Microscopic Sources of Solid-State NMR Shielding in Titanate of Alkaline Earth Perovskite Metals

Javad Nematollahi and Saeid Jalali-Asadabadi*

Department of Physics, Faculty of Sciences, University of Isfahan (UI), Hezar Gerib Avenue, Isfahan 81746-73441, Iran

ABSTRACT: Nuclear magnetic resonance (NMR) parameters are calculated and analyzed in a series of titanate of alkaline earth perovskites to explore microscopic sources of their magnetic shieldings using a full-potential-based NMR scheme. In this method, there is no approximation to calculate the induced current density. The slope of the correlation between various approaches and available experimental data is successfully reproduced very close to the required ideal value (−1). Our NMR results are consistent with the experimental data and the available theoretical results calculated by the gauge-including projector augmented-wave (GIPAW) method. Moreover, we have predicted the chemical shifts of the compounds in which their experimental values have not been measured yet. Isotropic and anisotropic chemical shift parameters as well as associated asymmetries are analyzed. The analysis explores the relation between atomic and orbital characters of the valence and conduction bands wave functions as well as the 17O NMR shielding. Our results show that the NMR shielding varies by around 180 ppm through the materials under question. We, in agreement with the results reported on alkali fluorides, show that the variation of the NMR shielding in our investigated alkaline earth titanate perovskites is mostly related to the oxygen p-states. Furthermore, we show that the NMR chemical shifts strongly depend on the shape of the unoccupied titanium-d density of states (DOS) and alkaline-earth metals-d DOSs as well as their locations in the conduction region with respect to the Fermi level. It is also shown that the shielding calculated for the ordinary ice is less by 71.2 ppm than that derived for the water using TB-mBJ.

INTRODUCTION

Solid-states nuclear magnetic resonance (NMR) is one of the most powerful multidisciplinary experimental techniques.1,2 It has many applications in a variety of research fields.3–6 The NMR measurements can yield useful information about atomic and electronic structures of a material through its response to an external magnetic field.7–9 This information can be provided by measuring the transition frequency from one orientation of the nuclear magnetic moment to another one due to the external magnetic field exerted on the material.10 This external magnetic field can cause the electrons of the material to produce an induced electric current.11 The latter current in turn can induce a magnetic field at the nucleus of the sample.12 The induced magnetic field, which is a screened field of the external magnetic field at the nucleus by the electrons, is proportional to the external magnetic field.13 This proportionality constant is called the magnetic shielding tensor.14,15

It is approximately possible to theoretically interpret the measured NMR data of light molecules using empirical models.16,17 However, accurate electronic structures are necessary for interpreting NMR spectra of heavier systems such as macromolecules and solids.22–24 Hence, a relation as a connecting bridge is demanded between the experimental NMR data and theoretical ab initio results to interpret the measured NMR spectra and realize the chemical bonding of materials. The interpretations of the NMR spectra by ab initio calculations were first restricted to nonperiodic systems such as molecules and clusters.25,26 Nowadays, there are several density functional theory (DFT)27,28 based methods for the prediction of NMR shielding tensor in solids employing a perturbation scheme29 to calculate the induced current and hence the induced magnetic field using the Biot-Savart law.30 However, the calculation of the induced current is rather difficult for solids as extended systems.31 This is because in the presence of the external magnetic field the Hamiltonian does not remain invariant under translation.32 This thereby violates the condition of Bloch’s theorem. Moreover, the position operator is not also well-defined.33 These difficulties have been resolved by Mauri, Pfommer, and Louie (MPL) by proposing a linear response approach based on a periodic modulation of the external magnetic field by a finite wave vector.34 Although the MPL method has been implemented in a variety of reliable pseudopotential codes,35–37 in practice its applications have been restricted to light systems.38–40 This is because of omitting the pseudoization effects on the induced current, which are remarkable in the heavier systems.22 Pickard and Mauri have solved the latter problem by introducing the gauge-including projector augmented-wave (GIPAW) method.25 The

Received: June 4, 2018
Revised: August 15, 2018
Published: August 20, 2018
GIPAW method using pseudopotential calculations has been successfully applied on various heavy systems.\textsuperscript{41–43} In addition to the above methods, several other methods\textsuperscript{6,44–46} have been introduced to calculate magnetic shielding for a wide range of materials from nanosystems\textsuperscript{49–51} to biosystems\textsuperscript{52,53} using both pseudopotential\textsuperscript{14,55} and full-potential codes.\textsuperscript{56}

The role of the relation between experimental NMR spectra and theoretical \textit{ab initio} chemical shielding calculations can be compared to the role of the relation between experimental nuclear quadrupole spectra and theoretical \textit{ab initio} electric field gradient (EFG) calculations. Around three decades ago, a reliable approach was proposed\textsuperscript{57,58} to perform accurate EFG calculations employing the FP-LAPW method instead of using the unreliable point charge model for providing satisfactory descriptions of chemical bonding of materials including solids.\textsuperscript{59–64} Consequently very recently, Laskowski and Blaha\textsuperscript{11,14} have developed a new direct perturbative formalism of the NMR chemical shielding calculations based on a linear-response theory for the FP-APW plus regular local and their proposed NMR local orbitals (FP-APW+lo-NMR-LO) method in the extended solid systems without imposing any restriction on or approximation to the induced current density and the integration of the all-electron current performed by a pseudopotential technique. Although the idea of developing the FP-APW+lo-NMR-LO approach\textsuperscript{11} is similar to that of the reliable FP-APW+lo-EFG-LO approach,\textsuperscript{57,58} evidently their physics and formulations are totally different. The FP-APW+lo-NMR-LO approach has been reliably implemented in the WIEN2k program package\textsuperscript{65} and applied successfully on a variety of systems\textsuperscript{11–16} as well.

Here, we systematically analyze the relation between NMR shielding and electronic structure. By this, the NMR chemical shift measurements are interpreted to satisfactorily describe the chemical bonding of our desired materials. To this end, the NMR chemical shifts at oxygen sites are calculated using the full-potential APW+lo+NMR-LO approach\textsuperscript{11} to find the microscopic sources of the chemical shifts variation through a series of titinate of alkaline-earth perovskites, MgTiO\textsubscript{3}, CaTiO\textsubscript{3}, SrTiO\textsubscript{3}, and BaTiO\textsubscript{3}.\textsuperscript{17} O\textsuperscript{17} is the only stable oxygen isotope that can be detected by NMR techniques. It is worth to mention that NMR study is not a very easy and straightforward experimental task in these compounds due to the presence of the O\textsuperscript{17} nucleus at site R by its nuclear magnetic shielding, \(\tilde{\sigma}(R)\), which is generally a tensor of rank 2.\textsuperscript{74} This tensor can be diagonalized in the principle axes system (PAS). The PAS axes can be chosen such that \(\sigma_{zz} \geq \sigma_{yy} \geq \sigma_{xx}\), where \(\sigma_{zz}\) is the principle component of the \(\tilde{\sigma}(R)\) tensor.\textsuperscript{75} Here, we briefly describe the approach utilized to calculate the NMR magnetic shielding to elucidate the pros and cons of our study. For further details and a more complete discussion on the foundations of this approach, we refer readers to ref 11 and references therein. The approach is based on a linear response theory\textsuperscript{22–24} which is widely used for NMR calculations in solids.\textsuperscript{11–16} This formalism is implemented by Laskowski and Blaha\textsuperscript{11,14} in the WIEN2k code.\textsuperscript{58} A uniform external magnetic field \(B\) applied to a sample of matter produces an electronic current. This current in turn induces a nonuniform magnetic field \(B_{\text{ind}}\) at nucleus site R. The NMR shielding tensor \(\tilde{\sigma}(R)\) can linearly relate the induced field \(B_{\text{ind}}\) to the external field \(B\):\textsuperscript{11}

