All-electron magnetic response with pseudopotentials: NMR chemical shifts

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A theory for the *ab initio* calculation of all-electron NMR chemical shifts in insulators using pseudopotentials is presented. It is formulated for both finite and infinitely periodic systems and is based on an extension to the projector augmented-wave approach of Blöchl [P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994)] and the method of Mauri *et al.* [F. Mauri, B. G. Pfrommer, and S. G. Louie, Phys. Rev. Lett. **77**, 5300 (1996)]. The theory is successfully validated for molecules by comparison with a selection of quantum chemical results, and in periodic systems by comparison with plane-wave all-electron results for diamond.

I. INTRODUCTION

The experimental technique of nuclear magnetic resonance (NMR) is widely used in structural chemistry and increasingly in solid-state studies.[1] Chemical shift (σ) spectra give information about the atomic structure of the sample under investigation. In the case of molecular systems, empirical rules are commonly used to extract this information from the raw experimental data. However, this approach cannot be applied in the solid state, as the atomic configurations often cannot be modeled by chemical analogs or reference compounds. In these cases *ab initio* calculations of the chemical shifts are the only way to obtain an unambiguous determination of the microscopic structure.

Until recently, there has been no theory for the calculation of NMR chemical shifts in extended periodic systems, and the conventional approach to the theoretical interpretation of solid-state NMR spectra has been to approximate the infinite solid by a cluster.[2] In this way, the traditional quantum chemical approaches[3–6] can be used to calculate the chemical shifts. Unfortunately, true convergence with respect to basis set and cluster size is often not possible due to the limitations of available computational resources.

The work of Mauri, Pfrommer, and Louie[7] (MPL) solved the problem of calculating NMR chemical shifts in the solid state with an all-electron Hamiltonian. Integrated with their approach to the calculation of magnetic susceptibility,[8] they presented a theory for the *ab initio* computation of NMR chemical shifts in condensed matter systems using periodic boundary conditions (hereafter referred to as the MPL method). Although the MPL theory has been derived using an all-electron Hamiltonian, so far it has only been implemented in an electronic structure code based on norm-conserving pseudopotentials. In such implementation the complications inherent within the pseudopotential approximation have been neglected. For this reason, while several useful applications have emerged,[9–14] the method's use has been restricted to the calculation of chemical shifts of light elements (hydrogen, carbon, and nitrogen) and of silicon. Moreover, the description of the silicon chemical shifts re-

quired the explicit inclusion of the $2s$ and $2p$ silicon orbitals as valence and the use of a very high, and computationally expensive, plane-wave energy cutoff of 600 Ry.[14] In the above applications of the MPL method the pseudopotential error had been assumed to be small and controllable. To compute the NMR chemical shifts of nuclei heavier than neon and to truly exploit the ability of pseudopotentials to calculate the properties of complex, low-symmetry structures (which is well established for a wide range of structural properties), a theory is required that does not ignore the pseudopotential approximation.

Apart from the early and isolated attempt of Ridard, Levy, and Millie,[15] it has been widely expected within the quantum chemical community that any theory for the calculation of NMR chemical shifts for nuclei described with a pseudopotential would fail[16] due to the nonrigid nature of the core contributions to the total chemical shift.[3] However, a careful separation of core and valence contributions that ensures that they are individually gauge invariant, by Gregor, Mauri and Car,[17] has shown that this is not the case and that the core contributions are rigid. This suggests that a pseudopotential based theory of NMR might, in fact, exist.

One of the most obvious deficiencies of the pseudopotential approach is that the pseudopotential approximation explicitly neglects the form of the electronic wave functions near the nucleus. The pseudo-wave-functions are chosen to be as smooth as possible in the core region, and the correct nodal structure of the wave functions is lost. This leads to a good approximation for the calculation of total energies and their derivatives, and properties for which the matrix elements are dominated by the regions outside the core. However, the quantitative calculation of many properties—hyperfine parameters, core-level spectra, electric-field gradients, and the NMR chemical shifts—depend critically on the details of the all-electron wave functions at the nucleus. Van de Walle and Blöchl presented a solution to this problem for the calculation of hyperfine parameters[18] based on Blöchl's projector augmented-wave (PAW) electronic structure method,[19] which is itself closely related to Vanderbilt's ultrasoft pseudopotential scheme.[20] While in all

but a few reported cases (where core-electron polarization effects are important[21] or in some magnetic systems[22]) the PAW method gives similar results to pseudopotential approaches, it does provide an extremely useful framework for the unification of all-electron (full-potential) linearized augmented-plane-wave[23] and pseudopotential approaches. Indeed, it it becoming clear that the PAW approach, which will be described in more detail in Sec. III A, offers a general approach to the calculation of all-electron properties from pseudopotential-based schemes. Following the work of Van de Walle and Blöchl, core-level spectra,[24,25] momentum matrix elements,[26] and electric-field gradients[27] have all been calculated using the PAW scheme.

In this paper we present a theory for all-electron magnetic response within the pseudopotential approximation and its application to the calculation of first-principles NMR chemical shifts. The connection between the current response and the chemical shifts is outlined in Sec. II. We introduce an extension of Blöchl's PAW approach, which we call the gauge-including projector augmented-wave (GIPAW) approach. This will be described in Sec. III. A Hamiltonian constructed using GIPAW has the required translational invariance in the presence of a magnetic field. This is not true for the original PAW formulation. In Sec. IV we present our theory for finite systems. In Sec. V we reformulate our expressions for extended systems. To be useful, these expressions must be restricted to *periodic* extended systems, and the periodic theory is presented in Sec. VI. Both the theories for finite and extended periodic systems summarized in Sec. VII have been implemented in a plane-wave pseudopotential electronic structure code. Details of our implementation are given in Sec. VIII. We validate the method by comparison with IGAIM (individual gauges for atoms in molecules) calculations by Gregor *et al.*[17] for a selection of small molecules. The theory for extended systems is further validated by comparison to results obtained by an all-electron plane-wave calculation for a crystalline material, diamond.

II. NMR CHEMICAL SHIFTS

A uniform, external magnetic field **B** applied to a sample of matter induces an electric current. In an insulating non-magnetic material, only the orbital motion of the electrons contributes to this current. Moreover, for the field strengths typically used in NMR experiments, the induced electronic current is proportional to the external field **B** and is the first-order-induced current, $\mathbf{j}^{(1)}(\mathbf{r}')$. The current $\mathbf{j}^{(1)}(\mathbf{r}')$ produces a nonuniform magnetic field,

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

The chemical shift is defined as the ratio between the induced magnetic field and the external uniform applied magnetic field,

$$\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r}) \mathbf{B}. \tag{2}$$

Here $\overleftrightarrow{\sigma}(\mathbf{r})$ is the chemical shift tensor, and the isotropic chemical shift is given by $\sigma(\mathbf{r}) = \text{Tr}[\overleftrightarrow{\sigma}(\mathbf{r})]/3$. NMR experi-

ments can measure $\overleftrightarrow{\sigma}(\mathbf{r})$ at the nuclear positions. To compute the chemical shift tensor we first obtain $\mathbf{j}^{(1)}(\mathbf{r})$ by perturbation theory and then we evaluate $\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r})$ using Eq. (1). We now describe our new approach to the calculation of an induced all-electron current $\mathbf{j}^{(1)}(\mathbf{r}')$ using pseudopotentials and in Sec. VIII the computational procedure we use to obtain $\mathbf{j}^{(1)}(\mathbf{r}')$, and finally $\sigma(\mathbf{r})$, is detailed.

III. PSEUDOPOTENTIALS IN A MAGNETIC FIELD

In this section we develop the gauge-including projector augmented wave method, first describing the original projector augmented-wave method, and then extending it to the case of a uniform applied magnetic field.

A. Projector augmented-wave method

In Ref. 19, Blöchl introduced a linear transformation operator $\mathcal{T}$ that maps the valence pseudo-wave-functions $|\tilde{\Psi}\rangle$ onto the corresponding all-electron wave functions, $|\Psi\rangle = \mathcal{T}|\tilde{\Psi}\rangle$. The operator is defined by specifying a set of target all-electron partial waves $|\phi_{\mathbf{R},n}\rangle$ obtained by the application of $\mathcal{T}$ on to a set of pseudo-partial-waves $|\tilde{\phi}_{\mathbf{R},n}\rangle$ with

$$\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} [|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle] \langle \tilde{p}_{\mathbf{R},n}|, \tag{3}$$

and $\langle \tilde{p}_{\mathbf{R},n}|$ are a set of projectors such that $\langle \tilde{p}_{\mathbf{R},n}|\tilde{\phi}_{\mathbf{R}',m}\rangle = \delta_{\mathbf{R},\mathbf{R}'}\delta_{n,m}$. Each projector and partial wave is an atomic-like function centered on an atomic site **R**, and the index n refers to the angular momentum quantum numbers and to an additional number, used if there is more than one projector per angular-momentum channel. The expectation value of an operator O between all-electron wave functions can be expressed as the expectation value of a pseudo-operator $\tilde{O} = \mathcal{T}^+ O \mathcal{T}$ between the corresponding pseudo-wave-functions.

