 used the experimental structures as described in Chapter 6. PBC-GIPAW used a $k$-point sampling of $6 \times 6 \times 6$. Embedded clusters were constructed as above (Section 8.2.1), and results are given for 21 and 65 QM atom clusters. The 21 QM atom cluster results are from non-relativistic calculations using the PW91 DFT functional. The 65 QM atom clusters are from scalar relativistic PBE calculations. Differences between PW91 and PBE (not shown in the Table) and relativistic effects are small, as expected. Tests on the 65 QM atom ST cluster show that non-relativistic PBE produced $\sigma_{x,y}$ and $\sigma_{zz}$ values that are $\simeq 6$ and 1.5 ppm more positive, respectively, than PW91. Adding scalar-relativistic effects changed $\sigma_{x,y}$ and $\sigma_{zz}$ by $\simeq +12$ and +3 ppm, respectively, independent of the GGA functional. These effects are negligible for the corresponding chemical shifts, as expected, due to cancellation of errors.

The ST and PT 65 QM atom relativistic PBE $\sigma_{x,y}$ and $\sigma_{zz}$ are in good agreement with PBC values, differing at most by $\simeq 33$ and 20 ppm respectively. Isotropic values for both systems are within 24 ppm of PBC-GIPAW. A larger discrepancy is seen in BT, where the cluster values are rigidly shifted by about +50 ppm. Size effects between the 21 and 65 QM atom results are evident in the table. The 21 QM atom values are more shielded [i.e., more positive (see Eq. (7.1))] than either the 65 QM atom values or the PBC methods. Rigidly shifting all 21 QM atom brings these into better agreement, indicating good cancellation of errors. This is evident in the chemical shifts shown in Table 7.3 in the next section, where 21 and 65 QM atom clusters are seen to give nearly identical chemicals shifts.

These results demonstrate that the embedded cluster and PBC-GIPAW approaches produce comparable agreement with measured isotropic chemical shifts, regardless of cluster size and methodology. Differences due to cluster size, DFT functionals, relativistic effects, and PSPs largely cancel in the chemical shifts, i.e., they are absorbed in the constant chemical shielding reference value $\sigma_{\text{ref.}}^{\text{th.}}$. 
7.3 Results

In this section, we first describe the calculation of the theoretical oxygen chemical shielding reference $\sigma_{\text{ref}}^{\text{th}}$ [Eq. (7.4)]. As mentioned, this is done using linear regression of the calculated chemical shieldings with the corresponding measured chemical shifts, where available [47, 109]. We next present calculated $^{17}$O chemical shifts for two perovskite-based B-site alloys, PZT and PMN, using the derived values of $\sigma_{\text{ref}}^{\text{th}}$.

7.3.1 Determination of the theoretical $^{17}$O chemical shielding reference

A linear regression was separately evaluated for the PBC and embedded cluster calculations [47, 109]. Additionally for the clusters, separate regressions were performed for different cluster sizes and DFT functionals. Table 7.3 shows derived $\sigma_{\text{ref}}^{\text{th}}$ values for each case, along with the rms error and maximum deviation in the isotropic chemical shifts. The table compares the resulting calculated isotropic chemical shifts to the measured values. As in Chapter 6, experimental structures were used for all systems except PZ. For PZ, experimental lattice parameters from neutron scattering measurements were used together with internal coordinates determined from first-principles calculations [84]. Calculated cluster results (21 an 65 QM atoms) with B3LYP and PW91 exchange-correlation are shown together with GIPAW-PBC with PBE exchange-correlation. The last column shows other GIPAW results, where available. For the 65 QM clusters, $\sigma_{\text{ref}}^{\text{th}}$ is derived from a more limited set of calculations, as shown in the Table. For comparison, the effect of this limited sampling is also shown for PBC-GIPAW and is seen to be only a few ppm. B3LYP results are seen to give slightly better agreement with experiment. Using the same exchange-correlation treatment, both the 21 and 65 atom QM clusters are seen to give nearly identical chemical shifts. The values of $\sigma_{\text{ref}}^{\text{th}}$ in Table 7.3 are used below to determine the theoretical chemical shifts for PZT and PMN in Tables 7.4 and 7.5. Given the small difference between the PW91 and PBE GGA functionals and cancellation effects in chemical shifts, both PW91 and PBE are labeled as GGA in all further results below.
7.3.2 Results for Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_3$ (PZT) and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PMN)

PZT is a homovalent mixture of Ti$^{4+}$ and Zr$^{4+}$ transition metal cations, while Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ (PMN) is a heterovalent 2:1 mixture of the Nb$^{5+}$ transition metal cation and the Mg$^{2+}$ alkaline earth cation. Both embedded cluster and GIPAW calculations were carried out for PZT, while PMN results were obtained only with the GIPAW method, using PBC.

Disordered PZT 50/50 was modeled using first-principles relaxed structures [89] with different imposed B-site ordering and symmetry: i) [001] ordering parallel to the ferroelectric polarization, with tetragonal P4mm symmetry (a x a x 2c; c/a = 1.045); ii) [001] ordering perpendicular to the [100] ferroelectric polarization, with orthorhombic P2mm symmetry (a' x a x 2a; a'/a = 1.04); iii) [111] ordering (rocksalt B sublattice) parallel to the ferroelectric polarization, with R3m symmetry. Theoretical PZT isotropic, axial, and anisotropic chemical shifts are summarized in Table 7.4. [As mentioned, the axial and anisotropic components in Eq. (7.2) were calculated using the convention that the “xz” principal axis is that most nearly parallel to the B-O-B bond direction of the target O atom.] For comparison, results for ST, BT, PT and PZ are reproduced from Table 7.3. For each inequivalent target O atom in the above structural models, the corresponding 21 QM atom embedded cluster was used to calculate the chemical shielding tensor with both B3LYP and GGA exchange-correlation. Results from PBC-GIPAW with GGA exchange-correlation are also shown. Chemical shifts were determined using the corresponding values of $\sigma_{ref}^{th}$ in Table 7.3. The GGA 21 QM atom embedded cluster and PBC-GIPAW RMS errors differ by 4 ppm. As seen in Tables 7.3, the 21 QM atom embedded cluster chemical shifts are also in excellent agreement with those from the larger 65 QM atom cluster.

