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Calculation of NMR chemical shifts for extended systems using ultrasoft pseudopotentials

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We present a scheme for the calculation of magnetic response parameters in insulators using ultrasoft pseudopotentials. It uses the gauge-including projector augmented wave method [C. J. Pickard and F. Mauri, Phys. Rev. B **63**, 245101 (2001)] to obtain all-electron accuracy for both finite and infinitely periodic systems. We consider in detail the calculation of NMR chemical shieldings. The approach is successfully validated first for molecular systems by comparing calculated chemical shieldings for a range of molecules with quantum chemistry results and then in the solid state by comparing ^{17}O NMR parameters calculated for silicates with experiment.

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I. INTRODUCTION

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful experimental probe of structure and dynamics on an atomic scale. It has been widely applied to problems in chemistry, material science, biology, physics, and geology. However, there is no simple theorem which allows the measured spectrum to be related to the underlying chemical structure. For simple organic molecules and certain crystal structures, empirical rules have been found, but for more complex systems, interpretation of the experimental spectra can be difficult and often ambiguous.

First principles quantum mechanical calculations of NMR parameters have the potential to provide the vital missing link between NMR spectra and the underlying microscopic structure. Traditional quantum chemical techniques[1] have been successfully applied to assign the solution-state NMR spectra of molecular systems and establish key conformational and structural trends.[2] In order to apply these techniques to solid-state NMR, it has been necessary to devise finite clusters of atoms which model the local environment around a site of interest in the true extended structure. While this has led to successful studies of NMR chemical shifts in systems such as molecular crystals,[3] supramolecular assemblies,[4] and organometallic compounds,[5] it is clear that there are advantages in an approach that inherently takes account of the long-range electrostatic effects in extended systems. Mauri *et al.*[6] and Sebastiani and Parrinello[7] have presented approaches to calculate NMR chemical shieldings for systems with periodic boundary conditions. While both of these methods were formulated for an all-electron Hamiltonian, they were applied in the context of calculations based on norm-conserving pseudopotentials. The methods took no account of the complications introduced by the use of pseudopotentials and as a result were limited to light elements in which the pseudization error could be made to be small. Nevertheless, some valuable applications have been presented.[8–10] Recently, Pickard and Mauri introduced the gauge-including projector augmented wave (GIPAW) method[11] to correctly account for the use of pseudopotentials. This is an adaption of Blöchl's projector augmented wave[12] (PAW) method to respect the translational invariance of a system in a magnetic field. The GIPAW method enables NMR parameters to be calculated within the plane-wave pseudopotential formalism of density functional theory with all-electron accuracy. The technique has been applied, in combination with experimental NMR spectroscopy, to systems such as minerals,[13–15] glasses,[16,17] and molecular crystals.[18–20] The GIPAW method was originally implemented using norm-conserving pseudopotentials (NCPs); however, first row elements, transition, and rare-earth metals require very large numbers of plane waves to accurately describe the valence wave functions. As both the calculation time and the memory requirement scale as roughly the three-halves power of the maximum plane wave cutoff energy, it is clearly desirable to use softer and hence more efficient pseudopotentials. In this respect, the current "state of the art" are Vanderbilt's "ultrasoft" pseudopotentials (USPs).[21] These are designed to be as soft as possible in the core region and require a minimum number of plane waves for full convergence. This softness is achieved at the cost of relaxing the property of norm conservation and so the pseudo-wave-functions obey a generalized orthonormality condition.

In this paper, we develop the necessary computational tools to calculate magnetic resonance parameters in extended systems with USPs and examine the particular case of NMR chemical shieldings. The response of a system to an external magnetic field is treated within density functional perturbation theory (DFPT). DFPT expressions with USPs have previously been reported in connection with band curvature,[22] phonon dispersion spectra,[23] and dielectric tensors.[24] Our expressions can be applied with local and semilocal density functionals such as local density approximation (LDA) or generalized gradient approximation.

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The paper is organized as follows: In Sec. II, we briefly review the use of the GIPAW method to reconstruct all-electron properties from a pseudopotential calculation. In Secs. III and IV, we obtain expressions for the all-electron induced current density; first for molecular systems and then for infinitely periodic systems. Details of the practical implementation of the method and its use to calculate NMR chemical shielding tensors are presented in Sec. V. Finally, in Sec. VI, we present a validation of the method for a variety of systems.

II. ULTRASOFT PSEUDOPOTENTIALS AND THE GIPAW METHOD

When a diamagnetic material is placed in magnetic field, electronic currents will be induced in the material. These induced currents cause a small variation in the local magnetic field which can be detected in a NMR experiment, giving rise to the so called chemical shielding effect. The chemical shielding tensor $\vec{\sigma}(\mathbf{r})$ is defined as the ratio between a uniform external magnetic field $\mathbf{B}_{\text{ext}}$ and the induced magnetic field $\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r})$,

$$\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r}) = -\vec{\sigma}(\mathbf{r})\mathbf{B}_{\text{ext}} = \frac{1}{c}\int d^3r'\,\mathbf{j}^{(1)}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}, \tag{1}$$

where $\mathbf{j}^{(1)}$ is the first-order induced electric current. It is clear from Eq. (1) that the question of calculating chemical shielding is essentially that of calculating the induced current. It can also be seen from Eq. (1) that the chemical shielding is strongly dependent on the induced current close to the nucleus. This is problematic for calculations based on the use of pseudopotentials as is precisely in this region that the pseudo-wave-functions have an unphysical form. The now well established approach to deal with such a problem is the PAW method introduced by Blöchl[12] in which the all-electron wave function Ψ is derived from the pseudo-wave-function $\tilde{\Psi}$ by means of a linear transformation. The PAW method has been used to calculate electron paramagnetic resonance (EPR) hyperfine parameters,[12] electric field gradient tensors,[25] and electron energy loss spectroscopy[26] from calculations based on norm-conserving pseudopotentials. Although the PAW scheme could be applied to a system in a magnetic field, it is not a computationally feasible approach. In a uniform magnetic field, a rigid translation of all the atoms in the system by a vector $\mathbf{t}$ causes the wave functions to pick up an additional field-dependent phase factor, which can we written as, using the symmetric gauge for the vector potential, $\mathbf{A}(\mathbf{r}) = 1/2\mathbf{B}\times\mathbf{r}$,

$$\langle \mathbf{r}|\Psi_n'\rangle = e^{(i/2c)\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\langle \mathbf{r}-\mathbf{t}|\Psi_n\rangle. \tag{2}$$

In the original PAW approach, a large number of projectors would be required to describe the oscillations in the wave functions due to this phase. Pickard and Mauri introduced[11] a field-dependent transformation operator which, by construction, imposes the translational invariance exactly. In their GIPAW approach for an all-electron operator O, the corresponding pseudo-operator $\bar{O}$ is given by

$$\begin{aligned}\bar{O} = O + \sum_{\mathbf{R},n,m} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{p}_{\mathbf{R},n}\rangle \\ \times[\langle\phi_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}Oe^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\phi_{\mathbf{R},m}\rangle \\ -\langle\tilde{\phi}_{\mathbf{R},i}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}Oe^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}.\end{aligned} \tag{3}$$

$|\phi_{\mathbf{R}n}\rangle, |\tilde{\phi}_{\mathbf{R}n}\rangle$ are all-electron and pseudo-partial-waves and $\langle\tilde{p}_{\mathbf{R}n}|$ are a set of projectors such that $\langle\tilde{p}_{\mathbf{R}n}|\tilde{\phi}_{\mathbf{R}'m}\rangle = \delta_{\mathbf{R}\mathbf{R}'}\delta_{nm}$. Each projector and partial wave is an atomiclike function centered on an atomic site $\mathbf{R}$, and n is a composite index which refers to both the angular momentum quantum numbers and to an additional number which is used if there is more than one projector per angular momentum channel. Pickard and Mauri commented the connection between the GIPAW approach and the gauge-including atomic orbital[27] (GIAO) and the independent gauge for localized orbital[28] (IGLO) methods. They also noted that in the GIPAW approach, the phase required to maintain translational invariance is carried by the operators, while in the GIAO and IGLO approaches, the field-dependent phase is attached to the basis functions and to the occupied electronic orbitals, respectively. Following Ref. 11, we indicate with a bar operators obtained using the GIPAW transformation, Eq. (3). Operators obtained with the PAW transformation [the $\mathbf{B}=0$ limit of Eq. (3)] are indicated with a tilde.

III. THEORY

We now derive each of the ingredients necessary to calculate the induced current. We will need to expand quantities as a power series in the applied magnetic field and we introduce a notation such that $O^{(0)}$ and $O^{(1)}$ represent quantities to zeroth and linear orders in the field.