To obtain a useful formalism we must make some further assumptions. In particular, for each atomic site we define an augmentation region $\Omega_{\mathbf{R}}$ and suppose that (i) outside the augmentation region $\Omega_{\mathbf{R}}$, the $|\tilde{\phi}_{\mathbf{R},n}\rangle$ coincide with the $|\phi_{\mathbf{R},n}\rangle$, (ii) outside the augmentation region $\Omega_{\mathbf{R}}$, the $|\tilde{p}_{\mathbf{R},n}\rangle$ vanish, (iii) within the augmentation region $\Omega_{\mathbf{R}}$, the $|\phi_{\mathbf{R},n}\rangle$ form a complete set for the valence wave functions, i.e., any physical valence all-electron wave function can be written, within $\Omega_{\mathbf{R}}$, as a linear combination of all-electron partial waves, and finally (iv) the augmentation regions of different sites do not overlap. Blöchl has shown that given these assumptions, if O is a local or a semilocal (such as **p** or p^2) operator

$$\tilde{O} = O + \sum_{\mathbf{R},n,m} |\tilde{p}_{\mathbf{R},n}\rangle [\langle \phi_{\mathbf{R},n}|O|\phi_{\mathbf{R},m}\rangle - \langle \tilde{\phi}_{\mathbf{R},n}|O|\tilde{\phi}_{\mathbf{R},m}\rangle]$$

$$\times \langle \tilde{p}_{\mathbf{R},m}|. \tag{4}$$

For simplicity, we shall further suppose that the norms computed within $\Omega_{\mathbf{R}}$ of $|\tilde{\phi}_{\mathbf{R},n}\rangle$ and $|\phi_{\mathbf{R},n}\rangle$ coincide. We then recover the norm-conserving pseudopotential formalism in

the Kleinman-Bylander[28] form. The pseudo-wave-functions that correspond to the all-electron valence eigenstates of the all-electron Hamiltonian H are eigenstates of the pseudo-Hamiltonian $\tilde{H}$ with the same eigenvalues. In the absence of a magnetic field the pseudo-Hamiltonian is

$$\tilde{H} = \mathcal{T}^+ H \mathcal{T} = \frac{1}{2} \mathbf{p}^2 + V^{\text{loc}}(\mathbf{r}) + \sum_{\mathbf{R}} V_{\mathbf{R}}^{\text{nl}}, \quad (5)$$

where $\mathbf{p}$ is the momentum operator, and $V^{\text{loc}}(\mathbf{r})$ is the local part of the pseudopotentials, which includes the self-consistent part of the Hamiltonian. The nonlocal part of the pseudopotential at the atomic site $\mathbf{R}$ in the above expression is

$$V_{\mathbf{R}}^{\text{nl}} = \sum_{n,m} |\tilde{p}_{\mathbf{R},n}\rangle a_{n,m}^{\mathbf{R}} \langle \tilde{p}_{\mathbf{R},m}|. \quad (6)$$

The $a_{n,m}^{\mathbf{R}}$ are the strengths of the nonlocal potential in each channel, and they depend on $\mathbf{R}$ since each atomic site may be occupied by a different chemical species.

The choice of the pseudo-partial-waves and projectors is largely arbitrary. However, for a scheme to be useful, all the lowest eigenvalues of $\tilde{H}$ should coincide with a valence eigenvalue of H up to an given energy $E_{\text{val}}^{\text{max}}$, i.e., no ghost states should be introduced into the pseudospectrum up to an energy $E_{\text{val}}^{\text{max}}$. The energy $E_{\text{val}}^{\text{max}}$ depends on the specific property we wish to compute, and should at least be larger than the highest occupied eigenvalue.

In contrast to the traditional formulation of pseudopotentials, using the PAW formulation it is possible to obtain the expectation values of all-electron operators in terms of pseudo-wave-functions using the pseudo-operators defined in Eq. (4).

B. A single augmentation region in a uniform magnetic field

In the presence of a uniform external magnetic field $\mathbf{B}$ the all-electron Hamiltonian is

$$H = \frac{1}{2} \left(\mathbf{p} + \frac{1}{c} \mathbf{A}(\mathbf{r}) \right)^2 + V(\mathbf{r}), \quad (7)$$

where c is the speed of light, $V(\mathbf{r})$ is the all-electron local potential, and $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})$. We want to construct the corresponding pseudo-Hamiltonian for a complex system, which will contain many augmentation regions. However, before treating this general case, we consider a simplified system with just a single augmentation region. The spatial origin is chosen to coincide with the atomic site of the augmentation region. In the symmetric gauge $\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{d})$, where $\mathbf{d}$ is a constant vector that indicates the gauge origin. The expectation values of the all-electron eigenstates for observable operators do not depend on the gauge origin $\mathbf{d}$. However, the number of partial waves required to correctly describe the valence all-electron eigenstates in the augmentation region critically depends on the choice of $\mathbf{d}$. To minimize the number of partial waves required we must put the gauge origin at the atomic site of the augmentation region, setting $\mathbf{d} = \mathbf{0}$. Making this choice, we minimize the effect of the magnetic

field on the all-electron wave functions in the augmentation region, where $|\mathbf{A}(\mathbf{r})|^2$ and its spatial derivatives attain their minimum value. Moreover, with this choice of gauge, the interaction between the valence and core states of the augmented atom is negligibly small.[17] This is essential if we are to make the pseudopotential approximation. With

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \quad (8)$$

the all-electron Hamiltonian becomes

$$H = \frac{1}{2} \mathbf{p}^2 + V(\mathbf{r}) + \frac{1}{2c} \mathbf{L} \cdot \mathbf{B} + \frac{1}{8c^2} (\mathbf{B} \times \mathbf{r})^2, \quad (9)$$

where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is the angular-momentum operator computed with respect to the atomic site within the augmentation region. Using Eqs. (4) and (5), we obtain the corresponding pseudo-Hamiltonian,

$$\tilde{H} = \frac{1}{2} \mathbf{p}^2 + V^{\text{loc}}(\mathbf{r}) + V_{\mathbf{0}}^{\text{nl}} + \frac{1}{2c} \mathbf{L} \cdot \mathbf{B} + \frac{1}{8c^2} (\mathbf{B} \times \mathbf{r})^2$$

$$+ \sum_{n,m} |\tilde{p}_{\mathbf{0},n}\rangle (b_{n,m}^{(1)} + b_{n,m}^{(2)}) \langle \tilde{p}_{\mathbf{0},m}|, \quad (10)$$

where

$$b_{n,m}^{(1)} = \frac{1}{2c} \mathbf{B} \cdot [\langle \phi_{\mathbf{0},n} | \mathbf{L} | \phi_{\mathbf{0},m} \rangle - \langle \tilde{\phi}_{\mathbf{0},n} | \mathbf{L} | \tilde{\phi}_{\mathbf{0},m} \rangle] \quad (11)$$

and

$$b_{n,m}^{(2)} = \frac{1}{8c^2} [\langle \phi_{\mathbf{0},n} | (\mathbf{B} \times \mathbf{r})^2 | \phi_{\mathbf{0},m} \rangle - \langle \tilde{\phi}_{\mathbf{0},n} | (\mathbf{B} \times \mathbf{r})^2 | \tilde{\phi}_{\mathbf{0},m} \rangle]. \quad (12)$$

If just one projector per angular momentum channel is used, as is usually the case with norm conserving pseudopotentials,[29,30] $b_{n,m}^{(1)}$ exactly vanishes, since $|\phi_{\mathbf{0},n}\rangle$ and $|\tilde{\phi}_{\mathbf{0},n}\rangle$ are eigenstates of L and L_z with the same norm within the augmentation region. Moreover, since $(\mathbf{B} \times \mathbf{r})^2$ goes to zero in the center of the augmentation region, for norm-conserving pseudopotentials the term $b_{n,m}^{(2)}$ can also be neglected. Thus, with one augmentation region centered at the gauge origin, the coupling with the magnetic field in the pseudo- and all-electron Hamiltonians has the same form, i.e.,

$$\tilde{H} = \frac{1}{2} \mathbf{p}^2 + V^{\text{loc}}(\mathbf{r}) + V_{\mathbf{0}}^{\text{nl}} + \frac{1}{2c} \mathbf{L} \cdot \mathbf{B} + \frac{1}{8c^2} (\mathbf{B} \times \mathbf{r})^2. \quad (13)$$

C. Translations in a uniform magnetic field

The derivation in Sec. III B is not useful for systems with several augmentation regions. Indeed, the gauge origin can coincide with just one augmentation site at any given time. As a result, the number for projectors of the other augmentation regions would have to be increased to reach complete-

ness in those regions. The cause of this problem is that the PAW approach does not preserve translational invariance in a uniform magnetic field.