PMN PBC-GIPAW calculations were based on a low symmetry (3 x 2 x 2) 60-atom perovskite supercell structure with relaxed internal coordinates [114], with B-site cations arranged according to the random-site model [115]. X-ray patterns of well-annealed PMN samples indicate a homogeneous average structure, which exhibits rocksalt-like 1:1 B-site ordering, which is well described by the random-site model. Locally, the random-site model corresponds to B-site...
TABLE 7.4: Calculated oxygen isotropic, axial and anisotropic components (ppm) of the chemical shift tensor for three PZT 50/50 structural models from Ref. [89]. The notation B--O--B indicates O atoms with two equidistant nn B atoms, and B--O--B indicates an O atom with one short and one long nn B bond. For cluster-GGA results, numbers in parenthesis show the difference with GIPAW. For cluster-B3LYP results, numbers in square brackets show the difference with cluster-GGA values. For cases where $\delta_{\text{aniso}} = 0$ by symmetry, this is indicated by a dash.

<table>
<thead>
<tr>
<th></th>
<th>Cluster $\delta_{\text{iso}}$</th>
<th>B3LYP</th>
<th>GGA</th>
<th>Cluster $\delta_{\text{ax}}$</th>
<th>B3LYP</th>
<th>GGA</th>
<th>Cluster $\delta_{\text{aniso}}$</th>
<th>B3LYP</th>
<th>GGA</th>
</tr>
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<tbody>
<tr>
<td>ST (cubic)</td>
<td>491 [-3]</td>
<td>494</td>
<td>-144</td>
<td>-133</td>
<td>-145</td>
<td>-142</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BT (P4mm)</td>
<td>OAX (Ti--O--Ti)</td>
<td>591</td>
<td>-207</td>
<td>-183</td>
<td>-186</td>
<td>-184</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>OEQ (Ti--O--Ti)</td>
<td>515</td>
<td>-155</td>
<td>-140</td>
<td>-147</td>
<td>-145</td>
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<td>OAX (Ti--O--Ti)</td>
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<td>-236</td>
<td>-234</td>
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<tr>
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<td>OEQ (Ti--O--Ti)</td>
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<td>O1 (Zr--O--Zr)</td>
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<td>O3 (Zr--O--Ti)</td>
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<td>-118</td>
<td>-135</td>
<td>-133</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>O4 (Ti--O--Ti)</td>
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<td>-86</td>
<td>-84</td>
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<td></td>
<td>O6 (Ti--O--Zr)</td>
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<td>-130</td>
<td>-166</td>
<td>-164</td>
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<td></td>
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<tr>
<td>PZT (P2mm)</td>
<td>O1 (Zr--O--Zr)</td>
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<td>-80</td>
<td>-74</td>
<td>-96</td>
<td>-94</td>
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<tr>
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<td>O2 (Zr--O--Zr)</td>
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<td>-118</td>
<td>-137</td>
<td>-135</td>
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<tr>
<td></td>
<td>O4 (Ti--O--Ti)</td>
<td>408</td>
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<td>-57</td>
<td>-74</td>
<td>-72</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>O5 (Ti--O--Ti)</td>
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<td>-232</td>
<td>-238</td>
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<td>400</td>
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<td>-72</td>
<td>-92</td>
<td>-90</td>
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<tr>
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<td>394</td>
<td>-90</td>
<td>-84</td>
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<td>-105</td>
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<tr>
<td></td>
<td>O6 (Ti--O--Zr)</td>
<td>466</td>
<td>-127</td>
<td>-114</td>
<td>-135</td>
<td>-133</td>
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</tr>
</tbody>
</table>

Note: The notation B--O--B indicates O atoms with two equidistant nn B atoms, and B--O--B indicates an O atom with one short and one long nn B bond. For cluster-GGA results, numbers in parenthesis show the difference with GIPAW. For cluster-B3LYP results, numbers in square brackets show the difference with cluster-GGA values. For cases where $\delta_{\text{aniso}} = 0$ by symmetry, this is indicated by a dash.
planes, alternating between pure Nb and mixed Nb/Mg layers. Thus there are twice as many Nb-O-Mg as Nb-O-Nb O-sites in the 60-atom supercell, since the Mg atoms all reside in the mixed planes. Similarly, there are no Mg-O-Mg O-sites. Unlike earlier models, the random-site model satisfies charge neutrality locally. The previously accepted space-charge model was based on the apparent inability to fully anneal samples [115]. The 60-atom perovskite supercell structure [114], used in the present calculations, is consistent with the random-site model, Grinberg et al. [114] found good agreement between this relaxed 60-atom supercell structure and pair distribution functions obtained by neutron scattering experiments [116]. This indicates that this structural model reasonably represents the local structure in PMN. Calculations for PMN were done only with PBC-GIPAW, and the results are shown in Table 7.5.

7.4 Discussion

As previously noted in Chapter 6, there is a large anisotropy between the $\sigma_{x,y}$ and $\sigma_{zz}$ principal values in Table 7.2. The $\sigma_{x,y}$ principal values are large and negative (deshielded), while $\sigma_{zz}$ values tend to be considerably smaller and positive (shielded). (As mentioned, the "zz" principal axis is identified as that most closely aligned with the B-O-B bond direction of the target O atom.) The present calculations show that this anisotropy is also found in PZT and PMN and is reflected in the large $\delta_{xx}$ values (Eq. 7.2) in Tables 7.4 and 7.5.

As shown in Chapter 6 for prototypical perovskites, the large $\delta_{xx}$ values are due to paramagnetic contributions to $\sigma_{x,y}$ from virtual transitions between O(2p) and unoccupied B(nd) states. The p-d hybridization contributes predominantly to $\sigma_{x,y}$, due to O atoms having only two nearest neighbors in perovskites, with linearly arranged B-O-B structural units. As the B-O-B bond distances vary, large variations in the chemical shielding can occur, resulting in a strong dependence on $r_b$. We find a similar dependence for the PZT and PMN alloy systems.
7.4.1 PZT

Figure 7.1 plots PZT isotropic and axial chemical shifts as a function of $r_s$, the shortest B-O bond length of the targeted O atom. The B3LYP 21 QM atom cluster results from Table 7.4 are plotted. For comparison, results for ST, BT, PT, and PZ and from experiment are also shown Chapter 6. The dashed straight lines are the linear fits to the calculated results for these prototypical perovskites, taken from Chapter 6. A plot of PBC-GIPAW results from Table 7.4 (not shown) is very similar, which is consistent with the generally good agreement of the chemical shift results in the Table between the two calculational approaches. A nearly linear dependence on $r_s$ (with slope $\sim 850 \text{ ppm/Å}$) is seen in both $\delta_{iso}$ and $\delta_{ax}$, across all the systems studied. The axial shift is plotted as $2\delta_{ax} = \delta_{zz} - \delta_{iso}$ (Eq. 7.2) to emphasize that the linear dependence is largely due to $\delta_{x,y}$, while $\delta_{zz}$ has a much weaker dependence on $r_s$, as previously noted for the prototypical perovskites (Chapter 6). As seen in the figure, the calculated PZT 50/50 results follow the same trends as in Chapter 6.