A. Ultrasoft Hamiltonian in zero magnetic field

The key ingredient of the ultrasoft scheme is that norm of the pseudo-partial-waves in the augmentation region is different from that of the corresponding all-electron partial waves. We can thus define a nonzero charge augmentation term $q_{\mathbf{R},n,m}$:

$$q_{\mathbf{R},nm} = \langle\phi_{\mathbf{R},n}|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|\tilde{\phi}_{\mathbf{R},m}\rangle. \tag{4}$$

The norm of a pseudo-wave-function can be computed as expectation value of the pseudo-operator $\tilde{1} = S^{(0)}$. Using Eq. (1),

$$S^{(0)} = 1 + \sum_{\mathbf{R},n,m}|\tilde{p}_{\mathbf{R},n}\rangle q_{\mathbf{R},nm}\langle\tilde{p}_{\mathbf{R},m}| = 1 + \sum_{\mathbf{R}} Q_{\mathbf{R}}. \tag{5}$$

As a result, a normalized eigenstate of the pseudo-Hamiltonian obeys the generalized equations:

$$\tilde{H}^{(0)}|\tilde{\Psi}_o^{(0)}\rangle = \varepsilon_o^{(0)}S^{(0)}|\tilde{\Psi}_o\rangle, \tag{6}$$

and

$$\langle\tilde{\Psi}_o^{(0)}|S^{(0)}|\tilde{\Psi}_{o'}\rangle = \delta_{o,o'}. \tag{7}$$

B. First-order GIPAW Hamiltonian

The pseudo-Hamiltonian in the presence of a uniform magnetic field can be obtained from the all-electron Hamiltonian and the GIPAW transformation [Eq. (3)] (see Appendix A). The contribution to zeroth order in the field is given by Eq. (6) and the first-order term, $\bar{H}^{(1)}$, is

$$\bar{H}^{(1)} = \frac{1}{2c}\left(\mathbf{L} + \sum_{\mathbf{R}} \mathbf{R} \times \frac{1}{i}[\mathbf{r}, V^{\mathrm{nl}}_{\mathbf{R}}] + \sum_{\mathbf{R}} \mathbf{L}_{\mathbf{R}} Q_{\mathbf{R}}\right) \cdot \mathbf{B}, \tag{8}$$

where $L_{\mathbf{R}}$ is the angular momentum operator centered on the atomic site $\mathbf{R}$ $[L_{\mathbf{R}}=(\mathbf{r}-\mathbf{R})\times\mathbf{p}]$ and $V^{\mathrm{nl}}_{\mathbf{R}}$ is the nonlocal pseudopotential operator at the atomic site $\mathbf{R}$.

C. Translational invariance of the S operator

For the eigenenergies in Eq. (6) to be invariant under a translation in the presence of a uniform magnetic field, it is not sufficient to consider just the field dependence of the pseudo-Hamiltonian; the $S=\bar{1}$ overlap operator, obtained with the GIPAW transformation, Eq. (3), also shows a dependence on $\mathbf{B}$,

$$S = 1 + \sum_{\mathbf{R}} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} Q_{\mathbf{R}} e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}. \tag{9}$$

The zeroth order term is given by Eq. (5) and the term linear in the field may be written as

$$S^{(1)} = \frac{1}{2c}\sum_{\mathbf{R}} \mathbf{R} \times \frac{1}{i}[\mathbf{r}, Q_{\mathbf{R}}] \cdot \mathbf{B}. \tag{10}$$

For later convenience, we introduce what we will call the augmented velocity operator

$$\begin{aligned}\mathbf{v}(\varepsilon_o^{(0)}) &= \frac{1}{i}[\mathbf{r}, (\bar{H}^{(0)} - \varepsilon_o^{(0)} S^{(0)})] \\ &= \frac{1}{i}\nabla + \frac{1}{i}\sum_{\mathbf{R}} [\mathbf{r}, (V^{\mathrm{nl}}_{\mathbf{R}} - \varepsilon_o^{(0)} Q_{\mathbf{R}})].\end{aligned} \tag{11}$$

D. Current operators

We can apply the GIPAW transformation to obtain an expression for the gauge invariant current pseudo-operator. In this case, we can use directly the result obtained in Ref. 11 for norm-conserving pseudopotentials. Indeed, the norm-conservation condition was not used to derive this result. We recall that the all-electron current operator, $\mathbf{J}(\mathbf{r}')$, is

$$\mathbf{J}(\mathbf{r}') = \mathbf{J}^d(\mathbf{r}') + \mathbf{J}^p(\mathbf{r}'), \tag{12}$$

where the diamagnetic current, $\mathbf{J}^d(\mathbf{r}')$, is given by

$$\mathbf{J}^d(\mathbf{r}') = \frac{1}{c}\mathbf{A}(\mathbf{r}')|\mathbf{r}'\rangle\langle\mathbf{r}'| \tag{13}$$

and the paramagnetic current, $\mathbf{J}^p(\mathbf{r}')$,

$$\mathbf{J}^p(\mathbf{r}') = -\frac{\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}}{2}. \tag{14}$$

Using the GIPAW transformation and expanding in powers of the magnetic field the resulting current pseudo-operator, one obtains[11]

$$\bar{\mathbf{J}}(\mathbf{r}') = \bar{\mathbf{J}}^{(0)}(\mathbf{r}') + \bar{\mathbf{J}}^{(1)}(\mathbf{r}') + O(B^2), \tag{15}$$

with

$$\bar{\mathbf{J}}^{(0)}(\mathbf{r}') = \mathbf{J}^p(\mathbf{r}') + \sum_{\mathbf{R}} \Delta\mathbf{J}^p_{\mathbf{R}}(\mathbf{r}'), \tag{16}$$

and

$$\begin{aligned}\bar{\mathbf{J}}^{(1)}(\mathbf{r}') = -\frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'| + \sum_{\mathbf{R}}\Bigg\{&\Delta\mathbf{J}^d_{\mathbf{R}}(\mathbf{r}') \\ &+ \frac{1}{2ci}[\mathbf{B}\times\mathbf{R}\cdot\mathbf{r}, \Delta\mathbf{J}^p_{\mathbf{R}}(\mathbf{r}')]\Bigg\},\end{aligned} \tag{17}$$

where

$$\begin{aligned}\Delta\mathbf{J}^p_{\mathbf{R}}(\mathbf{r}') = \sum_{n,m} &|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{J}^p(\mathbf{r}')|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{J}^p(\mathbf{r}')|\tilde{\phi}_{\mathbf{R},m}\rangle] \\ &\times\langle\tilde{p}_{\mathbf{R},m}|\end{aligned} \tag{18}$$

is the paramagnetic augmentation operator, and

$$\begin{aligned}\Delta\mathbf{J}^d_{\mathbf{R}}(\mathbf{r}') = -\frac{\mathbf{B}\times(\mathbf{r}'-\mathbf{R})}{2c}\sum_{n,m}&|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\phi_{\mathbf{R},m}\rangle \\ &- \langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}|\end{aligned} \tag{19}$$

is the diamagnetic augmentation operator.

E. Current within DFPT

In the NCP formalism, the only contribution to an observable, such as the current density, arises from components of the first-order wave function projected into the unoccupied subspace.[29] In the USP formalism, components of first-order wave function in the occupied subspace may also contribute to an observable. As shown in Appendix B, this gives rise to an additional term in the expression for current density as compared to the NCP case. The total induced valence current can be written as

$$\begin{aligned}\mathbf{j}^{(1)}(\mathbf{r}') = 4\sum_{o} &\mathrm{Re}\{\langle\bar{\Psi}^{(0)}_o|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')\mathcal{G}(\varepsilon^{(0)}_o)(\bar{H}^{(1)} - \varepsilon^{(0)}_o S^{(1)})|\bar{\Psi}^{(0)}_o\rangle\} \\ &- 2\sum_{oo'}\langle\bar{\Psi}^{(0)}_o|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}^{(0)}_{o'}\rangle\langle\bar{\Psi}^{(0)}_{o'}|S^{(1)}|\bar{\Psi}^{(0)}_o\rangle \\ &+ 2\sum_{o}\langle\bar{\Psi}^{(0)}_o|\bar{\mathbf{J}}^{(1)}(\mathbf{r}')|\bar{\Psi}^{(0)}_o\rangle,\end{aligned} \tag{20}$$

(21)

where the sums over o and o' are sums over the set of occupied states. The Green's function operator projected onto the empty subspace is given by

$$\mathcal{G}(\varepsilon) = \sum_e \frac{|\bar{\Psi}_e^{(0)}\rangle\langle\bar{\Psi}_e^{(0)}|}{\varepsilon - \varepsilon_e}, \tag{22}$$

with the sum running over the empty orbitals e.

IV. INDUCED CURRENT

We now possess all the ingredients necessary to obtain an expression for the all-electron induced current in terms of properties from a calculation using ultrasoft pseudopotentials. In Ref. 11, three distinct approaches to calculate the induced current are outlined; two applicable only to finite systems and one that is valid for infinitely periodic systems. We now present equations for each of the three methods within the USP formalism; we follow the method of Ref. 11 but use the expressions for $\bar{H}^{(1)}$, $S^{(1)}$, and $\mathbf{j}^{(1)}$ given in the previous section.