\[
B_{\text{ind}}(R) = -\tilde{\sigma}(R)B
\]

where \(B_{\text{ind}}\) is calculated by the Biot-Savart law as follows:\textsuperscript{11,76}

\[
B_{\text{ind}}(R) = \frac{1}{c} \int \frac{\mathbf{j}_{\text{ind}}(r) \times (R - r)}{|R - r|^3} \, dr
\]

where \(c\) is the speed of light in a vacuum, \(r\) is a vector in real space inside the unit cell with respect to the origin of the crystal coordinate axes system, \(R\) is the position vector of an atom (atomic position or nucleus site) inside the unit cell with respect to the origin of the crystal coordinate axes system, and \(\mathbf{j}_{\text{ind}}(r)\) is the induced current density vector which can be simplified into the following form:\textsuperscript{16}

\[
\mathbf{j}_{\text{ind}}(r) = 1/c \sum_{\omega} \mathcal{R}([\Psi_0^{(\omega)}]^{*} \mathbf{j}(r) |\Psi_0^{(\omega)})]
\]

where \(\mathcal{R}\) symbol stands for the real part, \(\mathbf{j}(r)\) is the unperturbed (paramagnetic) part of the current operator, and the occupied perturbed state \(|\Psi_0^{(\omega)}\rangle\) is related to the empty unperturbed \(|\Psi_0^{(\omega)}\rangle\) states via the Green function \(G(\epsilon) = \sum_e \langle \Psi_0^{(\omega)} | (\Psi_0^{(\omega)})^* \rangle \delta(\epsilon - \epsilon_e)\) as\textsuperscript{11}

\[
|\Psi_0^{(\omega)}\rangle = \sum_e |\Psi_0^{(\omega)}\rangle (\Psi_0^{(\omega)})^* (r - r') \times \mathbf{p} \mathbf{B} |\Psi_0^{(\omega)}\rangle / (\epsilon - \epsilon_e)
\]

It is worth noting that the linear relation expressed in eq 1 is valid provided that \(|\mathbf{B}|\) is sufficiently small.\textsuperscript{77} In this case, the perturbation theory can be practically applicable using its first order equations for determining \(\tilde{\sigma}(R)\).\textsuperscript{24} The nonzero components of \(\tilde{\sigma}(R)\) can be determined in the PAS by the following three quantities: (i) isotropic average of the diagonal

\[
\epsilon_e = \langle \Psi_0^{(\omega)} | \mathbf{B} |\Psi_0^{(\omega)}\rangle
\]

\[
|\psi(r)|^2 = \frac{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}
\]

\[
\mathbf{j}(r) = e \sum_e \langle \psi^{(\omega)} | (\Psi_0^{(\omega)})^* \rangle \delta(\epsilon - \epsilon_e) \mathbf{p} \mathbf{B} \langle \Psi_0^{(\omega)} | \Psi_0^{(\omega)}\rangle
\]

\[
\epsilon_e = \langle \Psi_0^{(\omega)} | \mathbf{B} |\Psi_0^{(\omega)}\rangle
\]

\[
|\psi(r)|^2 = \frac{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}
\]

\[
\mathbf{j}(r) = e \sum_e \langle \psi^{(\omega)} | (\Psi_0^{(\omega)})^* \rangle \delta(\epsilon - \epsilon_e) \mathbf{p} \mathbf{B} \langle \Psi_0^{(\omega)} | \Psi_0^{(\omega)}\rangle
\]

\[
\epsilon_e = \langle \Psi_0^{(\omega)} | \mathbf{B} |\Psi_0^{(\omega)}\rangle
\]

\[
|\psi(r)|^2 = \frac{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}
\]

\[
\mathbf{j}(r) = e \sum_e \langle \psi^{(\omega)} | (\Psi_0^{(\omega)})^* \rangle \delta(\epsilon - \epsilon_e) \mathbf{p} \mathbf{B} \langle \Psi_0^{(\omega)} | \Psi_0^{(\omega)}\rangle
\]

\[
\epsilon_e = \langle \Psi_0^{(\omega)} | \mathbf{B} |\Psi_0^{(\omega)}\rangle
\]

\[
|\psi(r)|^2 = \frac{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}
\]

\[
\mathbf{j}(r) = e \sum_e \langle \psi^{(\omega)} | (\Psi_0^{(\omega)})^* \rangle \delta(\epsilon - \epsilon_e) \mathbf{p} \mathbf{B} \langle \Psi_0^{(\omega)} | \Psi_0^{(\omega)}\rangle
\]

\[
\epsilon_e = \langle \Psi_0^{(\omega)} | \mathbf{B} |\Psi_0^{(\omega)}\rangle
\]

\[
|\psi(r)|^2 = \frac{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}{\langle\psi^{(\omega)}|\psi^{(\omega)}\rangle}
\]

\[
\mathbf{j}(r) = e \sum_e \langle \psi^{(\omega)} | (\Psi_0^{(\omega)})^* \rangle \delta(\epsilon - \epsilon_e) \mathbf{p} \mathbf{B} \langle \Psi_0^{(\omega)} | \Psi_0^{(\omega)}\rangle
\]