Pb(Zr$_{1-x}$Ti$_x$)O$_3$ NMR $^{17}\text{O}$ magic angle spinning (MAS) central peak spectra were presented by Baldwin et al. [4] for a range of concentrations $x$. Tabulated chemical shifts were given only for the endpoint PT and PZ compounds (reproduced here in Table 7.3), whose spectra consist of well-defined narrow peaks. MAS removes broadening due to chemical shift anisotropy in powder samples, but only partly averages second-order quadrupolar broadening. The narrow peaks in the endpoint PT and PZ compounds indicate that electric field gradients (EFGs) at the $^{17}\text{O}$ nuclei are small [4]. This is consistent with first-principles calculations of O EFGs [84, 89]. Indeed, the $^{17}\text{O}$ peak positions are within a few ppm of the experimental isotropic chemical shifts [4]. There are two inequivalent O atoms in PT, two “equatorial” O$_{eq}$ (which has two equidistant nn Ti atom) and one “axial” O$_{ax}$ atom (which has one short and one long Ti-O bond). A narrow peak at 443 ppm has twice the (integrated) relative intensity of the peak at 647 ppm, and these were assigned to the O$_{eq}$ and O$_{ax}$ atoms, respectively. These are in good agreement with the calculated results in Table 7.3. The B3LYP calculation accurately reproduces this splitting, while GGA underestimates
it by ≈ 45 ppm. In PZ, there are five inequivalent O sites, which corresponds to five MAS peaks, centered near 350 ppm, within ± ~ 40 ppm. Measured and calculated values in Table 7.3 are in good agreement.

![Graph](image)

**FIG. 7.1:** Calculated PZT oxygen isotropic $\delta_{iso}$ and axial $2\delta_{ax}$ chemical shifts (B3LYP 21 QM atom cluster values from Tables 7.4), plotted as a function of $r_s$, the shortest B-O bond length of the targeted O atom. For comparison, calculated results for ST, BT, PT, and PZ and from experiment (hollow symbols) are also shown in Chapter 6. The dashed straight lines are linear fits to calculated values for ST, BT, PT, and PZ from Chapter 6.

At intermediate Ti and Zr concentrations, the spectra in Fig. 3 of Ref. [4] show that only a few of the narrow endpoint peaks persist. As Zr is added to PT, the narrow 647 ppm PT peak decreases quickly in intensity. It can no longer be observed in the $x = 0.55$ sample. A broad feature, between about 350 and 450 ppm is fully developed near $x = 0.50$, with narrower embedded features at ≈ 370 and 430 ppm. This broad feature reflects a distribution of inequivalent O-sites in the disordered PZT solid solution samples. The 430 ppm feature, which is close to the PT $O_{eq}$ 447 ppm peak, is observed to persist down to 25% Ti concentration. Baldwin *et al.* [4] assign the 430 ppm feature to a site similar to that of the PT $O_{eq}$ atom, *i.e.* a locally Ti-$O_{eq}$-Ti (undimerized)
chain-like configuration. They further suggest that this peak could indicate Ti clustering on a spatial scale of at least two unit cells in PZT.

Our results suggest an alternative explanation for the persistence of the observed 430 ppm feature. Our calculations show similar chemical shifts for a range of B-O-B' environments, with \( r_s \) ranging between \( \sim 2.0 - 2.1 \) Å in all the PZT 50/50 structural models, as seen in Table 7.4 and Fig. 7.1. Thus Ti clustering need not be invoked to explain the persistence of the 430 ppm feature in the measured spectra.

The apparent disappearance, at intermediate concentrations, of the 647 ppm peak does, however, indicate a reduced occurrence of a PT-like O\(_{\text{ox}}\) site with a short 1.77 Å Ti-O bond. We find such a site only in the relaxed P4\(_{\text{mmm}}\) and P2\(_{\text{mmm}}\) PZT 50/50 simulations. The P4\(_{\text{mmm}}\) and P2\(_{\text{mmm}}\) models have [100] type B-site ordering. The absence of the 647 ppm peak in the measurements indicates that local occurrences of [100] type B-site ordering are rare. Instead, the lack of the 647 ppm peak in our R3m PZT 50/50 simulations suggests that local rocksalt-like B-site ordering is more prevalent in disordered PZT. This conclusion is also supported by the R3m structural model having the lowest total energy of all the structural models by \( \sim 23 \) mRy [89]. Moreover, the calculated Ti EFG's for 50/50 R3m were significantly smaller and in better agreement with measured values, than the other B-site orderings [89].

Baldwin et al. [4] also remark a narrow 287 ppm peak that appears in their \( x = 0.48 \) sample. This peak is broader in \( x = 0.55 \) and \( x = 0.25 \) samples and is absent in PZ. These authors note that \( x = 0.48 \) is the composition corresponding to the morphotropic phase boundary (MPB) and conjecture that the 287 ppm peak evidences a new oxygen environment in a distinct crystalline monoclinic phase, which has been suggested to bridge the MPB [4]. They suggest that the new environment at \( x = 0.48 \) is a Ti-O-Zr site, which becomes ordered in the crystallographic sense as the long-range order of the monoclinic phase is established. As indicated by Fig. 7.1, isotropic chemical shifts near 287 ppm are associated with large \( r_s \approx 2.15 \) Å. As most Zr-O bond lengths are larger than those of Ti-O in the PZ and PZT 50/50 structural models, the 287 ppm feature could also be attributed to Zr-O-Zr sites with bond lengths distributed near \( \sim 2.15 \) Å.
FIG. 7.2: GIPAW calculated PMN oxygen isotropic $\delta_{\text{iso}}$ and axial $2\delta_{\text{ax}}$ chemical shifts, plotted as a function of $r_s$. The PMN chemical shifts are from Table 7.5, and the symbols indicate the B-O-B' configuration, using the convention in that table. For comparison, results for cubic and tetragonal KNbO$_3$ are also shown. The dashed lines are the same as that in Fig. 7.1. As plotted, the $r_s$ values have been increased by 0.12 Å (see text). The unshifted values are shown in the inset.