Following Ref. 11, we order the contributions to $\mathbf{j}^{(1)}(\mathbf{r}')$ into a contribution from the pseudized valence wave functions $\mathbf{j}_{\text{bare}}^{(1)}(\mathbf{r}')$ and two terms, one diamagnetic $\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r}')$ and one paramagnetic $\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r}')$, which account for the deviation of the pseudized valence wave function from the true all-electron wave function close to the nucleus,

$$\mathbf{j}^{(1)}(\mathbf{r}') = \mathbf{j}_{\text{bare}}^{(1)}(\mathbf{r}') + \mathbf{j}_{\Delta p}^{(1)}(\mathbf{r}') + \mathbf{j}_{\Delta d}^{(1)}(\mathbf{r}'). \tag{23}$$

A. Molecular approaches

The first approach is to directly substitute Eqs. (8) and (10) in Eq. (20). The resulting expressions define what we call the molecular method. The contribution $\mathbf{j}_{\text{bare}}^{(1)}(\mathbf{r}')$ is

$$\begin{aligned}\mathbf{j}_{\text{bare}}^{(1)}(\mathbf{r}') = {} & 4\sum_o \text{Re}\{\langle\bar{\Psi}_o^{(0)}|\mathbf{J}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle\} \\ & - \frac{1}{2c}\rho_{\text{soft}}^{\text{ps}}(\mathbf{r}')\mathbf{B}\times\mathbf{r}' - 2\sum_{oo'}\langle\bar{\Psi}_o^{(0)}|\mathbf{J}^p(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle \\ & \times\langle\bar{\Psi}_{o'}^{(0)}|S^{(1)}|\bar{\Psi}_o^{(0)}\rangle,\end{aligned} \tag{24}$$

where $\rho_{\text{soft}}^{\text{ps}}(\mathbf{r}') = 2\Sigma_o\langle\bar{\Psi}_o^{(0)}|\mathbf{r}'\rangle\langle\mathbf{r}'|\bar{\Psi}_o^{(0)}\rangle$ is the soft ground state pseudodensity formed from the pseudo-wave-functions without the addition of the hard atom centered augmentation charges. The paramagnetic augmentation to the current is

$$\begin{aligned}\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r}') = \sum_{\mathbf{R}',o} \Bigg(& 4\,\text{Re}\{\langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)}) \\ & \times(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle\} \\ & + 2\left\langle\bar{\Psi}_o^{(0)}\left|\frac{1}{i2c}[\mathbf{B}\times\mathbf{R}'\cdot\mathbf{r},\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')]\right|\bar{\Psi}_o^{(0)}\right\rangle\Bigg) \\ & - 2\sum_{oo'}\langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\langle\bar{\Psi}_{o'}^{(0)}|S^{(1)}|\bar{\Psi}_o^{(0)}\rangle,\end{aligned} \tag{25}$$

and the diamagnetic augmentation is

$$\mathbf{j}_{\Delta d}^{(1)}(\mathbf{r}') = 2\sum_{\mathbf{R},o}\langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}}^d(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle. \tag{26}$$

We cannot apply Eqs. (24) and (25) directly to extended systems as they contain expectation values of the position operator. However, we can use Eqs. (24)–(26) to calculate the induced current for molecules, within the supercell approximation, by applying the position operator as a smooth sawtooth function. We note that in the all-electron limit, the molecular method is equivalent to Eq. (3) of Ref. 30 (i.e., the "single gauge origin approach").

Equation (24) has both diamagnetic and paramagnetic components. As the diamagnetic component is related to the ground state charge density, it will converge faster with respect to the basis set than the paramagnetic contribution which contains a sum over unoccupied states. This is the so-called "gauge origin problem" which leads to a dependence of the chemical shift on a change in the gauge origin. The problem is less acute for a plane-wave basis compared to localized basis sets; however, it is still desirable to reformulate Eq. (24) and correspondingly Eq. (25) so that both terms converge at the same rate. We use the generalized f-sum rule established in Appendix C, Eq. (C8). Noting that the operators $\mathbf{J}^p(\mathbf{r}')$ and $\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')$ are odd and $\mathbf{r}$ even under time reversal symmetry, we obtain

$$\begin{aligned}\mathbf{j}_{\text{bare}}^{(1)}(\mathbf{r}') = 4\sum_o \text{Re}\Bigg\{ & \langle\bar{\Psi}_o^{(0)}|\mathbf{J}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle - \left\langle\bar{\Psi}_o^{(0)}\left|\mathbf{J}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})\sum_{\mathbf{R}}\frac{\mathbf{B}\times\mathbf{r}'}{2c}\cdot\mathbf{v}(\varepsilon_o^{(0)})\right|\bar{\Psi}_o^{(0)}\right\rangle\Bigg\} \\ & - \sum_{\mathbf{R}oo'}\langle\bar{\Psi}_o^{(0)}|\mathbf{J}^p(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\left\langle\bar{\Psi}_{o'}^{(0)}\left|(\mathbf{R}-\mathbf{r}')\times\frac{1}{2ci}[\mathbf{r},Q_{\mathbf{R}}]\cdot\mathbf{B}\right|\bar{\Psi}_o^{(0)}\right\rangle,\end{aligned} \tag{27}$$

and

$$\begin{aligned}\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r}') = 4\sum_{\mathbf{R}',o} \text{Re}\Bigg\{ & \langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle - \left\langle\bar{\Psi}_o^{(0)}\left|\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})\sum_{\mathbf{R}}\frac{\mathbf{B}\times\mathbf{R}'}{2c}\cdot\mathbf{v}(\varepsilon_o^{(0)})\right|\bar{\Psi}_o^{(0)}\right\rangle\Bigg\} \\ & - \sum_{\mathbf{R}\mathbf{R}'oo'}\langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}'}^p(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\left\langle\bar{\Psi}_{o'}^{(0)}\left|(\mathbf{R}-\mathbf{R}')\times\frac{1}{2ci}[\mathbf{r},Q_{\mathbf{R}}]\cdot\mathbf{B}\right|\bar{\Psi}_o^{(0)}\right\rangle.\end{aligned} \tag{28}$$

In the all-electron limit, Eqs. (27), (28), and (26) are equivalent to Eq. (8) of Ref. 30 [i.e., a set of gauge transformation[31] method with a vector potential $A(\mathbf{r}')=1/2B\times(\mathbf{r}'-\mathbf{r})$]. Again, we note that Eqs. (27) and (28) contain expectation values of the position operator and so may only be applied to finite systems. However, both Eqs. (27) and (28) contain a term which is valid in extended systems. These contributions to Eqs. (27) and (28) arise from the final term of $\bar{H}^{(1)}$ [Eq. (8)] and for later use, we write them as

$$\mathbf{j}^{(1)}_{\text{bare},Q_{\mathbf{R}}}(\mathbf{r}')=\frac{2}{c}\sum_{\mathbf{R}o}\text{Re}[\langle\bar{\Psi}^{(0)}_o|\mathbf{J}^p(\mathbf{r}')\mathcal{G}(\varepsilon_o)\mathbf{B}\cdot\mathbf{L}_{\mathbf{R}}Q_{\mathbf{R}}|\bar{\Psi}^{(0)}_o\rangle] \tag{29}$$

and

$$\mathbf{j}^{(1)}_{\Delta p,Q_{\mathbf{R}}}(\mathbf{r}')=\frac{2}{c}\sum_{o}\text{Re}[\langle\bar{\Psi}^{(0)}_o|\Delta\mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}')\mathcal{G}(\varepsilon_o)\mathbf{B}\cdot\mathbf{L}_{\mathbf{R}}Q_{\mathbf{R}}|\bar{\Psi}^{(0)}_o\rangle]. \tag{30}$$

As $Q_{\mathbf{R}}$ is localized within the augmentation region centered on atomic site $\mathbf{R}$, the terms $\mathbf{j}^{(1)}_{\text{bare},Q_{\mathbf{R}}}(\mathbf{r}')$ and $\mathbf{j}^{(1)}_{\Delta p,Q_{\mathbf{R}}}(\mathbf{r}')$ can be applied to both finite and extended systems.

B. Infinitely periodic systems

Finally, we present expressions for the induced current applicable to infinitely periodic systems. Note that these expressions may also be applied to nonperiodic systems through a supercell approximation. We write the electronic states as Bloch functions, $|\bar{\Psi}^{(0)}_{n,\mathbf{k}}\rangle=e^{i\mathbf{k}\cdot\mathbf{r}}|\bar{u}^{(0)}_{n,\mathbf{k}}\rangle$, where $\mathbf{k}$ is a reciprocal space vector within the first Brillouin zone and the corresponding eigenvalues are $\varepsilon_{n,\mathbf{k}}$. The cell-periodic function $\langle\mathbf{r}|\bar{u}^{(0)}_{n,\mathbf{k}}\rangle$ is normalized within the unit cell. We introduce the following $\mathbf{k}$-dependent quantities. The Green's function, $\mathcal{G}_{\mathbf{k}}(\varepsilon)$,

$$\mathcal{G}_{\mathbf{k}}(\varepsilon)=\sum_e\frac{|\bar{u}^{(0)}_{e,\mathbf{k}}\rangle\langle\bar{u}^{(0)}_{e,\mathbf{k}}|}{\varepsilon-\varepsilon^{(0)}_{e,\mathbf{k}}}, \tag{31}$$

the paramagnetic current operator, $\mathbf{J}^p_{\mathbf{k},\mathbf{k}'}(\mathbf{r}')$,

$$\mathbf{J}^p_{\mathbf{k},\mathbf{k}'}(\mathbf{r}')=-\frac{(-i\nabla+\mathbf{k})|\mathbf{r}'\rangle\langle\mathbf{r}'|+|\mathbf{r}'\rangle\langle\mathbf{r}'|(-i\nabla+\mathbf{k}')}{2}, \tag{32}$$

the augmented velocity operator, $\mathbf{v}_{\mathbf{k},\mathbf{k}'}(\varepsilon^{(0)}_{o,\mathbf{k}'})$,

$$\mathbf{v}_{\mathbf{k},\mathbf{k}'}(\varepsilon^{(0)}_{o,\mathbf{k}'})=-i\nabla+\mathbf{k}'+\frac{1}{i}[\mathbf{r},V^{\text{nl}}_{\mathbf{k},\mathbf{k}'}-\varepsilon^{(0)}_{o,\mathbf{k}'}Q_{\mathbf{k},\mathbf{k}'}], \tag{33}$$

and the commutator of the position operator and $S^{(0)}$,

$$\mathbf{s}_{\mathbf{k},\mathbf{k}'}=\frac{1}{i}[\mathbf{r},Q_{\mathbf{k},\mathbf{k}'}]. \tag{34}$$