In a uniform magnetic field the description of the system should be invariant upon a rigid translation of all the atoms by a vector $\mathbf{t}$. Following the translation, the all-electron potential becomes $V'(\mathbf{r})=V(\mathbf{r}-\mathbf{t})$ and the corresponding Hamiltonian is

$$H'=\frac{1}{2}\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right)^2+V(\mathbf{r}-\mathbf{t}),\qquad(14)$$

where $\mathbf{A}(\mathbf{r})$ is still given by Eq. (8). Because of the translational invariance, the eigenenergies of H' coincide with the eigenenergies of the original Hamiltonian H. However, the new eigenstates $|\Psi_n'\rangle$ are not just obtained by a rigid translation of the original eigenstates $|\Psi_n\rangle$, but, upon translation, they pick up an additional phase factor proportional to the magnetic field

$$\langle\mathbf{r}|\Psi_n'\rangle=e^{(i/2c)\mathbf{r}\cdot\mathbf{t}\times\mathbf{B}}\langle\mathbf{r}-\mathbf{t}|\Psi_n\rangle.\qquad(15)$$

The PAW transformation does not ensure exact invariance upon translation, since the pseudo-wave-functions constructed with the $\mathcal{T}$ transformation operator of Eq. (3) do not transform according to Eq. (15).

D. Gauge-including projector augmented-wave method

To restore the translational invariance within a PAW-like approach, we introduce a field dependent transformation operator $\mathcal{T}_\mathbf{B}$, which, by construction, imposes the translational invariance exactly,

$$\mathcal{T}_\mathbf{B}=\mathbf{1}+\sum_{\mathbf{R},n}e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}[|\phi_{\mathbf{R},n}\rangle-|\tilde{\phi}_{\mathbf{R},n}\rangle]\langle\tilde{p}_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}.\qquad(16)$$

This new transformation defines our approach, which we call the gauge-including projector augmented-wave (GIPAW) method. In the following, we indicate with a bar the pseudo-wave-functions and operators obtained using the $\mathcal{T}_\mathbf{B}$ operator by analogy to Blöchl's use of the tilde. By construction, the pseudoeigenstates $|\bar{\Psi}\rangle$, generated from the all-electron eigenstates using $|\Psi\rangle=\mathcal{T}_\mathbf{B}|\bar{\Psi}\rangle$, satisfy the same translation relation as the all-electron eigenstates given by Eq. (15). The GIPAW pseudo-operator $\bar{O}=\mathcal{T}_\mathbf{B}^+O\mathcal{T}_\mathbf{B}$ corresponding to a local or a semilocal operator O is given by

$$\bar{O}=O+\sum_{\mathbf{R},n,m}e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{p}_{\mathbf{R},n}\rangle$$
$$\times[\langle\phi_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}Oe^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\phi_{\mathbf{R},m}\rangle$$
$$-\langle\tilde{\phi}_{\mathbf{R},n}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}Oe^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}|\tilde{\phi}_{\mathbf{R},m}\rangle]$$
$$\times\langle\tilde{p}_{\mathbf{R},m}|e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}.\qquad(17)$$

There are connections between our GIPAW approach and the gauge-including atomic orbitals[4] (GIAO) and the independent gauge for localized orbitals[3] (IGLO) methods, widely

used in the quantum chemical community. However, it should be recognized that in GIPAW the phase required to maintain the translational invariance is carried by the operators, whereas in the GIAO and in IGLO approaches the field-dependent phase is attached to the basis functions and to the occupied electronic orbitals, respectively.

E. GIPAW Hamiltonian

Using Eq. (17), the identity

$$e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r})\right)^n e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}=\left(\mathbf{p}+\frac{1}{c}\mathbf{A}(\mathbf{r}-\mathbf{R})\right)^n,\qquad(18)$$

for integer n, and the outcomes of the discussion concerning $b_{n,m}^{(1)}$ and $b_{n,m}^{(2)}$ in Sec. III B, we finally obtain the GIPAW pseudo-Hamiltonian

$$\bar{H}=\frac{1}{2}\mathbf{p}^2+V^{\mathrm{loc}}(\mathbf{r})+\sum_\mathbf{R}e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}V_\mathbf{R}^{\mathrm{nl}}e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$
$$+\frac{1}{2c}\mathbf{L}\cdot\mathbf{B}+\frac{1}{8c^2}(\mathbf{B}\times\mathbf{r})^2.\qquad(19)$$

The GIPAW Hamiltonian coincides with the PAW Hamiltonian, Eq. (5) for $\mathbf{B}=0$, and with the PAW Hamiltonian, Eq. (13), for $\mathbf{B}\neq0$ in systems with a single augmentation region centered at the origin. Moreover, as expected, the GIPAW eigenenergies are exactly invariant upon translation, in contrast to the PAW eigenenergies.

For later use in perturbation theory, $\bar{H}$ can be expanded in powers of B,

$$\bar{H}=\bar{H}^{(0)}+\bar{H}^{(1)}+O(B^2),\qquad(20)$$

where $\bar{H}^{(0)}=\tilde{H}^{(0)}$ is the unperturbed Hamiltonian given by Eq. (5) and

$$\bar{H}^{(1)}=\frac{1}{2c}\left(\mathbf{L}+\sum_\mathbf{R}\mathbf{R}\times\mathbf{v}_\mathbf{R}^{\mathrm{nl}}\right)\cdot\mathbf{B},\qquad(21)$$

where

$$\mathbf{v}_\mathbf{R}^{\mathrm{nl}}=\frac{1}{i}[\mathbf{r},V_\mathbf{R}^{\mathrm{nl}}],\qquad(22)$$

and with square brackets we indicate the commutator.

F. GIPAW current operator

Another observable required to compute the NMR chemical shifts is the current. The all-electron electric current operator evaluated at the position $\mathbf{r}'$ is

$$\mathbf{J}(\mathbf{r}')=\mathbf{J}^{\mathrm{p}}(\mathbf{r}')-\frac{\mathbf{A}(\mathbf{r}')}{c}|\mathbf{r}'\rangle\langle\mathbf{r}'|=\mathbf{J}^{\mathrm{p}}(\mathbf{r}')-\frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'|,\qquad(23)$$

where $\mathbf{J}^{\mathrm{p}}(\mathbf{r}')$ is the paramagnetic current operator,

$$\mathbf{J}^{\mathrm{p}}(\mathbf{r}') = -\frac{\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}}{2}. \qquad (24)$$

Using Eqs. (17) and (18), we obtain the corresponding GI-PAW operator

$$\bar{\mathbf{J}}(\mathbf{r}') = \mathbf{J}^{\mathrm{p}}(\mathbf{r}') - \frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'| + \sum_{\mathbf{R}} e^{(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}[\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{p}}(\mathbf{r}')$$

$$+ \Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{d}}(\mathbf{r}')]e^{-(i/2c)\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}, \qquad (25)$$

where

$$\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{p}}(\mathbf{r}') = \sum_{n,m} |\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{J}^{\mathrm{p}}(\mathbf{r}')|\phi_{\mathbf{R},m}\rangle$$

$$- \langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{J}^{\mathrm{p}}(\mathbf{r}')|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}| \qquad (26)$$

is what we call the paramagnetic augmentation operator, and

$$\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{d}}(\mathbf{r}') = -\frac{\mathbf{B}\times(\mathbf{r}'-\mathbf{R})}{2c}\sum_{n,m} |\tilde{p}_{\mathbf{R},n}\rangle[\langle\phi_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\phi_{\mathbf{R},m}\rangle$$

$$- \langle\tilde{\phi}_{\mathbf{R},n}|\mathbf{r}'\rangle\langle\mathbf{r}'|\tilde{\phi}_{\mathbf{R},m}\rangle]\langle\tilde{p}_{\mathbf{R},m}| \qquad (27)$$

is what we call the diamagnetic augmentation operator.