### 7.4.2 PMN

PMN, by contrast with PZT, is a heterovalent 2:1 mixture of the Nb$^{5+}$ transition metal cation and the Mg$^{2+}$ alkaline earth cation. Figure 7.2 plots Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) isotropic and axial chemical shifts (GIPAW results from Table 7.5) as a function of $r_s$, the shortest B-O bond length of the targeted O atom. As plotted, the PMN $r_s$ values, have been increased by 0.12 Å for both $\delta_{\text{iso}}$ and $\delta_{\text{ax}}$, as further discussed below. The unshifted values are plotted in the inset. The dashed lines are the same as that in Fig. 7.1. With the 0.12 Å rigid shift for all O-sites, the PMN chemical shifts are seen to follow the same linear trend as in the homovalent B-site systems.
in Fig. 7.1. For Nb-O-Mg coordinated O-atoms, $r_s$ is taken as the Nb-O bond length, since the hybridization mechanism does not apply to Mg, which has no low-lying unoccupied d-states. (As mentioned, the linear dependence is due to paramagnetic contributions to $\delta_{xy}$ from virtual transitions between O(2p) and unoccupied B(nd) states.) We are not aware of published NMR $^{17}$O spectra for PMN.

Although the linear dependence of $\delta_{iso}$ and $\delta_{ax}$ in Fig. 7.2 have the same slope as the homovalent B-site systems, a 0.12 Å $r_s$ offset is needed for the PMN values to fall on the same line. As mentioned, the linear dependence reflects variations in the magnitude of the paramagnetic O(2p)-Nb(4d) hybridization contributions to the $\delta_{x,y}$ principal values. This indicates that the effective $r_s$ is controlled by the spatial extent of the paramagnetic screening currents. The Nb$^{5+}$ cation could be expected to modify the spatial extent of these currents, compared to the B$^{4+}$ cations in the homovalent systems, due to the larger electrostatic attraction of the Nb$^{5+}$ cation. The 0.12 Å offset in PMN renormalizes, in effect, the strength of the O(2p)-Nb(4d) hybridization. This observation would appear to indicate that for these systems the $r_s$-dependence of $\delta_{x,y}$ is given by $\delta_{x,y} = m(r_s - r_0)$. where the slope $m$ is nearly the same for all transition-metal coordinated O atoms in perovskites, while the intercept $r_0$ depends on other factors, such as the ionic charge of the nearest neighbor cation. To further examine this, we performed GIPAW calculations for cubic and tetragonal KNbO$_3$[117], which are also plotted in Fig. 7.2. While the tetragonal axial O values (short Nb-O $r_s$) are consistent with the linear trend, the KNbO$_3$ tetragonal equatorial and cubic O results (two equidistant Nb-O bonds) show significant deviations. [Similar deviations occur in Fig. 7.1 for the tetragonal equatorial and cubic O BT results. We note that both K and Ba have larger crystalline ionic Shannon [118] radii, 1.78 and 1.75 Å, respectively, than Sr or Pb, 1.58 and 1.63 Å, respectively.] Smaller deviations are also seen in the two largest $r_s$ values for the PMN oxygen atoms with two nearly equidistant Nb atoms, but for somewhat larger values of $r_s$ than in KNbO$_3$. In the case of heterovalent B-site perovskites, the covalency of A-site atoms could also be important, as indicated by the smaller deviations, for long $r_s$ in PMN compared to KNbO$_3$. These observations warrant further investigation to clarify these issues.
PMN is an end-point of the solid-solution series \((x)\text{PbTiO}_3 - (1 - x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\) (PMN-PT). In the 60-atom PMN structural model, there are no Nb-O bonds as small as the short Ti-O\(_{ax}\) bond \(\simeq 1.7\) Å in PT, which is associated with its high degree of tetragonality \((c/a = 1.065)\). This short bond corresponds to the large \(\delta_{\text{iso}} \simeq 640\) ppm, which is also seen in the P4\(_{mm}\) and P2\(_{mm}\) PZT structural models, both of which also show a high degree of tetragonality. The tetragonality of PMN-PT decreases as the Ti concentration is reduced from PT-rich compositions, and the average symmetry switches from tetragonal to rhombohedral at the morphotropic phase boundary (MPB) \(x \simeq 0.35\). The largest piezoelectric response is typically achieved at concentrations near the MPB \([76]\). Polarization rotation has been proposed as the origin of the large piezoelectric response at the MPB, via intermediate monoclinic phases \([119-121]\), where the tetragonality increases as the polarization rotates from [111] to [100] (pseudocubic) directions, with applied electric field along a pseudocubic axis. Increased tetragonality, compared to PT, has been seen in some other perovskite based solid solutions, such as some Bi based materials \([122, 123]\). The present calculations indicate that \(^{17}\)O NMR chemical shift measurements could be a useful probe in this regard, as increased tetragonality is accompanied by shortened transition-metal/oxygen bonds.

### 7.5 Summary

First-principles oxygen NMR chemical shift tensors were calculated for PZT and PMN, which are representative, respectively, of homovalent and heterovalent perovskite-structure B-site alloys. Quantum chemistry methods for embedded clusters and the GIPAW method for periodic boundary conditions were used. Results from both methods are in good agreement for PZT and prototypical perovskites. PMN results were obtained using only GIPAW. Both isotropic and axial chemical shift components were found to vary approximately linearly as a function of the nearest-distance transition-metal/oxygen bond length, \(r_{5}\). Using these results, we argue against Ti clustering in PZT, as conjectured from recent \(^{17}\)O NMR measurements. Our findings indicate that
$^{17}$O NMR measurements, coupled with first-principles calculations, can be an important probe of local structure in complex perovskite solid solutions.
TABLE 7.5: GIPAW calculated oxygen isotropic, axial and anisotropic components (ppm) of the chemical shift tensor for PMN. A 60-atom supercell with relaxed internal coordinates was used [114]. The B-O--B' bond notation is the same as in Table 7.4; bond lengths are categorized as equidistant if they differ by less than 0.05 Å.

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CHAPTER 8

First-principles Ti NMR chemical shift calculations of ferroelectric perovskite oxides

8.1 Introduction

The reversible lattice polarization (ferroelectricity) and strong electro-mechanical coupling (piezoelectricity) of ferroelectric perovskite oxide materials have resulted in these materials becoming key components in many electronic and mechanical devices such as sensors, actuators, and random access memory [1, 2]. Studies have revealed that these macroscopic properties are directly related to the material’s local structure. For example, different amounts of Zr substitution for Ti in Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) (PZT) results in different macroscopic piezoelectric characteristics [2]. However, the exact chemical and structural recipe for achieving the desired strength and sensitivity of these properties is still unknown.