\[
\epsilon_e = \langle \Psi_0^{(\omega)} | \mathbf{B} |\Psi_0^{(\omega)}\rangle
\]
elements of the magnetic shielding tensor $\sigma_{\text{iso}}(\text{ppm}) = (1/3)(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \text{Tr}(\delta(R))/3$, (ii) magnetic shielding anisotropy $\sigma_{\text{aniso}}(\text{ppm}) = \sigma_{zz} - \sigma_{\text{iso}}$ and (iii) asymmetry parameter $\eta_{\text{asy}} = (\sigma_{yy} - \sigma_{xx})/\sigma_{\text{iso}}$. In practice, however, a quantity that can be measured experimentally is the isotropic average of the diagonal elements of the chemical shift tensor $\delta(R)$, viz. $\delta_{\text{iso}}(\text{ppm}) = (1/3)(\delta_{xx} + \delta_{yy} + \delta_{zz}) = \text{Tr}(\delta(R))/3$. Moreover, the isotropic chemical shift can be experimentally measured only with respect to some reference compounds. A reference often quoted for $^{17}$O is $\text{H}_2\text{O}$. In the Haeben notation, the nonzero components of $\delta(R)$ in the PAS can be ordered with respect to $\delta_{xx}$ as $\delta_{xx} \geq \delta_{yy} \geq \delta_{zz}$, where $\delta_{xx}$ is the main component of the $\delta(R)$ tensor. In analogues to $\delta(R)$, the nonzero components of $\delta(R)$ in the PAS can be also determined. From eqs 1 and 2, it is clear that the induced current density plays a crucial role for the calculation of the absolute chemical shift tensor. By these equations, the main task of the $ab$ initio NMR calculations is transformed from the calculation of $\delta(R)$ to that of $j_{\text{ind}}(r)$.

In this work, the induced current density is calculated in the framework of the (L)APW+lo method. Such an expansion of the wave functions can be considered as an advantage for the (L)APW+lo method, as by this the nodal structure of the wave functions can be predicted without any approximations. Laskowski and Blaha efficiently used this advantage to represent the induced current density in a compatible way with the (L)APW+lo formalism. Inside the atomic spheres, the LAPW and APW bases are confined to those energies that are distributed around the Fermi energy to optimize the calculations of the occupied valence states. The optimized LAPW set of the linearization energies and radial functions would not be fully appropriate for the NMR calculations within the perturbation approach. In order to overcome this problem, additional local orbitals are included at high energies in unoccupied states to make the basis set of the standard LAPW approach more suitable for the NMR calculations. It is important to note that the regular local orbitals of the LAPW or APW method are different from the NMR local orbitals. A local orbital of the LAPW method (lo) is added at the occupied semicore region to include an additional radial wave function at low energies, whereas an NMR local orbital (LO) is added at the unoccupied conduction region to include an extra radial wave function at high energies. The added extra function is called NMR local orbital.

Since there are no specific rules for determining the appropriate linearization energies (NMR-LO), the local orbitals can be added almost arbitrarily (for example, by increasing linearization energies in regular intervals). In the NMR calculations, these orbitals should be added at high energies. We have increased the interval of linearization energies from $-10000$ to $10000$ Ry. The issue that would be considered is that these orbitals should be linearly independent to prevent that the two radial functions are very similar to each other. In order to optimize the number of local orbitals needed to reach the convergence, we have determined them according to the number of nodes of the corresponding radial functions.

As a result, the linearization energy is adjusted such that each of these radial functions is zero at the boundary of the sphere, and the number of nodes inside the sphere increases by one. The first five radial functions of the $p$ orbital of oxygen atom, as determined by this method, are shown in Figure 1.

We have optimized the number of nodes according to the method described above for each of the compounds. As shown in Figure 2, the optimized number of nodes for all the compounds has been calculated to be $10$. The insets in Figure 2 show the convergence of magnetic shielding with respect to the number of augmented plane waves. The default value for $R_{\text{MTK}}^{\text{max}}$ in the WIEN2k code is $7$, which has a good performance for most cases. As shown in the insets of Figure 2, the optimized value of $R_{\text{MTK}}^{\text{max}}$ for performing accurate magnetic shielding calculations is also obtained to be $7$, which confirms the default value of the code.

Now in principle, $B_{\text{iso}}(R)$ can be evaluated using the above-discussed and determined $j_{\text{ind}}$ by substituting eq 3 into eq 2. However, in practice, there are some difficulties for evaluating
the integral in eq 2 for solids as infinite periodic systems.\(^{11}\)

The convergence of the integral may not be always guaranteed.

(2) Transformation from real space to reciprocal space may not simplify the integral in eq 2 to include the size and shape effects, because \(j_{\text{ind}}\) is small in the interstitial region and rapidly oscillates (see Figure 3) and hence cancels out around centers of the neighboring muffin-tin spheres; therefore, as we can see in Figure 4 the current density and hence absolute chemical shielding mainly originates from a small region around the center of the atomic muffin-tin sphere where the nucleus is positioned and low in the interstitial region. From Figure 4 it is also clearly seen that the induced current density of MgTiO\(_3\) is more asymmetric compared to those of the other compounds. This asymmetric distribution shape shows that the behavior of the induced current density of MgTiO\(_3\) is different from that of the other compounds.

\[ \text{Figure 3. The (010) component of induced current density } j_{\text{ind}}(r) \text{ along desired direction. The external magnetic field applied in the [001] direction.} \]

\[ \text{Figure 4. The calculated induced current density } j_{\text{ind}}(r) \text{ where external magnetic field applied in the [001] direction. This current density is plotted in a plane perpendicular to the external field cutting through oxygen atoms.} \]

of the neighboring muffin-tin spheres; therefore, as we can see in Figure 4 the current density and hence absolute chemical shielding mainly originates from a small region around the center of the atomic muffin-tin sphere where the nucleus is positioned and low in the interstitial region. From Figure 4 it is also clearly seen that the induced current density of MgTiO\(_3\) is more asymmetric compared to those of the other compounds. This asymmetric distribution shape shows that the behavior of the induced current density of MgTiO\(_3\) is different from that of the other compounds. The source of this different behavior originates from the fact that the asymmetry parameter \((\eta_{\text{asy}})\) of MgTiO\(_3\) is different from the asymmetry parameters of the other compounds. As can be clearly seen from Table 2, the asymmetry parameter at the oxygen site in the MgTiO\(_3\) is much larger than the asymmetry parameters at oxygen sites of the other compounds under question. The larger the asymmetry parameter, the more the aspherical distribution of the induced current density. This means that the induced current density deviates from spherical symmetry much more in MgTiO\(_3\) than the other compounds due to its larger \(\eta_{\text{asy}}\) as would be observed in Figure 4.

(3) Contribution of \(j_{\text{ind}}\) in the absolute shift is larger in compounds having light nuclei or strong covalent bonds than in compounds having heavy nuclei. However, even for compounds with heavy nuclei, contributions from the interstitial and neighboring spheres are larger than the accuracy of the very accurate FP-APW+lo+NMR-LO method and so should be considered.