As for the Hamiltonian, for perturbation theory purposes it is useful to expand the operator $\bar{\mathbf{J}}(\mathbf{r})$ in powers of B,

$$\bar{\mathbf{J}}(\mathbf{r}') = \bar{\mathbf{J}}^{(0)}(\mathbf{r}') + \bar{\mathbf{J}}^{(1)}(\mathbf{r}') + O(B^2), \qquad (28)$$

with

$$\bar{\mathbf{J}}^{(0)}(\mathbf{r}') = \mathbf{J}^{\mathrm{p}}(\mathbf{r}') + \sum_{\mathbf{R}} \Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{p}}(\mathbf{r}') \qquad (29)$$

and

$$\bar{\mathbf{J}}^{(1)}(\mathbf{r}') = -\frac{\mathbf{B}\times\mathbf{r}'}{2c}|\mathbf{r}'\rangle\langle\mathbf{r}'| + \sum_{\mathbf{R}} \left[\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{d}}(\mathbf{r}')\right.$$

$$\left. + \frac{1}{2ci}[\mathbf{B}\times\mathbf{R}\cdot\mathbf{r},\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{p}}(\mathbf{r}')]\right]. \qquad (30)$$

IV. CURRENT RESPONSE IN FINITE SYSTEMS

Within density-functional perturbation theory, the current can be computed using the GIPAW operators and wave functions as

$$\mathbf{j}^{(1)}(\mathbf{r}') = 2\sum_o [\langle\bar{\Psi}_o^{(1)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle + \langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(0)}(\mathbf{r}')|\bar{\Psi}_o^{(1)}\rangle$$

$$+ \langle\bar{\Psi}_o^{(0)}|\bar{\mathbf{J}}^{(1)}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle]. \qquad (31)$$

Here the factor of 2 accounts for spin degeneracy and the sum runs over the occupied orbitals o. The wavefunction $|\bar{\Psi}_n^{(0)}\rangle$ is an unperturbed eigenstate of $\tilde{H}^{(0)}$ with eigenvalue ε_n and $|\bar{\Psi}_n^{(1)}\rangle$ is its linear variation, projected in the empty subspace

$$|\bar{\Psi}_n^{(1)}\rangle = \mathcal{G}(\varepsilon_n)\bar{H}^{(1)}|\bar{\Psi}_n^{(0)}\rangle. \qquad (32)$$

The Green-function operator is

$$\mathcal{G}(\varepsilon) = \sum_e \frac{|\bar{\Psi}_e^{(0)}\rangle\langle\bar{\Psi}_e^{(0)}|}{\varepsilon - \varepsilon_e}, \qquad (33)$$

with the sum running over the empty orbitals e. Reordering the different contributions of Eq. (31) we obtain

$$\mathbf{j}^{(1)}(\mathbf{r}') = \mathbf{j}_{\mathrm{bare}}^{(1)}(\mathbf{r}') + \mathbf{j}_{\Delta\mathrm{p}}^{(1)}(\mathbf{r}') + \mathbf{j}_{\Delta\mathrm{d}}^{(1)}(\mathbf{r}'), \qquad (34)$$

where

$$\mathbf{j}_{\mathrm{bare}}^{(1)}(\mathbf{r}') = 4\sum_o \mathrm{Re}[\langle\bar{\Psi}_o^{(0)}|\mathbf{J}^{\mathrm{p}}(\mathbf{r}')\mathcal{G}(\varepsilon_o)\bar{H}^{(1)}|\bar{\Psi}_o^{(0)}\rangle]$$

$$- \frac{1}{2c}\rho^{\mathrm{ps}}(\mathbf{r}')\mathbf{B}\times\mathbf{r}'. \qquad (35)$$

Re stands for taking the real part and $\rho^{\mathrm{ps}}(\mathbf{r}') = 2\Sigma_o\langle\bar{\Psi}_o^{(0)}|\mathbf{r}'\rangle\langle\mathbf{r}'|\bar{\Psi}_o^{(0)}\rangle$ is the ground-state pseudodensity. The paramagnetic correction to the current is

$$\mathbf{j}_{\Delta\mathrm{p}}^{(1)}(\mathbf{r}') = \sum_{\mathbf{R}',o} \left\{ 4\mathrm{Re}[\langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}'}^{\mathrm{p}}(\mathbf{r}')\mathcal{G}(\varepsilon_o)\bar{H}^{(1)}|\bar{\Psi}_o^{(0)}\rangle] \right.$$

$$\left. + 2\langle\bar{\Psi}_o^{(0)}|\frac{1}{i2c}[\mathbf{B}\times\mathbf{R}'\cdot\mathbf{r},\Delta\mathbf{J}_{\mathbf{R}'}^{\mathrm{p}}(\mathbf{r}')]|\bar{\Psi}_o^{(0)}\rangle \right\}, \qquad (36)$$

and the diamagnetic correction is

$$\mathbf{j}_{\Delta\mathrm{d}}^{(1)}(\mathbf{r}') = 2\sum_{\mathbf{R},o} \langle\bar{\Psi}_o^{(0)}|\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{d}}(\mathbf{r}')|\bar{\Psi}_o^{(0)}\rangle. \qquad (37)$$

Notice that the last two current contributions, $\mathbf{j}_{\Delta\mathrm{p}}^{(1)}(\mathbf{r}')$ and $\mathbf{j}_{\Delta\mathrm{d}}^{(1)}(\mathbf{r}')$, are written as a sum over augmentation sites and vanish outside the augmentation regions, where the all-electron and pseudo-partial-waves coincide.

By construction, the current $\mathbf{j}^{(1)}(\mathbf{r}')$ computed within the GIPAW formalism is, as all physical observables should be, invariant upon translation of the system by a vector $\mathbf{t}$, i.e., after translation the new current should be $\mathbf{j}^{(1)}(\mathbf{r}'-\mathbf{t})$. Interestingly, all three terms, $\mathbf{j}_{\mathrm{bare}}^{(1)}(\mathbf{r}')$, $\mathbf{j}_{\Delta\mathrm{p}}^{(1)}(\mathbf{r}')$, and $\mathbf{j}_{\Delta\mathrm{d}}^{(1)}(\mathbf{r}')$, are individually invariant upon translation. The invariance of $\mathbf{j}_{\Delta\mathrm{d}}^{(1)}(\mathbf{r}')$ is obvious from the definition of the $\Delta\mathbf{J}_{\mathbf{R}}^{\mathrm{d}}(\mathbf{r}')$ operator, Eq. (27). The invariance of the other two contributions is less evident, and to prove it, we need to manipulate Eqs. (35) and (36). To this end, we notice that the second term in the right-hand side (rhs) of Eq. (35) can be rewritten as a commutator,

$$-\frac{1}{2c}\rho^{\mathrm{ps}}(\mathbf{r}')\mathbf{B}\times\mathbf{r}'$$

$$= 2\sum_o \frac{1}{2c}\langle\bar{\Psi}_o^{(0)}|\frac{1}{i}[\mathbf{B}\times\mathbf{r}'\cdot\mathbf{r},\mathbf{J}^{\mathrm{p}}(\mathbf{r}')]|\bar{\Psi}_o^{(0)}\rangle.$$

$$(38)$$

We can now use the generalized *f*-sum rule established in Appendix A, Eq. (A7), with the operators $\mathbf{J}^p(\mathbf{r}')$ and $\Delta \mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}')$ in the place of $\mathcal{O}$ and the operator $\mathbf{r}$ in the place of $\mathcal{E}$, to rewrite the second terms in the rhs of both Eqs. (35) and (36), obtaining

$$\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}') = 4 \sum_o \text{Re} \Bigg[\langle \bar{\Psi}^{(0)}_o | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\varepsilon_o) \bar{H}^{(1)} | \bar{\Psi}^{(0)}_o \rangle$$
$$- \langle \bar{\Psi}^{(0)}_o | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\varepsilon_o) \frac{\mathbf{B} \times \mathbf{r}'}{2c} \cdot \mathbf{v} | \bar{\Psi}^{(0)}_o \rangle \Bigg], \quad (39)$$

$$\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}') = 4 \sum_{\mathbf{R}',o} \text{Re} \Bigg[\langle \bar{\Psi}^{(0)}_o | \Delta \mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}') \mathcal{G}(\varepsilon_o) \bar{H}^{(1)} | \bar{\Psi}^{(0)}_o \rangle$$
$$- \langle \bar{\Psi}^{(0)}_o | \Delta \mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}') \mathcal{G}(\varepsilon_o) \frac{\mathbf{B} \times \mathbf{R}'}{2c} \cdot \mathbf{v} | \bar{\Psi}^{(0)}_o \rangle \Bigg],$$
$$(40)$$

where $\mathbf{v} = 1/i[\mathbf{r}, \bar{H}^{(0)}]$ is the velocity operator. Now the translational invariance of $\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}')$ and $\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}')$ is more explicit, since on translation both $\mathbf{B} \times \mathbf{r}' \cdot \mathbf{v}/2c$ and $\mathbf{B} \times \mathbf{R}' \cdot \mathbf{v}/2c$ generate an extra term equal to $\mathbf{B} \times \mathbf{t} \cdot \mathbf{v}/2c$, as does $\bar{H}^{(1)}$, if, after the translation, we rewrite $\bar{H}^{(1)}$ in terms of the variable of the translated coordinate system $(\mathbf{r} - \mathbf{t})$.