To address this uncertainty, nuclear magnetic resonance (NMR) measurements have been conducted on some ferroelectric perovskite oxide systems. NMR’s ability to determine the elec-
tric field gradient (EFG) and the chemical shielding at a nuclear site makes it an excellent tool for studying the short range chemical order of crystalline solid-state systems. The EFGs experienced by quadrupole nuclei indicate the local symmetry of a crystallographic site, while the chemical shielding tensor $\sigma$, which results from the electronic shielding of the applied magnetic field, uniquely identifies distinct crystallographic sites. Recently, $^{47/49}$Ti EFG measurements were made on single crystals of BaTiO$_3$ and SrTiO$_3$ [124, 125].

In the case of BaTiO$_3$, quite a few experiments have been performed to determine the Ti EFG [124–133] and chemical shifts [126, 128–135] for its various crystallographic phases. The experimental EFG measurements are similar, but various chemical shift measurements differ by approximately 120 ppm. Since the Ti chemical shift is believed to vary with the mean Ti-O bond length [129, 131], this 120 ppm discrepancy adds uncertainty to the understanding of the local structure surrounding the Ti atoms in the various phases of BaTiO$_3$. Either complex dynamics in the crystal structure of BaTiO$_3$, or the enormous challenges associated with Ti NMR, might account for the reported chemical shift discrepancies. The experimental difficulty of Ti NMR results from Ti having two NMR active isotopic forms. Both isotopes have similar gyromagnetic ratios, resulting in similar resonance frequencies, even when large magnetic fields are applied. The NMR spectrum is further complicated by the isotopes having very large electric quadrupole moments: $Q(^{47}$Ti) = $30.2 \times 10^{-30}$m$^2$; $Q(^{49}$Ti) = $24.7 \times 10^{-30}$m$^2$. These quadrupole moments lead to a large splitting of the central $\left(\frac{1}{2}, -\frac{1}{2}\right)$ transition, which manifests itself by broad NMR powder spectra. The combination of the broad spectral peak and similar resonance frequencies leads to an overlap of the $^{47}$Ti and $^{49}$Ti spectra. Additionally, a small signal-to-noise ratio is present in the NMR spectrum because of the low natural abundance of the two isotopes. For these reasons, it is difficult to extract chemical shielding tensors from measured spectra.

Knowledge of the NMR parameters from first-principles quantum mechanical calculations would aid in data analysis and interpretation. To date, $\sigma$(Ti) calculations have been carried out for only a limited number of transition metal oxide systems [47, 108, 136], and no systematic studies have been performed on ferroelectric perovskite oxide materials. Here, we present titanium
NMR chemical shift tensor $\hat{\delta}(\text{Ti})$ ($\hat{\delta}(\text{Ti})$ w.r.t. cubic SrTiO$_3$) from complementary calculations with embedded clusters and periodic boundary conditions (PBC). The embedded cluster calculations used standard quantum chemistry methods. While PBC calculations were performed with the GIPAW method within Quantum Espresso (QE) [5, 41]. Compared to oxygen chemical shifts $\hat{\delta}(\text{O})$ (Chapters 6 & 7), $\hat{\delta}(\text{Ti})$ calculations are more challenging for both approaches. Ti cluster calculations were found to be sensitive to size effects and termination (Chapter 4), while GIPAW results were found to be sensitive to the pseudopotential construction. The two approaches complemented each other in optimizing these factors. We find that the titanium isotropic chemical shift is strongly dependent on the perovskite TiO$_6$ octahedral volume.

The remainder of this chapter is organized as follows. The theoretical approaches are described in Sec. 8.2. Calculated results for the prototypical perovskites CaTiO$_3$ (CT), SrTiO$_3$ (ST), BaTiO$_3$ (BT), and PbTiO$_3$ (PT) as well as the complex perovskite PZT are presented in Sec. 8.3. Additionally, Sec. 8.3 contains the analysis of the calculated results along with a comparison with experimental measurements (where available). Sec. 8.4 summarizes the findings.

### 8.2 Calculational Details

As mentioned in Chapter 3 chemical shielding tensor $\hat{\sigma}$ is determined by its principal axis components and is usually reported in terms of isotropic and anisotropic. For non-cubic perovskite structure based crystals, $\sigma_{zz}(\text{Ti})$ will always be identified, in this chapter, with the principal along the polar direction. The titanium chemical shielding reference used here is cubic SrTiO$_3$.

#### 8.2.1 Embedded cluster calculations

Calculations were performed with the GAUSSIAN computational package [28–30], and the chemical shielding tensor was determined using the continuous set of gauge transformations (CSGT) method [16, 49]. Calculations were done using the DFT hybrid B3LYP [10], as well as GGA, using the PW91 [50] and PBE [51] forms. Douglas-Kroll-Hess 2nd order scalar rel-
ativistic calculations were performed on selected systems. Site-centered Gaussian type orbitals (GTO) basis functions were associated with all the QM atoms. All-electron treatments were used for the O, Ca, and Ti atoms, while the other QM atoms were represented using scalar-relativistic small core (scalar-RSC) pseudopotentials [also called effective core potentials (ECPs)]. The basis sets and ECPs used for these calculations were taken from the EMSL website [33], except for Ti(6-311G(2d,p)), which was taken from the internal Gaussian program directory [28–30].

For the Ti-centered clusters, the RSC ECPs for the QM atoms were Sr(28), Zr(28), Ba(46), Pb (60), where the number of core electrons is shown in parenthesis. These pseudopotentials are generally specified by the same label as their associated basis sets listed below, except where otherwise indicated. For ePSPs, ECPs used for these calculations were taken from the EMSL website [33] and are described in Chapter 7. The following GTO basis sets were found to give well-converged results: O(IGLO-III), target Ti(cc-pwCVQZ), remaining Ti(6-311G(2d,p)). Zr(def2-TZVP), Pb(cc-pVDZ-PP). Ca(cc-pVDZ); for the Sr and Ba atoms the associated Stuttgart RSC 1997 basis sets were used. The non-relativistic (NR) and relativistic (DK) versions of Ti(cc-pwCVQZ) were used for their respective calculations. Calculated relative chemical shifts with these basis sets showed small variations with respect to basis set size. For example, when going from TZ to QZ basis set on the target Ti atom, $\delta_{iso}$(Ti) change by $\approx 2$ ppm for cubic BT and tetragonal PT. Similarly, when the Pb, Ba, and Sr basis sets were change from DZ to TZ (def-TZVP was used for Sr and Ba), $\delta_{iso}$(Ti) changed by no more than $\approx 5.5$ ppm.