All the calculations, here, are carried out in the framework of the DFT employing the APW + lo method\(^{83}\) including scalar relativistic\(^{84}\) effects using Perdew−Burke−Ernzerhof generalized gradient approximation (PBE-GGA)\(^{73}\) and Beck-Johnson (BJ)\(^{85}\) as well as its modified version by Tran and Blaha (TB-mBJ)\(^{71}\) functionals as embodied in the WIEN2k code.\(^{65}\) The muffin-tin radii \((R_{\text{MT}}')s\) are set to 1.67 Bohr for O and 1.84 Bohr for Ti in all the compounds. The \(R_{\text{MT}}'s\) are also adjusted to 2.5 Bohr for Ba, Sr, and Ca in the cubic phase and 2.19 Bohr in the orthorhombic phase as well as 1.90 Bohr for Mg in the trigonal phase to avoid overlapping during optimization. The periodic charge density and potential are Fourier expanded up to \(G_{\text{max}} = 14 (\text{Bohr})^{-1}\). The maximum angular momentum quantum number \(l\) as a cutoff for expanding the Kohn−Sham wave functions in terms of the lattice harmonics inside the muffin-tin spheres is set to \(l_{\text{max}} = 12\). After a careful optimization, a mesh of 1000 special k-points is considered for performing the valence states integration in the irreducible wedge of the first Brillouin zone (1BZ) that corresponds to the grids of \(10 \times 10 \times 10\) in the Monkhorst−Pack scheme\(^{86}\) for all the compounds except for the tetragonal BaTiO\(_3\) and orthorhombic CaTiO\(_3\) compounds. For the latter two compounds, the grids are optimized to be \(10 \times 10 \times 9\) and
SPACE GROUPS AND LATTICE PARAMETERS

The materials that we have chosen for the calculations of the $^{17}$O NMR shielding contain titanate of alkaline-earth perovskite oxides, as shown in Figure 5. An ideal perovskite material, e.g., SrTiO$_3$, crystallizes in cubic symmetry ($Pm\bar{3}m$); however, many perovskite materials are not cubic at ambient conditions and can transit to cubic symmetry at high temperatures.$^{87-89}$ The space groups of the perovskite materials are listed in Table 1. In the ideal perovskite structures there is one ABO$_3$ formula per unit cell, where A and B denote two different cations and all the oxygens are equivalent. As the symmetry reduces, the number of nonequivalent oxygen sites increases to a maximum of three nonequivalent sites. Deviations of the perovskite structure from cubic to lower symmetry and the associated loss of a center of symmetry are critical, because they are directly linked to many of the technologically important properties of these materials. For example, BaTiO$_3$ is a widely used ferroelectric whose electric dipole is a result of the displacement of O$^{2-}$ and Ti$^{4+}$ from their ideal cubic positions.

To obtain the ground-state lattice parameter of the materials, the total energy-volume curves are calculated using PBE-GGA and fitted to the Birch–Murnaghan’s equation of state.$^{90,91}$ The results together with the available experimental and theoretical data are tabulated in Table 1. The comparison shows that our results are close to the experimental values. Our PBE-GGA results are also consistent with or even somewhat a little bit better than the previous theoretical LDA results. This confirms that our selected scheme may be appropriate for the study of these compounds.

RESULTS AND DISCUSSION

In this section, the NMR shielding is characterized and related to the electronic structure of $^{17}$O in the compounds listed in Table 1. By this characterization, we aim to explore the microscopic sources of the solid-states NMR shielding in the studied materials. In this way, the total NMR shielding is decomposed into atomic and orbital characters of the occupied and empty states to realize the variation of the NMR shift in the perovskite series. To this end, we follow step by step the subsequent procedure proposed by Laskowski and Blaha for understanding the variation of the NMR shift in fluorides$^{12}$ and sulfides$^{15}$ series: (1) The NMR shielding is decomposed into its valence and core contributions. (2) Moreover, by considering the peaks of the valence DOSs, we divide the energy interval of the valence contribution into smaller energy intervals. As expressed in eq 3, the induced current depends on both the unperturbed $|\Psi_{o}(0)\rangle$ and perturbed $|\Psi_{o}(1)\rangle$ wave functions. Therefore, the majority of the valence contributions to the induced current (and as a result to the magnetic shielding) can be more decomposed to the orbital characters of the (3) occupied wave functions $|\Psi_{o}(0)\rangle$ and (4) occupied perturbed wave functions $|\Psi_{o}^{(1)}\rangle$ as included in eq 3. As expressed in eq 4, the $|\Psi_{o}^{(1)}\rangle$ state itself depends on the empty but unperturbed $|\Psi_{e}^{(0)}\rangle$ state weighted by $(\Psi_{o}^{(0)}|\Psi_{e}^{(0)})(\epsilon - e_{o})$. (5) Hence, one can eventually also decompose $|\Psi_{o}^{(1)}\rangle$ to the orbital and atomic characters of $|\Psi_{e}^{(0)}\rangle$ according to eq 4.

In the rest of this section, by applying the above strategy, we characterize the main valence contribution to the NMR shielding by decomposing it to its atomic and orbital components of the occupied and empty states. Furthermore, we study the variation of the NMR shielding through our perovskite series with respect to their electronic structures.

The magnetic shielding tensors $(\tilde{\sigma}(R))$’s are calculated at the sites of oxygen atoms for the six compounds listed in the first column of Table 1 using PBE-GGA, BJ, and TB-mBJ functionals by the procedure discussed in the Methodology and Details of Calculations section. Then, the isotropic averages of the diagonal elements of the $(\tilde{\sigma}(R))$ tensors are obtained using $\sigma_{iso} = \text{Tr}[\tilde{\sigma}(R)]/3$, as discussed in the Methodology and Details of Calculations section.
calculated $\delta_{\text{iso}}$'s are linearly least-squares fitted to the available corresponding experimental isotropic chemical shift $\delta_{\text{iso}}$'s in Figure 6. It would be noted that the number of oxygen atoms with different magnetic shieldings increases as their point group symmetries reduce. In the conventional unit cells of each of MgTiO$_3$(R3), CaTiO$_3$(Pm3m), SrTiO$_3$(Pm3m), and BaTiO$_3$(Pm3m) compounds, there are three equivalent oxygen sites. Thus, primitive unit cells of each of the latter four compounds contain only one oxygen atom. Although in the conventional unit cells of each of CaTiO$_3$(Pbnm) and BaTiO$_3$(P4mm) compounds there are also three oxygen atoms, and only two of these two oxygens are equivalent. Thus, primitive unit cells of each of the latter two compounds contain two nonequivalent oxygen atoms. This is why in experiment two different values are measured for $\delta_{\text{iso}}$ in the cases of CaTiO$_3$(Pbnm) and BaTiO$_3$(P4mm), whereas only one single value is reported for $\delta_{\text{iso}}$ in the cases of MgTiO$_3$(R3), CaTiO$_3$(Pm3m), SrTiO$_3$(Pm3m), and BaTiO$_3$(Pm3m), as shown in Figure 6 and listed in the last column of Table 2. In agreement with experiment, we have also theoretically found two different values for $\sigma_{\text{iso}}$ in the cases of CaTiO$_3$(Pbnm) and BaTiO$_3$(P4mm), and only one single value for $\sigma_{\text{iso}}$ in the cases of MgTiO$_3$(R3), CaTiO$_3$(Pm3m), SrTiO$_3$(Pm3m), and BaTiO$_3$(Pm3m), as shown in Figure 6 and listed in the third column of Table 2. The results show that the magnetic shielding decreases by the atomic numbers of the alkaline earth metals. The calculated shielding and measured shifts align well along a straight line over a range of 180 ppm. A linear least-squares fit yields $\sigma_{\text{iso}} = 272.3 - 1.173\delta_{\text{iso}}$ with a good determination coefficient of $R^2 = 0.956$ for PBE-GGA calculations, and similar trends can be seen for BJ and TB-mBJ results. The slope is consistent with the previous calculations of ionic fluorides, chlorides, bromides, or oxides using PBE-GGA.