$V^{\text{nl}}_{\mathbf{k},\mathbf{k}'}$, is the generalized form of the nonlocal pseudopotential operator,

$$V^{\text{nl}}_{\mathbf{k},\mathbf{k}'}=\sum_\tau\sum_{n,m}|\tilde{p}^{\mathbf{k}}_{\tau,n}\rangle D^\tau_{n,m}\langle\tilde{p}^{\mathbf{k}'}_{\tau,m}|, \tag{35}$$

and $Q_{\mathbf{k},\mathbf{k}'}$ is the charge augmentation operator,

$$Q_{\mathbf{k},\mathbf{k}'}=\sum_\tau\sum_{n,m}|\tilde{p}^{\mathbf{k}}_{\tau,n}\rangle q^\tau_{n,m}\langle\tilde{p}^{\mathbf{k}'}_{\tau,m}|=\sum_\tau Q_{\tau,\mathbf{k},\mathbf{k}'}. \tag{36}$$

The $\mathbf{k}$-dependent projectors are given in terms of $|\tilde{p}_{\mathbf{R},n}\rangle$, the real space projectors,

$$|\tilde{p}^{\mathbf{k}}_{\tau,n}\rangle=\sum_{\mathbf{T}}e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{T}-\boldsymbol{\tau})}|\tilde{p}_{\mathbf{T}+\tau,n}\rangle, \tag{37}$$

where the $\mathbf{T}$ are lattice vectors and the $\boldsymbol{\tau}$ are the internal coordinates of the atoms. The operators $\mathbf{v}_{\mathbf{k},\mathbf{k}'}(\varepsilon^{(0)}_{o,\mathbf{k}'})$ and $\mathbf{s}_{\mathbf{k},\mathbf{k}'}$ can be evaluated numerically following the procedure outlined in Ref. 22.

With these definitions, the bare current can be expressed as

$$\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}')=\lim_{q\to 0}\frac{1}{2q}[\mathbf{S}_{\text{bare}}(\mathbf{r}',q)-\mathbf{S}_{\text{bare}}(\mathbf{r}',-q)]+\mathbf{j}^{(1)}_{\text{bare},Q_{\mathbf{R}}}(\mathbf{r}'), \tag{38}$$

where

$$\begin{aligned}\mathbf{S}_{\text{bare}}(\mathbf{r}',q)=\frac{2}{cN_{\text{k}}}\sum_{i=x,y,z}\sum_{o,\mathbf{k}}\text{Re}\Bigg[&\frac{1}{i}\langle\bar{u}^{(0)}_{o,\mathbf{k}}|\mathbf{J}^p_{\mathbf{k},\mathbf{k}+\mathbf{q}_i}(\mathbf{r}')\mathcal{G}_{\mathbf{k}+\mathbf{q}_i}(\varepsilon_{o,\mathbf{k}})\mathbf{B}\\&\times\hat{\mathbf{u}}_i\cdot\mathbf{v}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}}(\varepsilon_{o,\mathbf{k}})|\bar{u}^{(0)}_{o,\mathbf{k}}\rangle\\&-\sum_{o'}\langle\bar{u}^{(0)}_{o,\mathbf{k}}|\mathbf{J}^p_{\mathbf{k},\mathbf{k}+\mathbf{q}_i}(\mathbf{r}')|\bar{u}^{(0)}_{o',\mathbf{k}+\mathbf{q}_i}\rangle\\&\times\langle\bar{u}^{(0)}_{o',\mathbf{k}+\mathbf{q}_i}|\mathbf{B}\times\hat{\mathbf{u}}_i\cdot\mathbf{s}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}}|\bar{u}^{(0)}_{o,\mathbf{k}}\rangle\Bigg].\end{aligned} \tag{39}$$

$\hat{\mathbf{u}}_i$ are unit vectors in the three Cartesian directions and $\mathbf{q}_i=q\hat{\mathbf{u}}_i$. $N_{\mathbf{k}}$ is the number of $\mathbf{k}$ points included in the summation. In a similar fashion to Eq. (38), the paramagnetic augmentation current can be written as

$$\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}')=\lim_{q\to 0}\frac{1}{2q}[\mathbf{S}_{\Delta p}(\mathbf{r}',q)-\mathbf{S}_{\Delta p}(\mathbf{r}',-q)]+\mathbf{j}^{(1)}_{\Delta p,Q_{\mathbf{R}}}(\mathbf{r}'), \tag{40}$$

where

$$\begin{aligned}\mathbf{S}_{\Delta p}(\mathbf{r}',q)=\frac{2}{cN_{\text{k}}}\sum_{i=x,y,z}\sum_{\mathbf{T},\tau,o,\mathbf{k}}\text{Re}\Bigg[&\frac{1}{i}\langle\bar{u}^{(0)}_{o,\mathbf{k}}|\Delta\mathbf{J}^p_{\mathbf{T},\tau,\mathbf{k},\mathbf{k}+\mathbf{q}_i}(\mathbf{r}')\\&\times\mathcal{G}_{\mathbf{k}+\mathbf{q}_i}(\varepsilon_{o,\mathbf{k}})\mathbf{B}\times\hat{\mathbf{u}}_i\cdot\mathbf{v}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}}(\varepsilon_{o,\mathbf{k}})|\bar{u}^{(0)}_{o,\mathbf{k}}\rangle\\&-\sum_{o'}\langle\bar{u}^{(0)}_{o,\mathbf{k}}|\Delta\mathbf{J}^p_{\mathbf{T},\mathbf{k},\mathbf{k}+\mathbf{q}_i}(\mathbf{r}')|\bar{u}^{(0)}_{o',\mathbf{k}+\mathbf{q}_i}\rangle\\&\times\langle\bar{u}^{(0)}_{o',\mathbf{k}+\mathbf{q}_i}|\mathbf{B}\times\hat{\mathbf{u}}_i\cdot\mathbf{s}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}}|\bar{u}^{(0)}_{o,\mathbf{k}}\rangle\Bigg],\end{aligned} \tag{41}$$

and we have introduced the $\mathbf{k}$-dependent paramagnetic augmentation operator, $\Delta\mathbf{J}^p_{\mathbf{T},\tau,\mathbf{k},\mathbf{k}'}(\mathbf{r}')$,

$$\Delta\mathbf{J}^{p}_{\mathbf{T},\tau,\mathbf{k},\mathbf{k}'}(\mathbf{r}') = \sum_{n,m} |\tilde{p}^{\mathbf{k}}_{\tau,n}\rangle[\langle\phi_{\mathbf{T}+\tau,n}|\mathbf{J}^{p}(\mathbf{r}')|\phi_{\mathbf{T}+\tau,m}\rangle - \langle\tilde{\phi}_{\mathbf{T}+\tau,n}|\mathbf{J}^{p}(\mathbf{r}')|\tilde{\phi}_{\mathbf{T}+\tau,m}\rangle]\langle\tilde{p}^{\mathbf{k}'}_{\tau,m}|. \quad (42)$$

Together, Eqs. (19), (38), and (40) define the crystal approach to calculate the all-electron current in infinitely periodic systems. It can be seen that in the norm-conserving limit $(S=1)$, they reduce to the expressions given in Ref. 11.