8.2.2 GIPAW calculations

A detailed discussion of this approach and the calculation parameters for the systems discussed here (except for the Ca pseudopotential parameters) are given in Chapters 4 and 7. A brief summary of the key features is presented here.

Calculations for PBC used the GIPAW [5] functionality of the QuantumESPRESSO (QE) code [41]. These calculations are done in two steps. A standard ground state norm-conserving pseudopoten-
tial (PSP) calculation is first performed. This is followed by a linear response calculation in the
presence of an external magnetic field. The linear response calculation uses all-electron like va-
lence wave functions, which are represented using a projector augmented wave (PAW) basis. The
PAW basis functions are constructed when the PSP is generated.

Calculations reported below used well converged Monkhorst-Pack [110] Brillouin zone k-
point sampling, e.g. 6×6×6 for the prototypical perovskites (CT, ST, BT, and PT) and 6×6×4
for 10 atom unit cells systems (PZT and the mixed A-site perovskites, A = Sr, Ba, Pb). Unless
otherwise specified, the PBE GGA functional was used in all QE calculations.

GIPAW calculations can be complicated by the details of the pseudopotential construction.
For example, compared to oxygen, titanium contains additional core electrons and higher angular
character. Therefore, the additional parameters require significantly greater care and testing.

8.2.3 Comparison of Methods

GIPAW and cluster approaches are compared for the TiO₂ molecule, the rutile crystalline
solid, as well as results for the prototypical perovskites SrTiO₃ and PbTiO₃ in the cubic and
tetragonal phases, respectively, in Table 8.1. Where available, published PBC-GIPAW results [47]
are also given for comparison.

TiO₂ molecule and rutile atomic coordinates as well as the associate GIPAW parameters are
described in Chapter 7. The Gaussian calculation for the isolated molecule used a basis set of cc-
pwCVQZ-DK and IGLO-III for Ti and O, respectively. For the rutile structure, the cluster method
used a Ti₁₁₂O₄₄ QM cluster with cc-pwCVQZ-DK, 6-311G(2d,p) basis sets, respectively, for the
target and outer 10 Ti atoms; IGLO-III basis sets were used for all 44 O atoms. (Embedding with
ePSPs and point charges were done as described Chapter 7) QE calculations are in good agreement
with the finite size methods for both TiO₂ systems. Principle components of δ differ by at most
≃33 ppm and ≃ 19 ppm for the molecule and solid, respectively. Isotropically, the theoretical
discrepancy is reduced to ≃ 25 ppm and ≃ 14 ppm.
TABLE 8.1: Comparison of results, using embedded clusters and GIPAW. The principle values of the titanium chemical shielding tensor are present for TiO$_2$ molecule and rutile, cubic ST, and tetragonal PT. All values are from relativistic PBE-GGA calculations. Embedded cluster results are labeled as C-xx, where xx is the number of quantum atoms (see text) in the cluster. For PT, the depolarizing field was removed by comparing the LDA force to an LAPW calculation.

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$^a$ Ref. [47] determined the chemical shielding using a different experimental structure. Their lattice parameter, $a = 3.94$ Å, is larger compared to the lattice parameter, $a = 3.905$ Å, used in this study.
Calculations for the prototypical perovskites in Table 8.1 used the structures described in Chapter 7. Embedded clusters were constructed as in Chapter 4, and results are given for 75- and 111-QM atom clusters. Both the 75-QM atom and 111-QM atom cluster results are from scalar relativistic PBE calculations. Differences between PW91 and PBE (not shown in the Table) are small, as expected. Tests on the 75-QM atom ST cluster show that, relativistically, PBE produced $\tilde{\sigma}$ values that are $\simeq 11$ ppm more positive than PW91. In contrast, scalar-relativistic effects changed $\tilde{\sigma}$ by $\simeq +46$ ppm. For the chemical shifts, these effects are expected to negligible, due to cancellation of errors.

The ST and PT 111-QM atom relativistic PBE $\sigma_{xx} = \sigma_{yy}$ and $\sigma_{zz}$ are in good agreement with PBC values, differing at most by $\simeq 31$ and $\simeq 52$ ppm respectively. Isotropic values for both systems are within 31 ppm of PBC-QE.

Size effects between the 75- and 111-QM atom results are evident in the Table 8.1. The 75-QM atom values are more shielded [i.e., more positive (see Eq. (7.1))] than either the 111-QM atom values or the PBC methods. Rigidly shifting the 75 QM-atom brings these into better agreement with GIPAW, indicating good cancellation of errors. This is evident in Table 8.2, which compares the calculated non-relativistic PW91 isotropic chemical shifts to GIPAW results and experimental data, where available, for TiO$_2$ rutile, CT, ST (2 different lattice constants), cubic BT, P4mm BT, cubic PT, P4mm PT and 50/50 PZT with P4mm, P2mm, and R3m symmetries. As in Chapter 7, experimental structures were used for all systems except cubic CT [137], cubic ST with cubic BT lattice parameter, cubic PT [138] and the PZT structural models [89]. As will be discussed in the next section, calculated chemical shifts are in agreement between the theoretical methods.

These results demonstrate that the embedded cluster and PBC-GIPAW approaches produce comparable agreement with chemical shifts for the presented cluster sizes and methodology. Differences due to cluster size, DFT functionals, relativistic effects, and pseudopotentials largely cancel in the chemical shifts.
8.3 Results and Discussion

Table 8.2 presents calculated results for the titanium chemical shift tensor $\hat{\delta}(\text{Ti})$ tensor. In the cubic phase $\hat{\delta}(\text{Ti})$ is isotropic, while in the P4mm and R3m cases there is a two-fold degenerate pair, consistent with the relatively high site symmetry for the B-sites compared to the O-sites (Table XX in Chapter 4) in these structures. Table 8.2 compares calculated results to measured $\delta_{\text{iso}}(^{17/49}\text{Ti})$ chemical shifts from NMR powder spectra and a single crystal measurements. The experimental BaTiO$_3$ and PbTiO$_3$ values were referenced to cubic SrTiO$_3$, with the exception of cubic BaTiO$_3$ along with TiO$_2$, which were both referenced to liquid TiCl$_4$. Therefore, the measured chemical shift of cubic SrTiO$_3$ referenced to liquid TiCl$_4$ (-843 ppm [135]) was used to derive the experimental values shown in Table 8.2. The agreement between theory and experiment is good for TiO$_2$ and BaTiO$_3$ in the cubic and tetragonal phases, except for one reported tetragonal measurement. The calculated TiO$_2$ uniaxial chemical shifts (Eq. 7.2) of ~25 ppm (Cluster) and ~28 ppm (GIPAW) are small and consistent with the single crystal measurement of ~22.5 ± 20 ppm [139] (Eq. 7.2) and the powder measurement of ~30 ± 15 ppm [140]. The discrepancy is larger in tetragonal PbTiO$_3$ B3LYP improves upon the GGA. Calculated $\delta_{\text{iso}}$(Ti) values for the PZT 50/50 P4mm, P2mm, and R3m structural models, differ no more than 35 ppm from PT. This is qualitatively in agreement with the Ti NMR measurements of PT, PZT 25/75 and PZT 50/50, where the intrinsic line width (~3500 ppm) and location of the Ti NMR spectrum remains constant with changes in Ti concentration [4].