One using the theoretical relation of $\sigma_{\text{iso}}(\text{R}) = \sigma_{\text{ref}} - \delta_{\text{iso}}(\text{R})$ discussed in calculation section predicts that the slopes of the $\sigma_{\text{iso}}$ versus $\delta_{\text{iso}}$ lines should be equal to $-1$. In practice, however, there are some deviations from this theoretical prediction because of the approximations used in the exchange-correlation, basis set, and linear-response theory. Figure 6 clearly shows that the slopes of the $\sigma_{\text{iso}}$−$\delta_{\text{iso}}$ lines depend on the functional used. The linear fits are found to be $\sigma_{\text{iso}} = 272.3 - 1.173\delta_{\text{iso}}$ using PBE-GGA, $\sigma_{\text{iso}} = 270.1 - 1.085\delta_{\text{iso}}$ using BJ, and $\sigma_{\text{iso}} = 373.6 - 0.995\delta_{\text{iso}}$ using TB-mBJ. These linear fits show that the slope predicted by TB-mBJ ($−0.995$) is closer to the theoretical slope (−1) than those predicted by PBE-GGA (−1.173) and BJ (−1.085). The better performance of the TB-mBJ, which is merely developed to overcome the well-known bandgap-shortcoming of the DFT-based methods, may be related to the value calculated by TB-mBJ for the absolute isotropic shielding in MgTiO$_3$. As can be clearly seen from Figure 6, the latter single value is less scattered from (closer to) the fitted line obtained for TB-mBJ results than the

![Figure 6. Calculated absolute isotropic shielding, $\sigma_{\text{iso}}$(ppm), using PBE-GGA, BJ, and TB-mBJ versus experimental isotropic chemical shift, $\delta_{\text{iso}}$(ppm), at $^{17}$O sites of the compounds listed in Table 1. Data are shown by the same symbols and colors for nonequivalent oxygen atoms of the compounds. The data are linear-least-squares fitted and the solid lines show the fits. In the top inset our calculated chemical shifts by FP-APW$+\text{lo}$+NMR-LO-TB-mBJ method are compared with the available chemical shifts calculated by GIPAW-GGA method and the experimental data. The bottom inset shows the variation of magnetic shieldings using TB-mBJ through the compounds.](image)

Table 2. O−Ti and O−Alkaline-Earth-Metal (O−M) Bond Length in Å, Absolute Isotropic $^{17}$O NMR Shielding $\sigma_{\text{iso}}$ the Magnetic Shielding Anisotropy $\sigma_{\text{aniso}}$ (ppm) = $\sigma_{\text{ze}} - \sigma_{\text{iso}}$ and Asymmetry Parameter $\eta_{\text{asy}} = (\sigma_{\text{yy}} - \sigma_{\text{xy}})/\sigma_{\text{aniso}}$ of Investigated Materials for TB-mBJ Functional

<table>
<thead>
<tr>
<th>compound</th>
<th>O−Ti</th>
<th>O−M</th>
<th>$\delta_{\text{iso}}$(mm)</th>
<th>$\sigma_{\text{iso}}$</th>
<th>$\eta_{\text{asy}}$</th>
<th>$\delta_{\text{TB-mBJ}}$(mm)</th>
<th>$\sigma_{\text{GIPAW-PBE}}$</th>
<th>$\sigma_{\text{aniso}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgTiO$_3$(R3)</td>
<td>1.860</td>
<td>2.027</td>
<td>−12.82</td>
<td>198.30</td>
<td>0.349</td>
<td>388.36</td>
<td>398.0$^a$</td>
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</tr>
<tr>
<td>CaTiO$_3$(Pm3m)</td>
<td>1.898</td>
<td>2.684</td>
<td>−49.10</td>
<td>222.82</td>
<td>0.000</td>
<td>424.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaTiO$_3$(Pbnm)</td>
<td>1.953</td>
<td>2.353</td>
<td>−80.16</td>
<td>225.35</td>
<td>0.000</td>
<td>455.04</td>
<td>448.0$^d$</td>
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<tr>
<td>SrTiO$_3$(Pm3m)</td>
<td>1.951</td>
<td>2.373</td>
<td>−75.38</td>
<td>229.07</td>
<td>0.133</td>
<td>451.24</td>
<td>443.4$^d$</td>
<td></td>
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<tr>
<td>BaTiO$_3$(Pm3m)</td>
<td>1.953</td>
<td>2.761</td>
<td>−86.82</td>
<td>255.18</td>
<td>0.000</td>
<td>462.73</td>
<td>491.25$^b$</td>
<td>465.0$^b$</td>
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<tr>
<td>BaTiO$_3$(P4mm)</td>
<td>2.004</td>
<td>2.834</td>
<td>−165.95</td>
<td>287.90</td>
<td>0.000</td>
<td>542.26</td>
<td>560.52$^b$</td>
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<tr>
<td></td>
<td>1.970</td>
<td>2.828</td>
<td>−148.76</td>
<td>270.76</td>
<td>0.103</td>
<td>524.98</td>
<td>532.23$^b$</td>
<td>523.0$^b$</td>
</tr>
</tbody>
</table>