V. CURRENT RESPONSE IN EXTENDED SYSTEMS

In Sec. III we developed a theory for a system containing a single augmentation region located at the origin, and then later for several augmentation regions. We must now check that our results are still useful in situations involving an infinite number of these augmentation regions, as is the case in the solid state.

The expression for $\mathbf{j}^{(1)}_{\Delta d}(\mathbf{r}')$ given by Eq. (37) can be straightforwardly applied to solid state calculations. But, the contributions to the all-electron current $\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}')$ and $\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}')$ given in Eq. (39) and Eq. (40) involve expectation values of the position operator. As these are not generally defined in an extended system, one might worry that Eqs. (39) and (40) are not valid. However, if they are rewritten in the following way:

$$\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}') = \frac{2}{c} \sum_o \text{Re} \Bigg[\langle \bar{\Psi}^{(0)}_o | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\varepsilon_o) \Bigg((\mathbf{r} - \mathbf{r}') \times \mathbf{p}$$
$$+ \sum_{\mathbf{R}} (\mathbf{R} - \mathbf{r}') \times \mathbf{v}^{\text{nl}}_{\mathbf{R}} \Bigg) \cdot \mathbf{B} | \bar{\Psi}^{(0)}_o \rangle \Bigg] \quad (41)$$

and

$$\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}') = \frac{2}{c} \sum_{\mathbf{R}',o} \text{Re} \Bigg[\langle \bar{\Psi}^{(0)}_o | \Delta \mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}') \mathcal{G}(\varepsilon_o) \Bigg((\mathbf{r} - \mathbf{R}') \times \mathbf{p}$$
$$+ \sum_{\mathbf{R}} (\mathbf{R} - \mathbf{R}') \times \mathbf{v}^{\text{nl}}_{\mathbf{R}} \Bigg) \cdot \mathbf{B} | \bar{\Psi}^{(0)}_o \rangle \Bigg] \quad (42)$$

then it becomes clear that they are indeed well defined. The Green-function operator $\mathcal{G}(\varepsilon_o)$, in an insulator, and both the paramagnetic augmentation operator $\Delta \mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}')$ and the nonlocal pseudopotential operator $\mathbf{v}^{\text{nl}}_{\mathbf{R}}$ are short ranged.[31] This ensures that contributions to the current response for large values of $(\mathbf{r} - \mathbf{r}')$, $(\mathbf{R} - \mathbf{r}')$, $(\mathbf{r} - \mathbf{R}')$, or $(\mathbf{R} - \mathbf{R}')$ in Eqs. (41) and (42) vanish.

VI. CURRENT RESPONSE IN INFINITELY PERIODIC SYSTEMS

The expressions given above are valid for any extended system. However, the only such computationally tractable systems are those exhibiting translational symmetry or infinitely periodic systems. We now develop the equations making this translational symmetry explicit, by writing 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.

In order to take full advantage of this translational symmetry we first define the functions $\mathbf{S}_{\text{bare}}(\mathbf{r}',q)$ and $\mathbf{S}_{\Delta p}(\mathbf{r}',q)$ as

$$\mathbf{S}_{\text{bare}}(\mathbf{r}',q) = \frac{2}{c} \sum_{i=x,y,z} \sum_o \text{Re} \Bigg[\frac{1}{i}$$
$$\times \langle \bar{\Psi}^{(0)}_o | \mathbf{J}^p(\mathbf{r}') \mathcal{G}(\varepsilon_o) \mathbf{B} \times \hat{\mathbf{u}}_i \cdot \Bigg(e^{iq\hat{\mathbf{u}}_i \cdot (\mathbf{r} - \mathbf{r}')} \mathbf{p}$$
$$+ \sum_{\mathbf{R}} e^{iq\hat{\mathbf{u}}_i \cdot (\mathbf{R} - \mathbf{r}')} \mathbf{v}^{\text{nl}}_{\mathbf{R}} \Bigg) | \bar{\Psi}^{(0)}_o \rangle \Bigg], \quad (43)$$

$$\mathbf{S}_{\Delta p}(\mathbf{r}',q) = \frac{2}{c} \sum_{i=x,y,z} \sum_{\mathbf{R}',o} \text{Re} \Bigg[\frac{1}{i}$$
$$\times \langle \bar{\Psi}^{(0)}_o | \Delta \mathbf{J}^p_{\mathbf{R}'}(\mathbf{r}') \mathcal{G}(\varepsilon_o) \mathbf{B} \times \hat{\mathbf{u}}_i \cdot \Bigg(e^{iq\hat{\mathbf{u}}_i \cdot (\mathbf{r} - \mathbf{R}')} \mathbf{p}$$
$$+ \sum_{\mathbf{R}} e^{iq\hat{\mathbf{u}}_i \cdot (\mathbf{R} - \mathbf{R}')} \mathbf{v}^{\text{nl}}_{\mathbf{R}} \Bigg) | \bar{\Psi}^{(0)}_o \rangle \Bigg], \quad (44)$$

where the $\hat{\mathbf{u}}_i$ are unit vectors in the three Cartesian directions. We can then write

$$\mathbf{j}^{(1)}_{\text{bare}}(\mathbf{r}') = \lim_{q \to 0} \frac{1}{2q} [\mathbf{S}_{\text{bare}}(\mathbf{r}',q) - \mathbf{S}_{\text{bare}}(\mathbf{r}',-q)], \quad (45)$$

$$\mathbf{j}^{(1)}_{\Delta p}(\mathbf{r}') = \lim_{q \to 0} \frac{1}{2q} [\mathbf{S}_{\Delta p}(\mathbf{r}',q) - \mathbf{S}_{\Delta p}(\mathbf{r}',-q)]. \quad (46)$$

This can be seen to be correct by expanding the exponentials in Eqs. (43) and (44) as $e^{iq\hat{\mathbf{u}}_i \cdot \mathbf{x}} = 1 + iq\hat{\mathbf{u}}_i \cdot \mathbf{x} + O((qx)^2)$, taking the limits in Eqs. (45) and (46) and comparing them to Eqs. (41) and (42). The limits taken using the expanded exponentials are valid since only finite values of $\mathbf{x}$ contribute to the total current (as established in Sec. V).

The description of the electronic states as Bloch functions allows us to rewrite the summations over the infinite number of occupied states in Eqs. (43) and (44) as summations over **k**-dependent quantities computed within a single unit cell. The **k**-dependent Green function is

$$\mathcal{G}_{\mathbf{k}}(\varepsilon) = \sum_e \frac{|\bar{u}_{e,\mathbf{k}}^{(0)}\rangle\langle\bar{u}_{e,\mathbf{k}}^{(0)}|}{\varepsilon - \varepsilon_{e,\mathbf{k}}}. \qquad (47)$$

A consequence of reexpressing the current contributions in terms of $\mathbf{S}_{\text{bare}}(\mathbf{r}',q)$ and $\mathbf{S}_{\Delta\text{p}}(\mathbf{r}',q)$ is that we must evaluate several quantities at **k** and **k**+**q** simultaneously. For example, the usual form of the **k**-dependent nonlocal pseudopotential operator is generalized,

$$V_{\mathbf{k},\mathbf{k}'}^{\text{nl}} = \sum_{\tau} \sum_{n,m} |\tilde{p}_{\tau,n}^{\mathbf{k}}\rangle a_{n,m}^{\tau} \langle\tilde{p}_{\tau,m}^{\mathbf{k}'}|. \qquad (48)$$

This operator acts on Bloch functions at **k** to the left, and **k**′ to the right. For **k**=**k**′, $V_{\mathbf{k},\mathbf{k}'}^{\text{nl}}$ coincides with the **k**-dependent nonlocal pseudopotential operator, as implemented in plane-wave pseudopotential codes. The **k**-dependent projectors in terms of $|\tilde{p}_{\mathbf{R},n}\rangle$, the real-space projectors, are given by

$$|\tilde{p}_{\tau,n}^{\mathbf{k}}\rangle = \sum_{\mathbf{L}} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{L}-\tau)}|\tilde{p}_{\mathbf{L}+\tau,n}\rangle, \qquad (49)$$

where the **L** are lattice vectors and the τ are the internal coordinates of the atoms. We arrive at analogous expressions for both the velocity operator,

$$\mathbf{v}_{\mathbf{k},\mathbf{k}'} = -i\nabla + \mathbf{k}' + \frac{1}{i}[\mathbf{r}, V_{\mathbf{k},\mathbf{k}'}^{\text{nl}}], \qquad (50)$$

and the paramagnetic current operator,

$$\mathbf{J}_{\mathbf{k},\mathbf{k}'}^{\text{p}}(\mathbf{r}') = -\frac{(-i\nabla+\mathbf{k})|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|(-i\nabla+\mathbf{k}')}{2}. \qquad (51)$$