Figure 8.1 plots the BT, PT, and PZT (P4mm, P2mm, and R3m symmetries) isotropic (Figure 8.1(a)), uniaxial (Figure 8.1(b)), $xx = yy$ (Figure 8.1(c)), and $zz$ (Figure 8.1(d)) chemical shifts as a function of the TiO$_6$ octahedral volume surrounding the targeted Ti atom. For the BT and PT systems, the unit cell volume was varied and for each volume the GGA relaxed structure was determined with 4 different c/a fixed ratios. As can be seen in Figure 8.1(a), $\delta_{\text{iso}}$(Ti) for both BT and PT show a linear dependence with respect to volume with a rigid 50 ppm offset in $\delta_{\text{iso}}$(Ti) for A-site substitution. The $\delta_{\text{iso}}$(Ti) values for the mixed B-site PZT compounds with P4mm and
### TABLE 8.2: Comparison of results, using embedded clusters, GIPAW-PBC, and available experiment. The principle values and the isotropic component of $\sigma$ (Ti) (in ppm) are presented for cubic CT, cubic ST, cubic ST with the cubic BT lattice parameter, cubic BT, cubic PT, tetragonal BT, tetragonal PT, and PZT clusters are based on [89] (P4mm, P2mm, R3m). In the non-cubic crystals, $zz$ denotes the principal axis along the polar direction. Embedded cluster results are for 75 QM atom clusters for the perovskites using B3LYP and PW91. All chemical shifts are referenced to cubic ST with the reference values of -75, -225, and -228 ppm used for B3LYP, PW91, and GIPAW-PBC, respectively. In the case of TiO$_2$, a 55 QM atom cluster was used in it was referenced to the chemical shielding of 111-atom QM cubic SrTiO$_3$ cluster (-247 ppm).

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>B3LYP</th>
<th>PW91</th>
<th>GIPAW</th>
<th>GIPAW$^a$</th>
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<tr>
<td><strong>TiO$_2$ (rutile)</strong></td>
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</tr>
<tr>
<td><strong>xz</strong></td>
<td>$-42 \pm 10^b$</td>
<td>-88</td>
<td>-122</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>yy</strong></td>
<td>$-42 \pm 10^b$</td>
<td>-42</td>
<td>-64</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>zz</strong></td>
<td>$28 \pm 10^c$</td>
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<td>-7</td>
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<tr>
<td><strong>iso</strong></td>
<td>$0^\circ, -17 \pm 10^c, -38 \pm 5^d$</td>
<td>-40</td>
<td>-64</td>
<td></td>
<td></td>
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<td><strong>CT cubic</strong></td>
<td>-88</td>
<td>-92</td>
<td>-91</td>
<td></td>
<td></td>
</tr>
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<td>0</td>
<td>0</td>
<td></td>
<td>0</td>
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<tr>
<td><strong>ST cubic</strong> ($a=BT$)</td>
<td>97</td>
<td>102</td>
<td>101</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>BT cubic</strong></td>
<td>112$^e$, 102$^f$</td>
<td>138</td>
<td>141</td>
<td>142</td>
<td>145</td>
</tr>
<tr>
<td><strong>PT cubic</strong></td>
<td>-13</td>
<td>-16</td>
<td></td>
<td></td>
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<td><strong>BT P4mm</strong></td>
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<tr>
<td><strong>xz = yy</strong></td>
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<tr>
<td><strong>iso</strong></td>
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<td>110</td>
<td>93</td>
<td>55</td>
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<td>-112</td>
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<tr>
<td><strong>iso</strong></td>
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<tr>
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</tr>
<tr>
<td><strong>zz</strong></td>
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</tr>
<tr>
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</tr>
<tr>
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<td>100</td>
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<td></td>
</tr>
<tr>
<td><strong>zz</strong></td>
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<td>113</td>
<td>-119</td>
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<td></td>
</tr>
<tr>
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<td>-134</td>
<td>66</td>
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<tr>
<td><strong>zz</strong></td>
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<td>148</td>
<td>96</td>
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<tr>
<td><strong>iso</strong></td>
<td>64</td>
<td>54</td>
<td>13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Ref. [47] cube ST and P4mm BT experimental structures; cubic BT relax structure

$^b$ Powder results Ref. [134]

$^c$ Single crystal experimental values are from Ref. [139]

$^d$ Powder results Ref. [140]

$^e$ Powder results Ref. [133]

$^f$ Single crystal experimental values are from Ref. [128]

$^g$ Single crystal experimental values are from Ref. [126, 134]

$^h$ Powder results Ref. [132]

$^i$ Powder results Ref. [129]

$^j$ Powder results Ref. [130]
FIG. 8.1: Calculated titanium isotropic chemical shifts are plotted as a function of the volume of the nn A-site cube surrounding the target titanium cation for a collection of PT and BT computational experiments. In the respective systems, the unit cell volume was varied and for each volume the GGA relaxed structure was determined with 4 different c/a fixed ratios. Results are also shown for PZT 50/50 models (P4mm, P2mm, and R3m) in Figures 8.1(a) and 8.1(b). The dotted lines connected the plotted points within each calculation set.

P2mm symmetries follow the linear trend of PT. Figure 8.1(b) indicates that \( \delta_{\text{ax}}(\text{Ti}) \) also has linear dependence on volume, but in contrast to \( \delta_{\text{iso}}(\text{Ti}) \), the BT slope is smaller than the Pb compounds.