V. PRACTICAL IMPLEMENTATION

We could calculate the total valence current by summing the three contributions $\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}')$, $\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}')$, and $\mathbf{j}^{(1)}_{\Delta d}(\mathbf{r}')$. Application of the Biot-Savart law would then give the chemical shielding at each atomic site due to the valence electrons. Such an approach would be computationally expensive as an extremely fine grid would be needed to store the highly oscillatory augmentation currents. Instead, we take advantage of the linearity of the Biot-Savart law and calculate the induced magnetic field due to each of $\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}')$, $\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}')$, and $\mathbf{j}^{(1)}_{\Delta d}(\mathbf{r}')$, giving $\mathbf{B}^{(1)}_{\text{bare}}(\mathbf{R})$, $\mathbf{B}^{(1)}_{\Delta p}(\mathbf{R})$, $\mathbf{B}^{(1)}_{\Delta d}(\mathbf{R})$ and $\sigma_{\text{bare}}(\mathbf{R})$, $\sigma_{\Delta d}(\mathbf{R})$, $\sigma_{\Delta p}(\mathbf{R})$, respectively. In doing this, we follow Ref. 11 and make the approximation that the augmentation current at one atomic site only affects the chemical shielding at that site, i.e., that it gives no contribution to the chemical shielding at neighboring sites. This on-site approximation is a less good approximation in the USP case as the augmentation currents are generally larger than with NCP. However, in both cases, the close agreement with all-electron results has demonstrated the validity of this approximation. Within this approximation the diamagnetic augmentation field, $\mathbf{B}^{(1)}_{\Delta d}(\mathbf{R})$, is given by combining Eqs. (1) and (19), we obtain

$$\mathbf{B}^{(1)}_{\Delta d}(\mathbf{R}) = 2\sum_{o,n,n'} \langle\bar{\Psi}^{(0)}_{o}|\tilde{p}_{\mathbf{R},n}\rangle \mathbf{e}^{\mathbf{R}}_{m,n}\langle\tilde{p}_{\mathbf{R},m}|\bar{\Psi}^{(0)}_{o}\rangle, \quad (43)$$

where

$$\mathbf{e}^{\mathbf{R}}_{m,n} = \left\langle \phi_{\mathbf{R},n}\left|\frac{(\mathbf{R}-\mathbf{r})\times[\mathbf{B}\times(\mathbf{R}-\mathbf{r})]}{2c^{2}|\mathbf{R}-\mathbf{r}|^{3}}\right|\phi_{\mathbf{R},m}\right\rangle - \left\langle \tilde{\phi}_{\mathbf{R},n}\left|\frac{(\mathbf{R}-\mathbf{r})\times[\mathbf{B}\times(\mathbf{R}-\mathbf{r})]}{2c^{2}|\mathbf{R}-\mathbf{r}|^{3}}\right|\tilde{\phi}_{\mathbf{R},m}\right\rangle. \quad (44)$$

A corresponding expression can be found for $\mathbf{B}^{(1)}_{\Delta p}(\mathbf{R})$. To evaluate the contribution of the bare current to the chemical shielding, we apply the Biot-Savart law in reciprocal space

$$\mathbf{B}^{(1)}_{\text{bare}}(\mathbf{G}) = \frac{4\pi}{c}\frac{i\mathbf{G}\times\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{G})}{G^{2}}. \quad (45)$$

We cannot apply this equation at $G=0$ (Ref. 32) as the $G=0$ component is related to the macroscopic magnetic susceptibility χ. For a spherical sample, we can write[33]

$$\mathbf{B}^{(1)}_{\text{in}}(\mathbf{G}=0) = \frac{8\pi}{3}\chi\mathbf{B}. \quad (46)$$

We follow Refs. 11 and 32 and use

$$\chi_{\text{bare}} = \lim_{q\to 0}\frac{F(q)-2F(0)+F(-q)}{q^{2}}, \quad (47)$$

where $F_{ij}(q)=(2-\delta_{ij})Q_{ij}(q)$, i and j are Cartesian indices,

$$Q(q) = -\frac{1}{c^{2}N_{\text{k}}V_{c}}\sum_{i=x,y,z}\sum_{o,\mathbf{k}}\text{Re}[\langle\bar{u}^{(0)}_{o,\mathbf{k}}|\hat{\mathbf{u}}_{i}\times(-i\nabla+\mathbf{k})\times\mathcal{G}_{\mathbf{k}+\mathbf{q}_{i}}(\varepsilon_{o,\mathbf{k}})\hat{\mathbf{u}}_{i}\times\mathbf{v}_{\mathbf{k}+\mathbf{q}_{i},\mathbf{k}}(\varepsilon_{o,\mathbf{k}})|\bar{u}^{(0)}_{o,\mathbf{k}}\rangle], \quad (48)$$

and V_c is the unit cell volume. The total chemical shielding σ_{tot} is given by the sum of these three terms plus a contribution from the core electrons σ_{core}. σ_{core} has been shown[30] to be chemically invariant and we can calculate it for each nuclear species using an atomic code. Finally, we comment on the projectors used for the GIPAW reconstruction. In the norm-conserving GIPAW approach, it was found to be necessary to use two projectors for each angular momentum channel, even though norm-conserving pseudopotentials give accurate ground state properties with a single projector in each channel. Ultrasoft pseudopotentials typically use two projectors for each channel, and we find that the reconstructed chemical shieldings are sufficiently accurate with two projectors per angular momentum channel. Generally, the projectors for the GIPAW augmentation are identical to the pseudopotential projectors; however, when a chemically relevant channel is described by a local potential, it is necessary to augment this channel. As an example, consider Si which can be described by an ultrasoft pseudopotential with two projectors for each of s and p and a local potential to represent the d states. For the GIPAW reconstruction, it is necessary to have two projectors for each of s, p, and d.

VI. VALIDATION

In order to show the validity of the approaches outlined in the previous sections, we first benchmark the method against existing quantum chemical techniques. In Ref. 30, chemical shieldings were presented for a range of small molecules calculated with the individual gauges for atoms in molecules (IGAIM) (Ref. 34) approach using large Gaussian basis sets. This same set of molecules was used to test the original GIPAW implementation based on norm-conserving pseudopotentials[11] and we begin by also considering this set of molecules.

We compute isotropic chemical shieldings $(\sigma_{\text{iso}}=1/3Tr[\vec{\sigma}])$ for this set of molecules using LDA and large supercells. We first compare the three approaches presented in this work: molecular, molecular sum rule, and crystal. We find that the chemical shielding computed with the three methods agrees closely across the set of molecules; the differences in isotropic chemical shieldings are less than 0.01 ppm for H and C, 0.1 ppm for Si, and 0.3 ppm for P.

In Fig. 1, we compare the isotropic chemical shieldings computed using the crystal method with the IGAIM all-electron values from Ref. 30. The upper figure shows the importance of the GIPAW augmentation terms; without these terms, most of the sensitivity to chemical environment is lost. This becomes increasingly significant as we descend the Periodic Table. From the lower figure, we can see that when

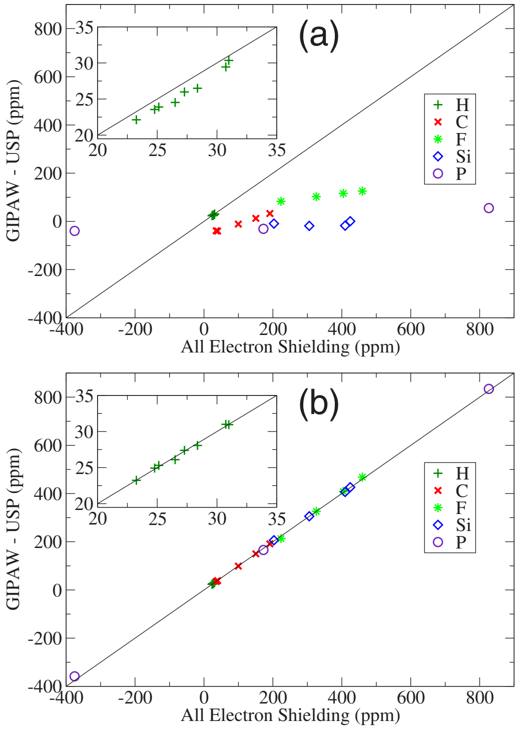

FIG. 1. (Color online) Isotropic chemical shielding for nuclear sites in a range of molecules (Ref. 35). The graphs show shieldings obtained with the GIPAW-USP method plotted against all-electron shielding (Ref. 30). The straight line represents perfect agreement. The upper figure (a) shows the contribution without GIPAW augmentation ($\sigma_{\text{bare}}+\sigma_{\text{core}}$); the lower figure (b) plots the total contribution.

the GIPAW augmentations are included, the agreement with the all-electron results is excellent. As for the norm-conserving case,[11] the largest absolute deviations are for phosphorus. However, these represent a small fraction of the total range of phosphorus chemical shieldings.

We next consider silicate compounds. In Ref. 15, O and Si chemical shielding tensors were computed for a small cluster derived from the α-quartz structure, both using the GIPAW approach with NCP and with the IGAIM approach with a large (pentuple zeta) Gaussian basis. In Table I, we compare isotropic chemical shieldings, chemical shielding anisotropy Δ_{aniso}, and chemical shielding asymmetry η computed with the three approaches. The agreement between the approaches is good. We also use this silicate cluster to examine the convergence of the chemical shielding with the size of the plane-wave basis. Clearly, the rate of convergence depends on the size of the pseudopotential augmentation region; a larger augmentation region allows for a softer pseudopotential and hence fewer plane waves are required for numerical convergence. However, the augmentation region should not be so large that neighboring augmentation regions have significant overlap; otherwise, errors will be introduced. The relatively large Si–O bond lengths in silicates allow for a large augmentation region for an oxygen pseudopotential and we consider values of 1.3 and 1.5 bohr. We note that for the shorter oxygen bonds found in organic materials, only the smaller augmentation region will be appropriate. In Fig. 2, we plot the convergence of the isotropic O chemical shielding against maximum plane-wave energy for NCPs and USPs with augmentation regions of both 1.3 and 1.5 bohr. The faster convergence rate of USPs is apparent. We also note that for both NCPs and USPs, the final converged result is independent of the size of augmentation region, demonstrating the stability of the GIPAW approach.