$^a$We compare our results with available measured and calculated GIPAW (where taken from) NMR chemical shifts. The experimental shifts $\delta_{\text{exp}}$ are given with reference H$_2$O. The theoretical shifts $\delta_{\text{theo}}$ are given using a reference taken from linear fit of the calculated absolute shieldings vs experimental shifts for compounds as shown in Figure 6. Reference 30. $^b$Reference 98. $^c$Reference 99. $^d$Reference 100.
corresponding absolute isotropic shielding values calculated by PBE-GGA and BJ functionals for the MgTiO₃. Anyway since the TB-mBJ results are closer to the experimental values, in the rest of this paper we only focus on the results obtained by the TB-mBJ functional. It is worth mentioning that the reference value of 373.6 ppm is approximately obtained from the fit, because the value of the absolute reference shielding cannot be exactly calculated because in experiments only the liquid phase of H₂O is used as a reference. A similar restriction has been reported for inorganic sulfides and sulfates. In principle, however, magnetic shielding can be also directly calculated for H₂O assuming an ice atomic structure. Therefore, it may be interesting to see how far the shielding of ice can be from the reference value of 373.6 ppm predicted for the liquid H₂O by the most successful functional used in this work, TB-mBJ. Consequently, we have calculated the absolute isotropic shielding for the ordinary ice or frozen water, i.e., H₂O ice Iₐ, using TB-mBJ. The ordinary ice crystallizes in the space group of P₆₃mc, which is a hexagonal structure with lattice parameters of a = b = 7.82, c = 7.36 Å. We have fully relaxed the internal atomic positions with the criterion of 1 mRy/Bohr on the exerted forces. The computed shielding is calculated to be 302.24 ppm for the ice Iₐ, which is less by 71.2 ppm than the reference value of 373.6 ppm obtained for the liquid H₂O using the linear fit of the calculated magnetic shielding versus experimental chemical shifts. One of the sources of this discrepancy (373.6 – 302.24 = 71.12 ppm) may be attributed to the different phases of the solid H₂O ice and the liquid H₂O water.

The variation of our calculated chemical shielding, σiso, with respect to the compounds is shown in the bottom-left inset of Figure 6 and Table 2. But, σiso cannot be directly compared with the experimental data. This is because in experiment chemical shift (δiso) is measured; however, in theory magnetic shielding (∆σiso) is calculated. Therefore, to compare our theoretical results with the experimental data, we have also theoretically predicted the chemical shift using TB-mBJ which we here call δiso to be distinguished from the experimental δiso. To this end, we have obtained δiso from the TB-mBJ linear relation of 373.6 – 0.995δiso as δiso = (373.6 – σiso)/0.995. Our theoretically predicted δiso using FP-APW+lo+NMR-LO-TB-mBJ together with the available experimental δiso and their perturbative expansion is expressed in terms of the unoccupied orbitals via green functions for the calculation of NMR magnetic shielding using perturbation method, as can be seen from eqs 3 and 4. As expressed in the numerator of eq 4, these occupied and unoccupied wave functions are coupled to each other, and therefore both of them can affect the induced current and hence the magnetic shielding. Furthermore, due to the energy that appears in the denominator of eq 4, it is expected that the improvement of the band gap employing the TB-mBJ functional can also affect the value of the NMR magnetic shielding. In other words, since the energy gap between VBM and CBM states predicted by TB-mBJ functional is larger than those predicted by PBE-GGA and BJ functionals and our perturbative expansion is expressed in terms of the unperturbed states, the change in the energy difference between these states can change the NMR magnetic shieldings, as well.

Moreover, it is noteworthy that the low-lying unoccupied Ca-3d orbitals problem is not seen here. Previous calculations have shown that the partially covalent Ca–O bond has a huge impact on the O chemical shieldings. The O sites with largest shielding errors are the ones closest to the calcium atoms. However, as can be seen in Table 2, in our calculations the nearest-neighbors of oxygens are Ti atoms and the covalent interactions between the O-2p and unoccupied Ti-3d states have the greatest impact on the observed trend. Furthermore, the correlations between experimental and theoretical electronic bandgaps using PBE-GGA, BJ, and TB-mBJ are quantitatively investigated. To this end, the calculated bandgaps using these three functionals are plotted in terms of the experimental bandgaps for the compounds under question. The data are then linearly least-squares fitted, as shown in Figure 8. As can be seen in this figure, the slopes of the fitted lines obtained for PBE-GGA, BJ, and TB-mBJ are 1.64, 1.53, and 1.14, respectively. The results show that the slope of the fitted line of the BJ functional (1.53) is closer to the ideal slope (+1) than that of the PBE-GGA functional (1.64). This shows that here the bandgaps are a little bit better predicted by BJ than PBE-GGA for the compounds under study. Furthermore, we clearly observe that the deviation of the TB-mBJ slope from the ideal slope (+1) is less than those of the PBE-GGA and BJ. This confirms that here TB-mBJ is the most successful functional for the bandgaps prediction over the PBE-GGA and...
BJ for these compounds. This is consistent with our last discussion regarding the deviation of the magnetic shielding from the ideal relation (slope $-1$ to the measured shift); see Figure 6 and the presented discussion on the slope of the fitted TB-mBJ-line.

Let us now turn our attention to the origin of the variations of the oxygen NMR magnetic shielding through the series of the compounds under question. To this purpose, first the partial densities of states (DOSs) are calculated for all the compounds, as shown in Figure 7. As can be seen from the valence regions, the O−DOSs of the compounds are mainly dominated by their O-2p states below the Fermi level ($E_F = 0$) in $(-5$ eV, $E_F$) energy interval, while O-2s states are distributed far from the Fermi level around $-18$ eV. The O-2p-DOSs almost independently of all the compounds, and their different crystal structures are broadened with bandwidths of around $5$ eV, whereas the O-2s DOSs of these compounds are narrow, showing a partial hybridization with the alkaline-earth-metals-p states. The DOS results show that the Mg-p-DOS in MgTiO$_3$(Pm3m) is almost empty in the energy interval $(-20, 20$ eV). In the other compounds, the alkaline-earth-metals-p-DOSs in this energy interval are located far from the Fermi level. Thus, contributions of the alkaline-earth-metals-p-DOSs to the physical properties may be smaller than those valence states such as O-2p-DOSs and Ti-d-DOSs which are closer to the Fermi level. In contrast to the alkaline-earth-metals-p-DOSs, the Ti-d-DOSs and O-2p-DOSs in all the compounds are then significantly contributed in the valence region close to the Fermi level. Thus, the physical properties of the systems under study can be considerably affected by the Ti-d-DOSs and O-2p-DOSs states. In addition to the valence region, the Ti-d-DOSs play a key role in the conduction regions of all the compounds, as well. The d-DOSs of all the alkaline-earth-metals can be also observed in the conduction regions of all the compounds under study except for MgTiO$_3$(Pm3m). The Ti-d-DOSs partially overlap with the d-DOSs of all the alkaline-earth-metals in all the compounds under study apart from the Mg case.