Combining the above we arrive at a compact expression for $\mathbf{S}_{\text{bare}}(\mathbf{r}',q)$:

$$\mathbf{S}_{\text{bare}}(\mathbf{r}',q) = \frac{2}{cN_{\mathbf{k}}} \sum_{i=x,y,z} \sum_{o,\mathbf{k}} \text{Re}\left[\frac{1}{i}\right.$$
$$\left. \times \langle\bar{u}_{o,\mathbf{k}}^{(0)}|\mathbf{J}_{\mathbf{k},\mathbf{k}+\mathbf{q}_i}^{\text{p}}(\mathbf{r}')\mathcal{G}_{\mathbf{k}+\mathbf{q}_i}(\varepsilon_{o,\mathbf{k}})\mathbf{B}\times\hat{\mathbf{u}}_i\cdot\mathbf{v}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}}|\bar{u}_{o,\mathbf{k}}^{(0)}\rangle\right], \qquad (52)$$

where $\mathbf{q}_i = q\hat{\mathbf{u}}_i$ and $N_{\mathbf{k}}$ is the number of **k** points included in the summation. Similarly, by also defining

$$\Delta\mathbf{J}_{\mathbf{L},\tau,\mathbf{k},\mathbf{k}'}^{\text{p}}(\mathbf{r}') = \sum_{n,m} |\tilde{p}_{\tau,n}^{\mathbf{k}}\rangle[\langle\phi_{\mathbf{L}+\tau,n}|\mathbf{J}^{\text{p}}(\mathbf{r}')|\phi_{\mathbf{L}+\tau,m}\rangle$$
$$- \langle\tilde{\phi}_{\mathbf{L}+\tau,n}|\mathbf{J}^{\text{p}}(\mathbf{r}')|\tilde{\phi}_{\mathbf{L}+\tau,m}\rangle]\langle\tilde{p}_{\tau,m}^{\mathbf{k}'}|, \qquad (53)$$

the expression for the paramagnetic augmentation term is

$$\mathbf{S}_{\Delta\text{p}}(\mathbf{r}',q) = \frac{2}{cN_{\mathbf{k}}} \sum_{i=x,y,z} \sum_{\mathbf{L},\tau,o,\mathbf{k}} \text{Re}\left[\frac{1}{i}\right.$$
$$\left. \times \langle\bar{u}_{o,\mathbf{k}}^{(0)}|\Delta\mathbf{J}_{\mathbf{L},\tau,\mathbf{k},\mathbf{k}+\mathbf{q}_i}^{\text{p}}(\mathbf{r}')\mathcal{G}_{\mathbf{k}+\mathbf{q}_i}(\varepsilon_{o,\mathbf{k}})\mathbf{B}\times\hat{\mathbf{u}}_i\cdot\mathbf{v}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}}|\bar{u}_{o,\mathbf{k}}^{(0)}\rangle\right]. \qquad (54)$$

These expressions for $\mathbf{S}_{\text{bare}}(\mathbf{r}',q)$ and $\mathbf{S}_{\Delta\text{p}}(\mathbf{r}',q)$ allow the evaluation of the all-electron current response through Eqs. (45), (46), and (37).

VII. SUMMARY OF APPROACHES

There are three different approaches that we could take in the calculation of the first-order current response to a uniform external applied magnetic field. If the current response in an extended periodic system is required, then the approach described in Sec. VI must be taken. In this case, the expressions given in Eqs. (45), (46), (52), (54), and (37) are evaluated, and it is referred to as the ''crystal approach.'' The total current response in a finite system can be calculated using Eqs. (35), (36), and (37). This approach is referred to as the ''molecular approach.'' Alternatively, using the results of the generalized f-sum rule, Eqs. (39), (40), and (37) can be used. This is the ''molecular sum-rule approach.'' Setting $\mathcal{T}_{\mathbf{B}}=1$ in the GIPAW formalism, i.e., in the all-electron case, the crystal approach becomes equivalent to the MPL method,[7] the molecular approach becomes equivalent to the single gauge method [Eq. (3) of Ref. 17], and the molecular sum-rule approach becomes equivalent to the continuous set of gauge transformation method[32] (CSGT) with the $\mathbf{d}(\mathbf{r})=\mathbf{r}$ gauge function [Eq. (8) of Ref. 17].

The crystal approach can be used to calculate molecular properties through the use of large supercells. If the generalized f-sum rule holds, then the results obtained by each of the three approaches should be equivalent. This is demonstrated in Sec. IX. If the generalized f-sum rule does not hold well (for example, if the basis set used is far from completeness as is the case for the atomic-orbital basis sets used in most quantum chemical calculations[17]), then the crystal approach and the molecular sum-rule approach will still give the same results. However, the results obtained using the molecular approach will be different. In particular, we expect that the molecular approach will require a much larger atomic-orbital basis set to converge the NMR chemical shifts than the other two methods, as it has been proved to be the case for all-electron Hamiltonians.[32] This is because the two terms in Eq. (35) [as well as the two terms in Eq. (36)] of the molecular approach converge at different rates with respect to the completeness of the basis set.[32,17]

VIII. CALCULATION OF NMR CHEMICAL SHIFTS

It is important to show that the GIPAW method is a practical approach to the calculation of NMR chemical shifts. We have therefore implemented the method into a parallelized plane-wave pseudopotential electronic structure code.[33] Such codes self-consistently calculate the ground-state electronic

structure. Specifically, the self-consistent Hamiltonian $\bar{H}^{(0)}$ and the corresponding wave functions $|\bar{\Psi}_n^{(0)}\rangle$ that appear in the above expressions are obtained. In this section we outline the features of the implementation that are specific to the GIPAW method, and not to the pseudopotential method in general. The plane-wave pseudopotential method is most naturally suited to the crystal approach for the calculation of NMR chemical shifts. However, we also implemented both molecular methods in our plane-wave code, for completeness. This is described in Sec. VIII D.

A. Application of the Green function

There are several points at which first-order wave functions of the form

$$|\bar{\Psi}_n^{(1)}\rangle = \mathcal{G}(\varepsilon_n)\bar{H}^{(1)}|\bar{\Psi}_n^{(0)}\rangle \qquad (55)$$

must be evaluated. The Green function $\mathcal{G}(\varepsilon)$ is given by

$$\mathcal{G}(\varepsilon) = \sum_e \frac{|\bar{\Psi}_e^{(0)}\rangle\langle\bar{\Psi}_e^{(0)}|}{\varepsilon - \varepsilon_e}, \qquad (56)$$

and a naive approach would require the explicit summation over all empty states. This is unnecessarily arduous. We can multiply Eq. (55) through by $(\varepsilon_n - \bar{H}^{(0)})$. If we then write $\mathcal{Q} = \Sigma_e|\bar{\Psi}_e^{(0)}\rangle\langle\bar{\Psi}_e^{(0)}| = 1 - \Sigma_o|\bar{\Psi}_o^{(0)}\rangle\langle\bar{\Psi}_o^{(0)}|$, where the sums over o and e are over the occupied and empty states, respectively, we obtain

$$(\varepsilon_n - \bar{H}^{(0)})|\bar{\Psi}_n^{(1)}\rangle = \mathcal{Q}\bar{H}^{(1)}|\bar{\Psi}_n^{(0)}\rangle. \qquad (57)$$

This is a linear system involving only the occupied states, and can be solved using a conjugate gradient minimization scheme,[34] as in Ref. 7. This approach ensures that our method is comparable in computational cost to the calculation of the ground-state electronic structure.

B. The velocity operator

The velocity operator $\mathbf{v} = 1/i\,[\mathbf{r}, \bar{H}^{(0)}]$ appears in various guises throughout the relevant expressions above. The velocity operator may also be written as the first derivative of the **k**-dependent Hamiltonian with respect to **k**. The term related to the kinetic energy is straightforward to evaluate, and is simply the momentum operator. The term due to the nonlocal potential, which is defined numerically, is best obtained numerically. In our implementation we simply take the appropriate numerical derivative of the **k**-dependent nonlocal potential operators. The derivatives are evaluated by calculating the nonlocal potential at, say, **k** and **k**+**q**, where **q** is chosen to be small enough that the resulting numerical derivative is accurate, but not so small so as to introduce numerical noise.

C. The crystal approach

The crystal approach requires that the limits of Eqs. (45) and (46) are evaluated. These are, in effect, similar to the numerical derivatives which must be take in reciprocal space in order to evaluate the velocity operators. And in practice we take the same value for the reciprocal-space step size in both cases. The same considerations apply. The step should be chosen to be small enough that the resulting limit is accurately approximated, but not so small that numerical noise dominates. A typical value is 0.01 Bohr^{-1}.