TABLE I. Chemical Shielding parameters for a O-$(SiH_3)_2$ cluster derived from the α-quartz structure. The all-electron calculations (Ref. 15) use the IGAIM method with cc-pCVxZ basis sets for O and Si. The GIPAW-NCP calculations (Ref. 15) use Troullier-Martins pseudopotentials with a 120 Ry plane-wave cutoff. The plane-wave cutoff for the GIPAW-USP calculation is 60 Ry.

	USP	NCP	All-electron
O σ_{iso}	317.62	315.62	316.49
Δ_{aniso}	−109.75	−111.12	−109.25
η	0.02	0.02	0.03
Si(1) σ_{iso}	340.55	345.23	340.98
Δ_{aniso}	150.61	147.89	151.07
η	0.08	0.09	0.08
Si(2) σ_{iso}	339.28	343.84	339.60
Δ_{aniso}	149.53	147.01	150.24
η	0.08	0.08	0.08

Finally, we consider truly crystalline systems, for which we compare to existing GIPAW calculations using NCP, and experiment. We now use the PBE density functional[36] which has been shown to give chemical shifts in good agreement with experiment.[15,19] In Table II, we present ^{17}O NMR parameters calculated using USPs for three silicate materials, together with results from Ref. 15 using NCP and experimental results. The structures of the materials and the details of the Brillouin zone integration are the same as used in Ref. 15. Plane waves up to a maximum energy of 40 Ry are used. The agreement of the parameters computed with USPs, both with the existing NCP results and experiment, is excellent. In particular, the assignment of the oxygen sites in coesite is consistent between the two sets of computational results. For these materials, we find that the use of USPs gives a 50%

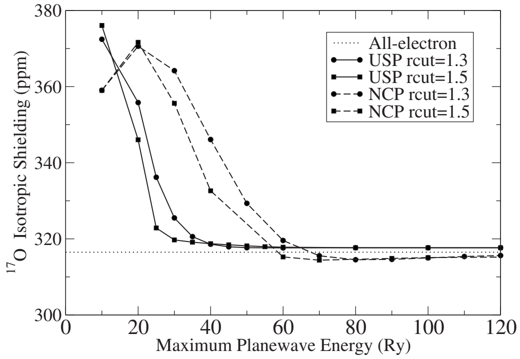

FIG. 2. Convergence with plan-ewave cutoff energy of the ^{17}O isotropic chemical shielding in a O-$(SiH_3)_2$ cluster derived from the α-quartz structure. The all-electron result is taken from Ref. 15.

TABLE II. ^{17}O NMR chemical shift and electric field gradient parameters for some silicate materials. Comparison of GIPAW calculations with USPs (this work) and NCPs (Ref. 15) with experiment (see references within Ref. 15).

	GIPAW USP			GIPAW NCP			Expt.		
	δ_{iso} (ppm)	C_Q (MHz)	η	δ_{iso} (ppm)	C_Q (MHz)	η	δ_{iso} (ppm)	C_Q (MHz)	η
Coesite O1	26.3	6.213	0.044	25.8	6.24	0.040	29	6.05	0.000
O2	40.0	5.571	0.196	39.2	5.56	0.190	41	5.43	0.166
O3	55.9	5.493	0.200	56.0	5.45	0.190	57	5.45	0.168
O4	52.3	5.614	0.172	52.4	5.73	0.166	53	5.52	0.169
O5	58.2	5.232	0.300	57.8	5.23	0.296	58	5.16	0.292
Cristobalite	39.0	5.30	0.145	39.3	5.30	0.145	37.2	5.21	0.13
Quartz	44.3	5.31	0.202	44.3	5.31	0.202	40.8	5.19	0.19

reduction in the amount of RAM required, and a 33% reduction in the overall CPU time, compared with NCPs.

VII. CONCLUSIONS

In conclusion, we have presented a scheme to compute NMR chemical shieldings in both finite and extended materials using ultrasoft pseudopotentials. The GIPAW approach is used to obtain chemical shieldings with all-electron accuracy and we describe the additional terms which must be included to account for the relaxation of norm conservation central to the ultrasoft formalism. This work allows NMR chemical shieldings to be calculated at reduced computational cost, extending the range of systems that can be studied both on large supercomputers and on personal desktop computers. Several applications of this technique, to perovskites[13] and to molecular crystals,[37,38] have already appeared.

Finally, we note that the formalism developed in this work allows other magnetic resonance parameters, such as the EPR g tensor[39] and NMR J couplings,[40] to be computed with ultrasoft pseudopotentials.

ACKNOWLEDGMENTS

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APPENDIX A: FIRST ORDER GIPAW HAMILTONIAN

In a uniform magnetic field, the all-electron Hamiltonian is

$$H = \frac{1}{2}\left[\mathbf{p} + \frac{1}{c}\mathbf{A}(\mathbf{r})\right]^2 + V(\mathbf{r}). \tag{A1}$$

We use the GIPAW transformation, Eq. (3), and the identity,

$$e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\left[\mathbf{p} + \frac{1}{c}\mathbf{A}(\mathbf{r})\right]^n e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} = \left[\mathbf{p} + \frac{1}{c}\mathbf{A}(\mathbf{r}-\mathbf{R})\right]^n, \tag{A2}$$

and, choosing the Coulomb gauge, we arrive at the corresponding GIPAW pseudo-Hamiltonian

$$\begin{aligned}\bar{H} = {} & \frac{1}{2}\mathbf{p}^2 + V^{\text{loc}}(\mathbf{r}) + \sum_{\mathbf{R}} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} V^{\text{nl}}_{\mathbf{R}} e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} + \frac{1}{2c}\mathbf{L}\cdot\mathbf{B} \\ & + \frac{1}{8c^2}(\mathbf{B}\times\mathbf{r})^2 + \sum_{\mathbf{R},n,m} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}(\beta^1 + \beta^2)e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}},\end{aligned} \tag{A3}$$

where

$$\beta^1 = \frac{1}{2c}\mathbf{B}\cdot|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_n|\mathbf{L}_{\mathbf{R}}|\phi_m\rangle - \langle\tilde{\phi}_n|\mathbf{L}_{\mathbf{R}}|\tilde{\phi}_m\rangle]\langle\tilde{p}_{\mathbf{R},m}| \tag{A4}$$

and

$$\begin{aligned}\beta^2 = {} & \frac{1}{8c^2}\mathbf{B}\cdot|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_n|[\mathbf{B}\times(\mathbf{r}-\mathbf{R})]^2|\phi_m\rangle \\ & - \langle\tilde{\phi}_n|[(\mathbf{B}\times(\mathbf{r}-\mathbf{R})]^2|\tilde{\phi}_m\rangle]\langle\tilde{p}_{\mathbf{R},m}|.\end{aligned} \tag{A5}$$

$\mathbf{L}_{\mathbf{R}}$ is the angular momentum operator with respect to the atomic position $\mathbf{R}$. We consider the term β^1. Without loss of generality, we consider a field in the direction of the z axis, $\mathbf{B}=B_z\hat{z}$, giving

$$\begin{aligned}\beta^1 & = \frac{1}{2c}B_z m_z|\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\phi_{\mathbf{R},m}\rangle - \langle\tilde{\phi}_{\mathbf{R},n}|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}| \\ & = \frac{1}{2c}B_z m_z|\tilde{p}_{\mathbf{R},n}\rangle q_{\mathbf{R},nm}\langle\tilde{p}_{\mathbf{R},m}| = \frac{1}{2c}\mathbf{L}_{\mathbf{R}}\cdot\mathbf{B}Q_{\mathbf{R}},\end{aligned} \tag{A6}$$

where m_z is the magnetic quantum number of the projector $|\tilde{p}_{\mathbf{R},n}\rangle$. Expanding $\bar{H}$ to first order in the applied field gives

$$\bar{H}^{(1)} = \frac{1}{2c}\left(\mathbf{L} + \sum_{\mathbf{R}}\mathbf{R}\times\frac{1}{i}[\mathbf{r},V^{\text{nl}}_{\mathbf{R}}] + \sum_{\mathbf{R}}\mathbf{L}_{\mathbf{R}}Q_{\mathbf{R}}\right)\cdot\mathbf{B}. \tag{A7}$$

The final term in Eq. (A7) represents the augmentation of the $\mathbf{L}$ operator resulting from the relaxation of norm conservation.