Keeping in mind the above-discussed DOSs and their distributions, we below show that the valence O-2p orbital together with the conduction d-orbitals of Ti and alkaline-earth-metals can explain the observed trend of the magnetic shielding through the series of the compounds under investigation. To this end, the total magnetic shielding of the oxygen atom ($\sigma_{\text{iso}-\text{total}}$), its atomic sphere contribution ($\sigma_{\text{iso}-\text{sphere}}$), and the interstitial contribution ($\sigma_{\text{iso}-\text{interstitial}}$) are calculated through the series. Furthermore, $\sigma_{\text{iso}-\text{sphere}}$ is decomposed into its contributions of $\sigma_{\text{iso-core}(1s)}$, $\sigma_{\text{iso}(2s)}$, and $\sigma_{\text{iso}(2p)}$; see Figure 9. As can be clearly seen in this figure, the major contribution of the total magnetic shielding is due to the integration of the current within the oxygen atomic sphere ($\sigma_{\text{iso-sphere}}$), while the other contributions from interstitial, titanium, and the alkaline earth metal spheres are small and approximately negligible. Therefore, we restrict our analysis to the contributions of oxygen atomic spheres. Note, however, that although the largest magnetic shielding contribution (275.2 ppm) comes from $\sigma_{\text{iso-core}(1s)}$, the magnitude of this contribution is constant through the series of the compounds. Hence, $\sigma_{\text{iso-core}(1s)}$ cannot explain the variation of the magnetic shielding. The $\sigma_{\text{iso}(2s)}$ is also almost constant and shows only a small variation (about 36–40 ppm). The other contributions to the magnetic shielding (not shown here) are less than 2 ppm. As can be seen from Figure 9, the main contribution to the magnetic shielding which can well describe the observed trend originates from $\sigma_{\text{iso}(2p)}$.

A key feature of the magnetic shieldings in these perovskites compounds is the covalent interactions between the O(2p) and unoccupied Ti(3d) states. By considering the optimized distances between titanium and oxygen atoms in the investigated structures, as indicated in Table 2, it is observed that all the bond lengths increase on moving from top to bottom down the group in the Periodic Table. Conversely, as can be seen in Table 2, the calculated magnetic shieldings decrease when moving down the group in the Periodic Table. In particular, it is observed that the $^{17}$O chemical shifts are sensitive to the hybridization between O(2p) and the Ti(3d) orbitals of neighboring atoms. The variation of O−Ti bond distances among the different O-sites in the perovskite crystals results in different O(2p)-Ti(3d) coupling strengths, which are reflected by the changes in the calculated oxygen magnetic shieldings. In fact, chemical shieldings vary approximately linearly as a function of the nearest-neighbor O−Ti bond length. Another striking point in Table 2 is the large positive $\sigma_{\text{dia}}$ versus $\sigma_{\text{iso}}$ for all the materials. This means that $\sigma_{\text{dia}}$ is
positive or shielded in comparison to $\sigma_n$ and $\sigma_p$ which are negative or deshielded. This is due to the hybridization between the O-2p and Ti-3d states.

In the next step, in order to understand the origin of these variations, we have decomposed the dominant oxygen p-band (O-p) contribution of isotropic shielding with respect to s-, p-, and d-components of the ground-state wave functions $\Psi^{(0)}_o$ and its first-order perturbation $\Psi^{(1)}_o$, as performed and shown in Figure 10. The reason for such further decomposition is that both $\Psi^{(0)}_o$ and $\Psi^{(1)}_o$ contribute to the induced current by $\langle \Psi^{(0)}_o \mid J_p(\mathbf{r}') \Psi^{(1)}_o \rangle$, as can be seen in eq 3. Therefore, the major contributions are shown for both $\Psi^{(0)}_o$ and $\Psi^{(1)}_o$ in Figure 10.

As expected, almost the main values of the shielding come from the O-p ($l = 1$) components of $\Psi^{(0)}_o$ and $\Psi^{(1)}_o$. Although it appears that the largest contribution in the first-order perturbation $\Psi^{(1)}_o$ comes from the O-d band, we should note that this contribution is almost constant and does not vary through the compounds, see Figure 10. Therefore, the variation of the O-p component of the shielding cannot be attributed to the O-d of $\Psi^{(1)}_o$, as well. On the other hand, for the first order perturbation, the O-p part varies and dominates and so dictates the trend, while the O-s components are fairly small and constant through the compounds, as shown in Figure 10. Thus, for investigation of the origin of the shielding variations, we can focus only on the $l = 1$ components of $\Psi^{(0)}_o$ and $\Psi^{(1)}_o$, and the effects of their contributions on the induced current.

In Figure 11, we have further decomposed the shielding considering the integral $\langle \Psi^{(0)}_o(\mathbf{r}) \mid \mathbf{r} \cdot \mathbf{B} \mid \Psi^{(0)}_o(\mathbf{r}') \rangle$ appearing in eq 4 into the angular components of the empty states $\Psi^{(0)}_e$. We recall that in eq 4, the first order perturbation $\Psi^{(1)}_e$ is expanded in terms of the unoccupied states $\Psi^{(0)}_e$. Thus, a state can contribute in this equation, only when it appears in $\Psi^{(0)}_e$. We should also note that the contribution is affected by both the value of the integral and the value of the energy difference $\epsilon - \epsilon_0$ in the denominator of the ratio $\langle \Psi^{(0)}_e(\mathbf{r}) \mid \mathbf{r} \cdot \mathbf{B} \mid \Psi^{(0)}_e(\mathbf{r}') \rangle / (\epsilon - \epsilon_0)$. The decomposition is performed as in Figure 10, only oxygen atomic sphere was taken into account, and the integral $\langle \Psi^{(0)}_e(\mathbf{r}) \mid \mathbf{r} \cdot \mathbf{B} \mid \Psi^{(0)}_e(\mathbf{r}') \rangle$ is considered over the whole of the unit cell. This integral is split into four regions, namely, oxygen (O), alkaline-metal (M), and titanium (Ti) spheres, and an interstitial (I) region, according to the APW method. Since within the atomic spheres, the empty conduction band orbitals are not localized, the interstitial part forms a large fraction of the integral which cannot be uniquely assigned to a specific atomic or orbital character of the corresponding wave functions. Although a significant part of $\langle \Psi^{(0)}_e(\mathbf{r}) \mid \mathbf{r} \cdot \mathbf{B} \mid \Psi^{(0)}_e(\mathbf{r}') \rangle$ (about 210 ppm) contributes to the resulting NMR shielding, it is relatively constant, and the variation rarely exceeds from 10 ppm; see Figure 11a. The component which comes from the oxygen sphere $\Psi^{(0)}_e(O)$ is larger and vary from $-340$ ppm to $-430$ ppm; however, they alone cannot explain the observed trends in total shielding variation. The other outstanding term which determines the observed trends of the total shielding is due to the integrals involving the alkaline-metal spheres, $\Psi^{(0)}_e(M)$, and titanium spheres, $\Psi^{(0)}_e(Ti)$, as shown in Figure 11a.

For better understanding, we have decomposed the contributions of atomic spheres of alkaline earth metals, titanium, and oxygen to the total magnetic shielding, according to the first order perturbation with respect to the empty states $\Psi^{(0)}_e$, which contribute to the first order perturbation $\Psi^{(1)}_e$ via the matrix elements $\langle \Psi^{(0)}_e(\mathbf{r}) \mid \mathbf{r} \cdot \mathbf{B} \mid \Psi^{(0)}_e(\mathbf{r}') \rangle$ in eq 4. (a) Decomposition of the integral according to the (a) empty states $\Psi^{(0)}_e$ in the muffin-tin spheres of the oxygen (O), titanium (T), alkaline metal (M), and the interstitial (I) region, and (b) angular momentums of the O, T, and M empty states $\Psi^{(0)}_e$. 