To investigate the difference in the BT and PT \( \delta_{\text{ax}} \) linear dependence, the principle components of the chemical shift tensor plotted. Figure 8.1(c) exhibits that \( \delta_{\text{xx}}(\text{Ti}) \) and \( \delta_{\text{yy}}(\text{Ti}) \) are not dependent on A-site species or the c/a ratio. While Figure 8.1(d) shows that \( \delta_{\text{zz}}(\text{Ti}) \) behaves differently with Ba and Pb occupying the A-site. \( \delta_{\text{zz}}(\text{Ti}) \) in BT changes linearly with volume whereas \( \delta_{\text{zz}}(\text{Ti}) \) is insensitive to volume in PT. This Pb compound volume insensitivity is responsible for the predicted
chemical shift anisotropy behavior as well as the 50 ppm offset in \( \delta_{\text{iso}}(\text{Ti}) \) between the two A-site species. This behavior can be attributed to Pb covalency, which, unlike the rigid-ion-like bonding of non-Pb A-site atoms, more easily accommodates structural adjustments and in turn lessen their impact on the surrounding the Ti cation.

The A-site dependence of the titanium chemical shift is further investigated by examining how \( \delta_{\text{iso}}(\text{Ti}) \) and \( \delta_{\text{ax}}(\text{Ti}) \) vary in mixed homovalent A-site compounds. Figure 8.2 displays calculated titanium isotropic (Figure 8.2(a)) and uniaxial (Figure 8.2(b)) chemical shifts plotted as a function of the TiO_6 volume for a collection of \((\text{A}_1/2\text{A'}_1/2)\text{TiO}_3\) systems, where A and A' = Sr, Ba, and Pb. It is apparent from Figure 8.2 that \( \delta_{\text{iso}}(\text{Ti}) \) has a low sensitivity to A-site alloying and the \( \delta_{\text{ax}}(\text{Ti}) \) volume dependence increases with Pb concentration.

![Figure 8.2](image.png)

**FIG. 8.2:** Calculated titanium isotropic and uniaxial chemical shifts, \( \delta_{\text{iso}}(\text{Ti}) \) and \( \delta_{\text{ax}}(\text{Ti}) \), are plotted as a function of the volume of the nn A-site cube surrounding the target titanium cation for a collection of \((\text{A}_1/2\text{A'}_1/2)\text{TiO}_3\), where A and A' = Sr, Ba, and Pb. 10 atom unit cells with a c/a ratio of 1.033 for each GGA relaxed structure at constant volume. The dotted lines connected the plotted points within each calculation set.

Unlike the P4mm and P2mm symmetries of PZT, the R3m \( \delta_{\text{iso}}(\text{Ti}) \) is not consistent with the \( \delta_{\text{iso}}(\text{Ti}) \) versus volume linear relationship followed by the other Pb compounds in this study. This apparent deviation due to symmetry was examined by performing a similar \( \delta_{\text{iso}}(\text{Ti}) \) versus volume study as done in Figure 8.1(a) with a collection of R3m PT and BT structures. Figure 8.3 shows these results along with selected results from Figure 8.1(a), which are included for comparison.
The plotted calculated values show that $\delta_{iso}(\text{Ti})$ has a low sensitivity to crystal symmetry and in the case of PT, $\delta_{iso}(\text{Ti})$ cannot distinguish between R3m and P4mm symmetries. In contrast, $\delta_{iso}(\text{Ti})$ can distinguish between BT R3m and P4mm symmetries at realistic volumes. However, the indistinguishably of symmetry for PT in Figure 8.3 and the nonconformity of the R3m symmetry of PZT in Figure 8.1(a) maybe due to the R3m structure having a different bonding environment than the P4mm and P2mm symmetries, which may allow for B-site dependence.

![Graph](image)

**FIG. 8.3:** Calculated titanium isotropic chemical shifts $\delta_{iso}(\text{Ti})$ are plotted as a function of the volume of the nn A-site cube surrounding the target titanium cation for a collection of R3m PT and BT structures. Selected results from Figure 8.1(a) are included for comparison. The dotted lines connected the plotted points within each calculation set.

### 8.4 Summary

Complementary titanium nuclear magnetic resonance chemical shift tensor calculations were carried out with embedded clusters, using quantum chemistry methods, and with periodic boundary conditions, using the GIPAW method within Quantum Espresso. Compared to oxygen chemical shifts $\delta(O)$ (Chapters 6 & 7), $\delta(Ti)$ calculations are more challenging for both approaches. Ti cluster calculations were found to be sensitive to size effects and termination (Chapter 4), while GIPAW results were found to be sensitive to the pseudopotential construction. The two approaches complemented each other in optimizing these factors. Tables 8.1 and 8.2 indicate that both methods produce chemical shifts that are consistent with each other. Figures 8.1, 8.2, and 8.3 show
that Ti chemical shifts have strong volume dependence. Both \( \delta_{\text{iso}}(\text{Ti}) \) and \( \delta_{\text{ax}}(\text{Ti}) \) show a near linearly dependence on TiO\(_6\) octahedral volume. \( \delta_{\text{iso}}(\text{Ti}) \) is relatively insensitive to A-site species (small offset) while \( \delta_{\text{ax}}(\text{Ti}) \) more so. Additionally, both components are fairly insensitive to c/a and B-site ordering.
Recently, Vijayakumar et al. [6] preformed a systematic experimental temperature and composition dependent $^{93}$Nb NMR study of PMN and their analysis revealed that Nb isotropic chemical shifts are dependent on the nearest neighbor B-site (nBn) configurations. A comparison of experimental results to first-principles Nb chemical shift calculations from various structural models could determine NbO$_6$ tetrahedral volumes. Perhaps nn B-B bond lengths could be extracted due to the Nb chemical shift sensitivity to nBn configurations. Initial calculations of on two 60 PMN supercells showed that the principle values of the Nb chemical shielding tensor are very sensitive to the nBn configurations and the isotropic chemical shielding range of $\approx$106 ppm is consistent with the experimental isotropic chemical shift range of $\approx$ 80 ppm. It would be interesting to further examine the Nb chemical shift sensitivity to PMN structural parameters not only to learn about the local structure of PMN, but also the potential of B-site NMR in studying other heterovalent B-site perovskites.


[79] The isotropic component should average out to zero when the measurement is performed under magic angle spinning (MAS). MAS measurements were made for most materials except for some of the SrTiO₃ and BaTiO₃. For cases when the sample is oriented at an angle other than the magic angle the magnetic susceptibility of the material will change the oxygen chemical shift by no more than 3 ppm if we assume that the samples are homogenous and in an infinite cylinder. See [78] for more information.


[92] The short B-O bond length $r_s$ can be expressed as $r_s = r_{\text{avg}} - \Delta / 2$, where $r_{\text{avg}}$ is the average of the short and long B-O distances and $\Delta$ describes the asymmetry of the B-O-B chain. Since $r_{\text{avg}} \approx 2 \, \text{Å}$ across these systems, $r_s$ is also a measure of the dimerization or bond length asymmetry of the B-O-B chain.