APPENDIX B: DFPT EXPRESSION FOR CURRENT DENSITY

If we denote the current operators to zeroth and first order in the magnetic field as $\bar{\mathbf{J}}^{(0)}(\mathbf{r}')$ and $\bar{\mathbf{J}}^{(1)}(\mathbf{r}')$, we can express the first-order induced current as

$$\begin{aligned}\mathbf{j}^{(1)}(\mathbf{r}') = 2\sum_{o} [&\langle\bar{\Psi}_o^{(1)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle + \langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(1)}\rangle \\ &+ \langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(1)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle].\end{aligned} \tag{B1}$$

Here, the factor of 2 accounts for spin degeneracy and the sum runs over the occupied orbitals o. The last term of Eq. (B1) represents the diamagnetic contribution to the current, arising from the unperturbed wave functions. The first two terms are the paramagnetic current response arising from the perturbed wave function, $|\bar{\Psi}_o^{(1)}\rangle$. It will be convenient to divide the paramagnetic current response into a contribution from the component of $|\bar{\Psi}_o^{(1)}\rangle$ projected in the empty subspace $|\bar{\Psi}_o^{(1e)}\rangle$ and the occupied subspace $|\bar{\Psi}_o^{(1o)}\rangle$. We introduce P_o and P_e projectors into the occupied and empty subspaces, respectively

$$P_o = \sum_{o} |\bar{\Psi}_o^{(0)}\rangle\langle\bar{\Psi}_o|S^{(0)},$$

$$P_e = \sum_{e} |\bar{\Psi}_e^{(0)}\rangle\langle\bar{\Psi}_e|S^{(0)}, \tag{B2}$$

where the sum over o and e runs over the occupied and empty states, respectively. Since $P_o + P_e = 1$,

$$|\bar{\Psi}_o^{(1)}\rangle = (P_o + P_e)|\bar{\Psi}_o^{(1)}\rangle = |\bar{\Psi}_o^{(1o)}\rangle + |\bar{\Psi}_o^{(1e)}\rangle. \tag{B3}$$

1. Empty subspace

We first obtain the current response arising from $|\bar{\Psi}_n^{(1e)}\rangle$. We start with the wave equation

$$H|\bar{\Psi}_o\rangle = \varepsilon_n S|\bar{\Psi}_o\rangle \tag{B4}$$

and take its first-order variation

$$(\varepsilon_o^{(0)}S^{(0)} - \bar{H}^{(0)})|\bar{\Psi}_o^{(1)}\rangle = (\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)} - \varepsilon_o^{(1)}S^{(0)})|\bar{\Psi}_o^{(0)}\rangle. \tag{B5}$$

By acting on both sides with P_e, we obtain the following linear equation;

$$(\varepsilon_o^{(0)}S^{(0)} - \bar{H}^{(0)})|\bar{\Psi}_o^{(1e)}\rangle = P_e(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle. \tag{B6}$$

As $P_e + P_o = 1$, we can write this in terms of occupied states only,

$$(\varepsilon_o^{(0)}S^{(0)} - \bar{H}^{(0)})|\bar{\Psi}_o^{(1e)}\rangle = (1 - P_o)(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle. \tag{B7}$$

Formally, the first-order wave functions can be written in terms of the Green's function projected on the empty subspace [Eq. (22)] as

$$|\bar{\Psi}_o^{(1e)}\rangle = \mathcal{G}(\varepsilon_o^{(0)})(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle. \tag{B8}$$

The contribution to $\mathbf{j}^{(1)}(\mathbf{r}')$ from the projection of $|\bar{\Psi}_o^{(1)}\rangle$ into the empty subspace, $\mathbf{j}_{emp}^{(1)}(\mathbf{r}')$, can thus be written as

$$\begin{aligned}\mathbf{j}_{emp}^{(1)}(\mathbf{r}') = 2\sum_{o} \{&\langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle \\ &+ \langle\bar{\Psi}_o^{(0)}|(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})\mathcal{G}(\varepsilon_o^{(0)})\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle\}\end{aligned} \tag{B9}$$

$$= 4\sum_{o} \mathrm{Re}\{\langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')\mathcal{G}(\varepsilon_o^{(0)})(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle\}. \tag{B10}$$

In the practical implementation, we obtain $|\bar{\Psi}_n^{(1e)}\rangle$ by minimizing via a conjugate gradient method the following functional of ϕ:

$$\begin{aligned}F[\phi] = {}&\langle\phi|(\bar{H}^{(0)} - \varepsilon_o^{(0)}S^{(0)} + \alpha_o S^{(0)}P_o)|\phi\rangle \\ &+ \langle\phi|(1 - P_o)(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})|\bar{\Psi}_o^{(0)}\rangle \\ &+ \langle\bar{\Psi}_o^{(0)}|(\bar{H}^{(1)} - \varepsilon_o^{(0)}S^{(1)})(1 - P_o)|\phi\rangle,\end{aligned} \tag{B11}$$

where $\alpha_o \geqslant (\varepsilon_o - \varepsilon_1)$ assures that the functional stationary point is a minimum. Indeed, at the minimum, $|\phi\rangle = |\bar{\Psi}_o^{(1e)}\rangle$.

2. Occupied subspace

The contribution to $\mathbf{j}^{(1)}(\mathbf{r}')$ from the projection of $|\bar{\Psi}_o^{(1)}\rangle$ into the occupied subspace, $\mathbf{j}_{occ}^{(1)}(\mathbf{r}')$, may be written as

$$\begin{aligned}\mathbf{j}_{occ}^{(1)}(\mathbf{r}') &= 2\sum_{o} [\langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(1o)}\rangle + \langle\bar{\Psi}_o^{(1o)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle] \\ &= 2\sum_{o}\sum_{o'} [\langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\langle\bar{\Psi}_{o'}^{(0)}|S^{(0)}|\bar{\Psi}_o^{(1)}\rangle \\ &\quad + \langle\bar{\Psi}_o^{(1)}|S^{(0)}|\bar{\Psi}_{o'}^{(0)}\rangle\langle\bar{\Psi}_{o'}^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle],\end{aligned} \tag{B12}$$

where the sum o' runs on the occupied states. Rearranging the last term and swapping the dummy indices give

$$\begin{aligned}\mathbf{j}_{occ}^{(1)}(\mathbf{r}') &= 2\sum_{oo'} [\langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\langle\bar{\Psi}_{o'}^{(0)}|S^{(0)}|\bar{\Psi}_o^{(1)}\rangle \\ &\quad + \langle\bar{\Psi}_{o'}^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle\langle\bar{\Psi}_o^{(1)}|S^{(0)}|\bar{\Psi}_{o'}^{(0)}\rangle] \\ &= 2\sum_{oo'} [\langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\langle\bar{\Psi}_{o'}^{(0)}|S^{(0)}|\bar{\Psi}_o^{(1)}\rangle \\ &\quad + \langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_{o'}^{(0)}\rangle\langle\bar{\Psi}_{o'}^{(1)}|S^{(0)}|\bar{\Psi}_o^{(0)}\rangle].\end{aligned} \tag{B13}$$

From the first-order variation of the generalized orthogonality condition [Eq. (7)], we obtain the relation

$$\langle\bar{\Psi}_i^{(0)}|S^{(0)}|\bar{\Psi}_j^{(1)}\rangle + \langle\bar{\Psi}_i^{(1)}|S^{(0)}|\hat{\Psi}_j^{(0)}\rangle = -\langle\bar{\Psi}_i^{(0)}|S^{(1)}|\bar{\Psi}_j^{(0)}\rangle. \tag{B14}$$

Substituting this into the expression for $\mathbf{j}_{occ}^{(1)}(\mathbf{r}')$, we arrive at the final expression

$$\mathbf{j}^{(1)}_{occ}(\mathbf{r}') = -2\sum_{oo'} \langle \bar{\Psi}^{(0)}_o|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}^{(0)}_{o'}\rangle\langle\bar{\Psi}^{(0)}_{o'}|S^{(1)}|\bar{\Psi}^{(0)}_o\rangle. \tag{B15}$$

Equations (B1), (B15), and (B9) together form an expression for the total induced current density. We note that similar expressions have been obtained in Ref. 23. The equations presented here are somewhat simpler for two reasons. First, we have restricted our derivation to insulating systems. Second, unlike the cases of a phonon displacement or applied electric field for an applied magnetic field, there is no change in charge density to linear order in the perturbation. It is therefore not necessary to consider the variation of the Hartree and exchange-correlation terms in the Hamiltonian (at least for the case of an exchange-correlation functional which depends solely on the charge density and its derivatives).

APPENDIX C: THE GENERALIZED *f*-SUM RULE

We must generalize the *f*-sum rule outlined in Ref. 11 such that it is valid for a Hamiltonian based on ultrasoft pseudopotentials. The generalized *f*-sum rule holds for any pair of Hermitian operators $\mathcal{O}$ and $\mathcal{E}$, where $\mathcal{O}$ and $\mathcal{E}$ are, respectively, odd and even on time reversal, i.e.,

$$\langle\phi|\mathcal{O}|\phi'\rangle = -\langle\phi'|\mathcal{O}|\phi\rangle \tag{C1}$$

and

$$\langle\phi|\mathcal{E}|\phi'\rangle = \langle\phi'|\mathcal{E}|\phi\rangle \tag{C2}$$

for any $|\phi\rangle$ and $|\phi'\rangle$ such that $\langle\mathbf{r}|\phi\rangle$ and $\langle\mathbf{r}|\phi'\rangle$ are real. It is straightforward to verify that $\mathbf{p}$, $\mathbf{L}$, $\mathbf{v}$, $\mathbf{v}^{\mathrm{nl}}_{\mathbf{R}}$, $\mathbf{J}^{p}(\mathbf{r}')$, and $\Delta\mathbf{J}^{p}_{\mathbf{R}}(\mathbf{r}')$ are odd and that $\mathbf{r}$ and operators that are a function of $\mathbf{r}$ are even. To derive the sum rule, we consider the quantity

$$s = -4\sum_o \mathrm{Re}\left\{\left\langle \bar{\Psi}^{(0)}_o \middle| \mathcal{O}\mathcal{G}(\varepsilon^{(0)}_o)\frac{1}{i}[\mathcal{E},\bar{H}^{(0)} - \varepsilon^{(0)}_o S^{(0)}] \middle| \bar{\Psi}^{(0)}_o\right\rangle\right\}. \tag{C3}$$