D. Finite systems in periodic boundary conditions

Both the molecular approach and the molecular sum-rule approach were implemented. The major difference between these approaches and the crystal approach, from a computational perspective, is that the reciprocal-space numerical derivative is replaced by a direct application of the position operator to the wave functions. Clearly, the position operator is not defined within periodic boundary conditions. But we can treat it approximately by constructing a periodic sawtoothlike function (in practice we build the function in reciprocal space). Near the center of the simulation cell, or about wherever the sawtooth is centered, this operator approximates the position operator. This approximation improves as the size of the simulation cell is increased, and for good results the magnitude of the induced current should be small on the surface where the sawtooth function changes sign.

E. From the current to the NMR chemical shifts

The GIPAW approach separates the contributions to the current response into a bare term, $\mathbf{j}_{bare}^{(1)}(\mathbf{r})$, and two correction terms, the paramagnetic and diamagnetic corrections, $\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r})$ and $\mathbf{j}_{\Delta d}^{(1)}(\mathbf{r})$, respectively. To compute the NMR chemical shifts, using Eq. (2), the induced magnetic field, $\mathbf{B}_{in}^{(1)}(\mathbf{R})$, must be evaluated at each nuclear position **R**. In principle, one could combine the three current contributions and obtain $\mathbf{B}_{in}^{(1)}(\mathbf{R})$ from the total current using Eq. (1). We use a different approach. We take advantage of the linearity of Eq. (1), and we solve it for each of the three current contributions, obtaining a bare induced field $\mathbf{B}_{bare}^{(1)}(\mathbf{R})$, a paramagnetic correction field, $\mathbf{B}_{\Delta p}^{(1)}(\mathbf{R})$, and a diamagnetic correction field, $\mathbf{B}_{\Delta d}^{(1)}(\mathbf{R})$.

To compute the correction fields, we suppose that just the correction currents, $\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r})$ and $\mathbf{j}_{\Delta d}^{(1)}(\mathbf{r})$, within the augmentation region $\Omega_{\mathbf{R}}$ contribute to $\mathbf{B}_{\Delta p}^{(1)}(\mathbf{R})$ and $\mathbf{B}_{\Delta d}^{(1)}(\mathbf{R})$ at the nuclear position **R**. Using this on-site approximation, combining Eqs. (1) and (37), we obtain

$$\mathbf{B}_{\Delta d}^{(1)}(\mathbf{R}) = 2 \sum_{o,n,m} \langle\bar{\Psi}_o^{(0)}|\tilde{p}_{\mathbf{R},n}\rangle \mathbf{e}_{n,m}^{\mathbf{R}} \langle\tilde{p}_{\mathbf{R},m}|\bar{\Psi}_o^{(0)}\rangle, \qquad (58)$$

where

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

$$- \langle\tilde{\phi}_{\mathbf{R},n}|\frac{(\mathbf{R}-\mathbf{r})\times[\mathbf{B}\times(\mathbf{R}-\mathbf{r})]}{2c^2|\mathbf{R}-\mathbf{r}|^3}|\tilde{\phi}_{\mathbf{R},m}\rangle. \qquad (59)$$

The coefficients $\mathbf{e}_{n,m}^{\mathbf{R}}$ depend only on the atomic species, and need only be calculated once. Similarly, within the on-site approximation, by combining Eq. (1) with the equations for the $\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r})$ correction current, we obtain expressions for the paramagnetic correction field, $\mathbf{B}_{\Delta p}^{(1)}(\mathbf{R})$, which depend linearly on the coefficients $\mathbf{f}_{n,m}^{\mathbf{R}}$,

$$\mathbf{f}_{n,m}^{\mathbf{R}} = \langle \phi_{\mathbf{R},n} | \frac{\mathbf{L}_{\mathbf{R}}}{|\mathbf{r}-\mathbf{R}|^3} | \phi_{\mathbf{R},m} \rangle - \langle \tilde{\phi}_{\mathbf{R},n} | \frac{\mathbf{L}_{\mathbf{R}}}{|\mathbf{r}-\mathbf{R}|^3} | \tilde{\phi}_{\mathbf{R},m} \rangle,$$
(60)

where $\mathbf{L}_{\mathbf{R}} = (\mathbf{r}-\mathbf{R}) \times \mathbf{p}$ is the angular momentum operator evaluated with respect to the atomic site $\mathbf{R}$. Again, the coefficients $\mathbf{f}_{n,m}^{\mathbf{R}}$ depend only on the atomic species, and need only be evaluated once.

To compute the bare induced field, $\mathbf{B}_{bare}^{(1)}(\mathbf{R})$, we Fourier transform Eq. (1) and $\mathbf{j}_{bare}^{(1)}(\mathbf{r}')$ into reciprocal space. The induced magnetic field can then be simply evaluated as,

$$\mathbf{B}_{bare}^{(1)}(\mathbf{G}) = \frac{4\pi}{c} \frac{i\mathbf{G} \times \mathbf{j}_{bare}^{(1)}(\mathbf{G})}{G^2},$$
(61)

where $\mathbf{G}$ is a reciprocal-lattice vector. We subsequently obtain $\mathbf{B}_{bare}^{(1)}(\mathbf{R})$ by a slow Fourier transform at the nuclear positions $\mathbf{R}$ (since the nuclear positions do not coincide, in general, with the points of the fast Fourier transform grid).

For $\mathbf{G} = \mathbf{0}$, Eq. (61) cannot be applied. Indeed the $\mathbf{G} = \mathbf{0}$ component of the induced magnetic field is not a bulk property.[7] The $\mathbf{G} = \mathbf{0}$ component of the induced field is affected by the surface currents that appear on the surface of the sample. In particular, its value depends on the the shape of the sample, and is determined by macroscopic magnetostatics. Following the experimental convention, we assume a spherical sample in our calculations, for which

$$\mathbf{B}_{in}^{(1)}(\mathbf{G}=\mathbf{0}) = \frac{8\pi}{3} \overleftrightarrow{\chi} \mathbf{B},$$
(62)

where $\overleftrightarrow{\chi}$ is the macroscopic magnetic susceptibility.[7] To be consistent with the on-site approximation for the correction currents, we should not take into account the contribution of $\mathbf{j}_{\Delta p}^{(1)}(\mathbf{r})$ and $\mathbf{j}_{\Delta d}^{(1)}(\mathbf{r})$ to $\mathbf{B}_{in}^{(1)}(\mathbf{G}=\mathbf{0})$, and so we use

$$\mathbf{B}_{in}^{(1)}(\mathbf{G}=\mathbf{0}) = \frac{8\pi}{3} \overleftrightarrow{\chi}_{bare} \mathbf{B},$$
(63)

where $\overleftrightarrow{\chi}_{bare}$ is the contribution to the macroscopic susceptibility coming from the bare current $\mathbf{j}_{bare}^{(1)}(\mathbf{r})$. Within the crystal approach, we use the following ansatz for $\overleftrightarrow{\chi}_{bare}$:

$$\overleftrightarrow{\chi}_{bare} = \lim_{q \to 0} \frac{\overleftrightarrow{F}(q) - 2\overleftrightarrow{F}(0) + \overleftrightarrow{F}(-q)}{q^2},$$
(64)

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

$$\overleftrightarrow{Q}(q) = - \sum_{i=x,y,z} \sum_{o,\mathbf{k}} \mathrm{Re} \left[\frac{1}{c^2 N_{\mathbf{k}} V_c} \right.$$

$$\left. \times \langle \bar{u}_{o,\mathbf{k}}^{(0)} | \hat{\mathbf{u}}_i \times (-i\boldsymbol{\nabla}+\mathbf{k}) \mathcal{G}_{\mathbf{k}+\mathbf{q}_i}(\varepsilon_{o,\mathbf{k}}) \hat{\mathbf{u}}_i \times \mathbf{v}_{\mathbf{k}+\mathbf{q}_i,\mathbf{k}} | \bar{u}_{o,\mathbf{k}}^{(0)} \rangle \right], \quad (65)$$

and V_c is the unit-cell volume. In support of this ansatz, one can show that when $\mathcal{T}_{\mathbf{B}} = \mathbf{1}$, i.e., in the all-electron case, the definition of $\overleftrightarrow{\chi}_{bare}$, Eq. (64) becomes equal to the expression for the calculation of the all-electron macroscopic magnetic susceptibility, as derived in Ref. 8.