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**Figure 10.** Decomposition of the dominant p-orbital of oxygen band contribution (O-p) into s-, p-, and d-components of the ground-state wave functions $\Psi^{(0)}_o$ and its first-order perturbation $\Psi^{(1)}_o$.

**Figure 11.** Dominant shielding contributions to the first order perturbation with O-p character $\Psi^{(1)}_o$ with respect to the empty states $\Psi^{(0)}_e$, which contribute to the first order perturbation $\Psi^{(1)}_e$ via the matrix elements $\langle \Psi^{(0)}_e \mid \mathbf{r} \cdot \mathbf{B} \Psi^{(0)}_e \rangle$ in eq 4. (a) Decomposition of the integral according to the (a) empty states $\Psi^{(0)}_e$ in the muffin-tin spheres of the oxygen (O), titanium (T), alkaline metal (M), and the interstitial (I) region, and (b) angular momentums of the O, T, and M empty states $\Psi^{(0)}_e$. 

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DOI: 10.1021/acs.jpcc.8b05356

*J. Phys. Chem. C* 2018, 122, 20597–20601
to their \( l \) characters of empty states \( (\Psi_{e}^{l}) \), as shown Figure 11b. Here, only the important components that have major contributions in the observed trend are shown; the other components are not shown since they are small and constant through the compounds, and their variations do not exceed 7 ppm. The operator in the matrix relation \( \langle \Psi_{e}^{(0)} | (\vec{r} - \vec{r}') \times \vec{p} \cdot \vec{B} \Psi_{e}^{(0)} \rangle \) is a product of position and momentum operators, and therefore, according to the selection rules just \( \Delta l = 0, \pm 1 \) components can appear in coupling between \( \Psi_{e}^{(0)} \) and \( \Psi_{e}^{(0)} \) wave functions. As shown before, the NMR magnetic shielding generally comes from oxygen \( l_{o} = 1 \) character and therefore can only be coupled with \( l_{e} = 0, 1, 2 \) components, where the \( o \) (\( e \)) index used in \( l_{o} (l_{e}) \) means occupied (empty). According to this point, after calculating the nonzero NMR magnetic shielding contributions, we have concluded that the contributions of the unoccupied parts of the oxygen \( s \), alkaline-metal \( s \) and \( p \), as well as of the titanium \( s \) and \( p \) components are small and vary from about 2 up to 7 ppm through the series of the compounds and therefore they are not shown here in Figure 11b. On the other hand, the \( l_{o} = 2 \) and \( l_{e} = 2 \) of the oxygen for both conduction and valence band states are large, but have no significant variation through the compounds, leading to a constant but large component in the magnetic shielding, see \( \Psi_{e}^{(0)}(O-d) \) in Figure 11b.

Finally, as can be seen in Figure 11b, the d-components of the alkaline earth metals and titanium as well as the p-components of the oxygen wave functions have the largest contributions to the observed magnetic shielding variations. This means that in addition to the p-character of the oxygen atom, the d-components of the alkaline-earth metals and titanium wave functions are effective in the observed trend of the magnetic shielding through the series of compounds. In addition, it is observed that when going down through the Periodic Table, the coupling of the oxygen valence states to the alkaline earths and titanium \( l_{o} = 2 \) characters of the conduction states leads to an increase in the absolute value of this contribution to the magnetic shielding.

**CONCLUSION**

In this paper, microscopic origins of the nuclear magnetic resonance (NMR) shielding have been theoretically analyzed and explored at the \( ^{17}O \)-sites of a variety of oxide-based (group II perovskites) materials. The NMR calculations are performed using an accurate and reliable full-potential APW-based NMR scheme, as recently developed by Laskowski and Blaha and implemented in the WIEN2k code. Unlike previous approaches, in this method no restriction or approximation is used to calculate the induced current density and its integration. To ensure the accuracy of the results, a variety of functionals such as PBE-GGA, B\( \text{J} \), and TB-mBJ have been tested. Linear fitting of the correlation between different calculated approaches and available experimental data has shown that the TB-mBJ functional is more successful to reproduce the ideal slope \((-1)\) than the other functionals. Thus, our chemical shielding results are further improved over the standard PBE-GGA by the TB-mBJ functional compared to the experimental data. In addition, comparing the results has shown that the calculated chemical shifts using the above new full potential APW-based NMR method are in agreement with the corresponding experimental data and with available results produced by the GIPAW method. To anticipate further experimental measurements in the future, using the equation derived from the linear fit we have theoretically predicted the chemical shifts of the compounds that their experimental values have not been measured or reported yet. Our results have shown that the NMR shielding varies by around 180 ppm through the materials. In order to realize the origins of these variations in the investigated materials, we have decomposed the induced current and consequently the total magnetic shielding into its components. The decompositions have revealed that the total magnetic shielding as well as the induced current originates from the oxygen-p \((l = 1)\) contribution. However, the variations cannot be attributed to this orbital alone. In the perturbative method which we used, the valence wave functions are expanded in terms of conduction wave functions and coupled together, and therefore the conduction orbitals contribute to the magnetic shielding too. We then decompose the total magnetic shielding in terms of the wave functions of the valence and conduction bands. The calculations have shown that although the d-band of oxygen has the largest contribution to the perturbative wave functions, its value is relatively constant throughout the compounds, and therefore this orbital has no contribution in the observed trend. In addition, apart from the d-bands of alkaline earth metals and titanium, other parts of the wave functions do not contribute to the total magnetic shielding and their values do not exceed 7 ppm. Our investigations showed that the observed trend of the magnetic shielding within the series originates not only from the oxygen-p character but also from the change of the coupling to the conduction band alkaline-metal-d and titanium-d character has an influence on it. In fact, the coupling of the oxygen valence states to the alkaline-earth and titanium \( l_{o} = 2 \) character of the conduction states leads to an increase of the absolute value of this contribution to the magnetic shielding when going down the Periodic Table. Furthermore, the isotropic magnetic shielding is also calculated for ordinary \( H_{2}O \) ice using the TB-mBJ functional, and the results are compared with the corresponding value derived from the linear fit of the calculated magnetic shielding using TB-mBJ versus experimental chemical shifts for the reference liquid \( H_{2}O \). The comparison shows that the shielding calculated for the \( H_{2}O \) in its ice \( \text{Ih} \) phase is less than that derived from the linear TB-mBJ-fit for the \( H_{2}O \) in its liquid water phase by 71.2 ppm.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: sjalali@sci.ui.ac.ir.*

**ORCID**

Saeid Jalali-Asadabadi: 0000-0002-7353-8923

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is supported by the University of Isfahan (UI), Isfahan, Iran.

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