The sums over o and o' (below) run over the occupied orbitals, and those over e' over the empty ones. Using the fact that $\bar{H}^{(0)}|\bar{\Psi}^{(0)}_n\rangle = \varepsilon^{(0)}_n S^{(0)}|\bar{\Psi}^{(0)}_n\rangle$, we can write

$$s = -4\sum_{oe'} \mathrm{Re}\left[\left\langle \bar{\Psi}^{(0)}_o \middle| \mathcal{O}\frac{1}{i} \middle| \bar{\Psi}_{e'}\right\rangle \langle\bar{\Psi}_{e'}|S^{(0)}\mathcal{E}|\bar{\Psi}^{(0)}_o\rangle\right]. \tag{C4}$$

Using $\Sigma_{e'} S|\hat{\Psi}_{e'}\rangle\langle\bar{\Psi}_{e'}| = 1 - \Sigma_{o'} S^{(0)}|\bar{\Psi}_{o'}\rangle\langle\bar{\Psi}_{o'}|$, the expression for s may be rewritten as

$$s = -4\sum_o \mathrm{Re}\left[\frac{1}{i}\langle\bar{\Psi}^{(0)}_o|\mathcal{O}\mathcal{E}|\bar{\Psi}^{(0)}_o\rangle\right] + 4\sum_{o,o'} \mathrm{Re}\left[\frac{1}{i}\langle\bar{\Psi}^{(0)}_o|\mathcal{O}|\bar{\Psi}^{(0)}_{o'}\rangle\langle\bar{\Psi}^{(0)}_{o'}|S^{(0)}\mathcal{E}|\bar{\Psi}^{(0)}_o\rangle\right]. \tag{C5}$$

This may be expressed as

$$s = 2\sum_o \left\langle \bar{\Psi}^{(0)}_o \middle| \frac{1}{i}[\mathcal{E},\mathcal{O}] \middle| \bar{\Psi}^{(0)}_o\right\rangle + 2\sum_{o,o'} \frac{1}{i}\langle\bar{\Psi}^{(0)}_o|\mathcal{O}S^{(0)}|\bar{\Psi}^{(0)}_{o'}\rangle \times\langle\bar{\Psi}^{(0)}_{o'}|[S^{(0)},\mathcal{E}]|\bar{\Psi}^{(0)}_o\rangle. \tag{C6}$$

From this expression, we finally obtain the generalized *f*-sum rule for an ultrasoft Hamiltonian:

$$2\sum_o \left\langle \bar{\Psi}^{(0)}_o \middle| \frac{1}{i}[\mathcal{E},\mathcal{O}] \middle| \bar{\Psi}^{(0)}_o\right\rangle - 2\sum_{o,o'} \frac{1}{i}\langle\bar{\Psi}^{(0)}_o|\mathcal{O}|\bar{\Psi}^{(0)}_{o'}\rangle\langle\bar{\Psi}^{(0)}_{o'}|[\mathcal{E},S^{(0)}]|\bar{\Psi}^{(0)}_o\rangle = -4\sum_o \mathrm{Re}\left[\left\langle \bar{\Psi}^{(0)}_o \middle| \mathcal{O}\mathcal{G}(\varepsilon^{(0)}_o)\frac{1}{i}[\mathcal{E},\bar{H}^{(0)} - \varepsilon^{(0)}_o S^{(0)}] \middle| \bar{\Psi}^{(0)}_o\right\rangle\right]. \tag{C7}$$

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[1] See, e.g., T. Helgaker, M. Jaszuski, and K. Ruud, Chem. Rev. (Washington, D.C.) **99**, 293 (1999); J. Gauss and J. F. Stanton, Adv. Chem. Phys. **123**, 355 (2002).

[2] *Calculation of NMR and EPR Parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley VCH, Weinheim, 2004).

[3] J. C. Facelli and D. M. Grant, Nature (London) **365**, 325 (1993).

[4] C. Ochsenfeld, S. P. Brown, I. Schnell, J. Gauss, and H. W. Spiess, J. Am. Chem. Soc. **123**, 2597 (2001).

[5] R. Salzmann, C. J. Ziegler, N. Godbout, M. T. McMahon, K. S. Suslick, and E. Oldfield, J. Am. Chem. Soc. **120**, 11323 (1998).

[6] F. Mauri, B. G. Pfrommer, and S. G. Louie, Phys. Rev. Lett. **77**, 5300 (1996).

[7] D. Sebastiani and M. Parrinello, J. Phys. Chem. A **105**, 1951 (2001).

[8] A. Hoffmann, D. Sebastiani, E. Sugiono, S. Yun, K. S. Kim, H. W. Spiess, and I. Schnell, Chem. Phys. Lett. **388**, 164 (2004).

[9] B. G. Pfrommer, F. Mauri, and S. G. Louie, J. Am. Chem. Soc. **122**, 123 (2000).

[10] D. Sebastiani and U. Rothlisberger, J. Phys. Chem. B **108**, 2807 (2004).

[11] C. J. Pickard and F. Mauri, Phys. Rev. B **63**, 245101 (2001).

[12] C. G. Van de Walle and P. E. Blöchl, Phys. Rev. B **47**, 4244 (1993).

[13] S. E. Ashbrook, L. L. Polles, R. Gautier, C. J. Pickard, and R. I. Walton, Phys. Chem. Chem. Phys. **8**, 3423 (2006).

[14] I. Farnan, E. Balan, C. J. Pickard, and F. Mauri, Am. Mineral. **88**, 1663 (2003).

[15] M. Profeta, F. Mauri, and C. J. Pickard, J. Am. Chem. Soc. **125**, 541 (2003).

[16] M. Benoit, M. Profeta, F. Mauri, C. J. Pickard, and M. E. Tuckerman, J. Phys. Chem. B **109**, 6052 (2005).

[17] T. Charpentier, S. Ispas, M. Profeta, F. Mauri, and C. J. Pickard, J. Phys. Chem. B **108**, 4147 (2004).

[18] C. Gervais, R. Dupree, K. J. Pike, C. Bonhomme, M. Profeta, C. J. Pickard, and F. Mauri, J. Phys. Chem. A **109**, 6960 (2005).

[19] J. R. Yates, T. N. Pham, C. J. Pickard, F. Mauri, A. M. Amado, A. M. Gil, and S. P. Brown, J. Am. Chem. Soc. **127**, 10216 (2005).

[20] J. R. Yates, C. J. Pickard, M. C. Payne, R. Dupree, M. Profeta, and F. Mauri, J. Phys. Chem. A **108**, 6032 (2004).

[21] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[22] C. J. Pickard and M. C. Payne, Phys. Rev. B **62**, 4383 (2000).

[23] A. DalCorso, Phys. Rev. B **64**, 235118 (2001).

[24] P. Umari, X. Gonze, and A. Pasquarello, Phys. Rev. B **69**, 235102 (2004).

[25] H. M. Petrilli, P. E. Blöchl, P. Blaha, and K. Schwarz, Phys. Rev. B **57**, 14690 (1998).

[26] C. J. Pickard and M. C. Payne, Inst. Phys. Conf. Ser. **153**, 179 (1997).

[27] R. Ditchfield, J. Chem. Phys. **56**, 5688 (1972).

[28] W. Kutzelnigg, U. Fleischer, and M. Schindler, *NMR Basic Principles and Progress* (Springer-Verlag, Berlin, 1990), Vol. 23, pp. 165–263.

[29] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[30] T. Gregor, F. Mauri, and R. Car, J. Chem. Phys. **111**, 1815 (1999).

[31] T. Keith and R. Bader, Chem. Phys. Lett. **210**, 223 (1993).

[32] F. Mauri and S. G. Louie, Phys. Rev. Lett. **76**, 4246 (1996).

[33] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1999).

[34] T. Keith and R. Bader, Chem. Phys. Lett. **194**, 1 (1992).

[35] Calculations were performed using a supercell of 6000 bohr^3, the LDA, and a maximum plane-wave energy of 80 Ry. The molecules are CH_4, CH_3F, CH_3NH_2, C_6H_12, C_6H_6, CF_4, C_5H_5N, SiF_4, SiH_3F, SiH_4, Si_2H_4, HCP, PF_3, P_2, and P_4. The ultrasoft pseudopotentials were constructed with augmentation regions of radius (in bohr): 0.8 (H), 1.4 (C), 1.5 (N), 1.3 (O), 1.4 (F), 1.8 (Si), and 1.8 (P).

[36] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[37] R. K. Harris, S. Cadars, L. Emsley, J. R. Yates, C. J. Pickard, R. Jetti, and U. J. Griesser, Phys. Chem. Chem. Phys. **9**, 360 (2006).

[38] R. K. Harris, S. A. Joyce, C. J. Pickard, S. Cadars, and L. Emsley, Phys. Chem. Chem. Phys. **8**, 137 (2006).

[39] C. J. Pickard and F. Mauri, Phys. Rev. Lett. **88**, 086403 (2002).

[40] S. A. Joyce, J. R. Yates, C. J. Pickard, and F. Mauri (unpublished).