F. Projectors

In our implementation, we use norm-conserving Troullier-Martins pseudopotentials[30] with single projectors for each angular-momentum channel. As a result, the argument in Section III B holds and the $b_{n,m}^{(1)}$ terms are zero. However, in contrast to what Van de Walle and Blöchl found for the calculation of hyperfine parameters,[18] we found that a minimum of two projectors per channel were required to ensure good transferability of the GIPAW current corrections. Otherwise, the projectors are constructed as described in Ref. 18, except that we choose a polynomial step function $f(r)$ so that the pseudo-wave-functions are cutoff smoothly at some distance less than the pseudopotential core radius.

IX. NUMERICAL TESTS OF THE GIPAW METHOD

A. Comparison with IGAIM results

Quantum chemical approaches have long been able to predict the NMR chemical shifts of small molecules, and one of the most widely used is the GAUSSIAN94[35] quantum chemical code. Rather than compare our GIPAW method directly to experimental chemical shifts, to avoid ambiguity we choose to benchmark our method against this established all-electron quantum chemical approach. The agreement of quantum chemically calculated chemical shifts with experiment has been comprehensively examined by Cheeseman *et al.*,[6] and so success in this benchmarking exercise would lead us to expect that the GIPAW method will show similar agreement with experiment. Gregor *et al.*[17] used the GAUSSIAN94 code to optimize the geometry and calculate the isotropic chemical shift of a selection of small molecules using both the GIAO and IGAIM methods.[6] We compare our GIPAW results [all chemical shifts reported here have been calculated within the local-density approximation[36] (LDA)] to the IGAIM results for several of these molecules (using exactly the same relaxed geometries) in Table I. The total isotropic chemical shifts computed with GIPAW agree very well in all cases with the GAUSSIAN94 results.

The GIPAW results presented in Table I were evaluated using the crystal approach, but results obtained using the molecular approaches differ typically by less than 0.1 parts per million (ppm) in sufficiently large simulation cells, as demonstrated in Table II.

The GIPAW results are converged to the 0.1 ppm level using a plane-wave cutoff of 100 Rydbergs, a super-cell volume of 6000 Bohr^3, and a $2 \times 2 \times 2$ Monkhorst-Pack

TABLE I. Isotropic absolute chemical shifts calculated using the IGAIM method by Gregor *et al* (Ref. 17) and the corresponding GIPAW-LDA results. The GIPAW calculations were performed using a plane-wave cut-off of 100 Ry and in a 6000 Bohr^3 simulation cell. With ''bare,'' ''Δd,'' and ''Δp,'' we indicate the valence GIPAW contributions to the chemical shifts, given by the bare field $\mathbf{B}_{\text{bare}}^{(1)}(\mathbf{R})$ and the two correction fields $\mathbf{B}_{\Delta d}^{(1)}(\mathbf{R})$ and $\mathbf{B}_{\Delta p}^{(1)}(\mathbf{R})$, respectively. The core contribution to the GIPAW chemical shifts is assumed to be constant and evaluated in an all-electron atomic code. All quantities are given as ppm.

Molecule		σ_{GIPAW}				σ_{IGAIM}
	Core	bare	Δd	Δp	Total	Total
H atom						
CH$_4$	0.00	30.47	0.40	0.00	30.87	30.99
CH$_3$F	0.00	25.71	0.41	0.00	26.13	26.50
C$_6$H$_6$	0.00	22.33	0.41	0.00	22.74	23.25
TMS	0.00	30.41	0.40	0.00	30.80	31.02
SiH$_3$F	0.00	24.92	0.38	0.00	25.30	25.13
Si$_2$H$_4$	0.00	24.53	0.36	0.00	24.90	24.78
SiH$_4$	0.00	26.96	0.37	0.00	27.33	27.28
C atom	1s					
CO	198.88	−126.25	4.59	−100.15	−22.93	−21.16
CH$_4$	198.88	16.86	3.97	−28.76	190.96	191.22
CH$_3$F	198.88	−49.64	3.93	−54.70	98.47	99.66
CH$_3$NH$_2$	198.88	−13.98	3.91	−39.05	149.77	150.44
C$_6$H$_6$	198.88	−89.51	4.07	−77.32	36.12	39.52
CF$_4$	198.88	−92.12	3.51	−76.05	34.22	35.29
TMS	198.88	9.12	3.97	−32.65	179.33	182.08
Si atom	1s2s2p					
SiF$_4$	832.39	−19.43	5.28	−408.26	409.97	409.69
SiH$_3$F	832.39	−19.50	5.70	−510.30	308.29	305.45
Si$_2$H$_4$	832.39	−9.04	5.80	−622.45	206.70	202.99
SiH$_4$	832.39	−0.21	5.98	−410.20	427.97	424.37
TMS	832.39	−17.39	5.70	−518.00	302.70	304.39
P atom	1s2s2p					
PF$_3$	902.47	−32.94	6.08	−697.61	178.00	172.52
P$_2$	902.47	−33.84	7.58	−1236.95	−360.75	−375.45
P$_4$	902.47	49.84	7.42	−126.79	832.94	826.62

k-point grid.[38] The states indicated in Table I were treated as core states in the pseudopotential calculations. The core contribution to the GIPAW chemical shifts is assumed to be constant (following the observations of Gregor *et al.*[17]), and evaluated in an all-electron atomic code. For hydrogen a pseudization core radius of 1.2 Bohr was used and only the s-channel was augmented. As a result, since the paramagnetic correction term is proportional to the angular momentum of the augmentation channel [see Eq. (60)], only the bare and diamagnetic correction terms contribute to the total isotropic chemical shifts. There is no core contribution for hydrogen. For the carbon shifts the s and p channels were augmented and a core radius of 1.6 Bohr used in the generation of the pseudopotential. For silicon and phosphorus the d channel was also augmented and core radii of 2.0 Bohr used in both cases. Gregor *et al.* attempted to converge the chemical shifts with respect to their localized basis-set size, and the convergence appears to be to the 1 ppm level for the carbon and silicon shifts (see Fig. 2 of Ref. 17). However, the convergence appears to be less complete for the phosphorus shifts. It is just these chemical shifts for which the GIPAW

and IGAIM results differ the most (although the errors as a fraction of the range of the chemical shifts are similar for all nuclei). So, the dominant reason for the small residual differences between the GIPAW and IGAIM results is due to the problems associated with achieving convergence with respect to localized basis functions. However, remaining sources of the discrepancies may be due to the small, much less than 1 ppm, nonrigidity of the core contributions,[17] and a difference in the parametrization of the local-density functional used. The GIPAW calculations use the parameterisation due to Ceperley-Alder,[36] while the IGAIM calculations use that due to Vosko-Wilk-Nusair.[37] While the diamagnetic correction term is found to be rigid with respect to the chemical environment, both the bare and paramagnetic correction terms are found to be strongly dependent on the system. The correction terms introduced by the GIPAW approach are therefore seen to be important even in the prediction of relative chemical shifts, and the rigid nature of the core contribution is reconfirmed.

In Table III we examine the robustness of the GIPAW method with respect to pseudopotentials used. A variety of

TABLE II. Comparison of the three different GIPAW approaches described in Sec. VII. The GIPAW-LDA calculations were performed using a plane-wave cutoff of 100 Ry and in a 6000 Bohr^3 simulation cell. The total isotropic chemical shifts are given as ppm.

Molecule	Molecular	Molecular sum rule	Crystal
H atom			
CH_4	30.75	30.76	30.87
CH_3F	26.02	26.01	26.13
C_6H_6	22.69	22.69	22.74
TMS	30.76	30.76	30.80
SiH_3F	25.40	25.40	25.30
Si_2H_4	24.92	24.93	24.90
SiH_4	27.57	27.58	27.33
C atom			
CO	−22.92	−22.90	−22.93
CH_4	191.08	191.09	190.96
CH_3F	98.53	98.52	98.47
CH_3NH_2	149.61	149.62	149.77
C_6H_6	36.13	36.14	36.12
CF_4	34.62	34.30	34.22
TMS	179.17	179.19	179.33
Si atom			
SiF_4	410.12	409.85	409.97
SiH_3F	308.27	308.23	308.29
Si_2H_4	206.50	206.49	206.70
SiH_4	427.95	427.95	427.97
TMS	302.61	302.61	302.70
P atom			
PF_3	177.90	177.70	178.00
P_2	−360.97	−360.97	−360.75
P_4	832.87	832.87	832.94

Troullier-Martins pseudopotentials,[30] with core radii ranging from 1.2 to 1.8 Bohr, were used to calculate the NMR chemical shift for carbon in methane. While the bare contribution to the chemical shift is observed to change by over 10 ppm, the total shifts, including the GIPAW correction terms, are constant to within 1 ppm. There is virtually no difference in the total shifts between potentials with core radii of 1.2 and 1.4 Bohr.

B. Comparison with all-electron plane-wave results for diamond

As the GIPAW method presented here is, to the authors' knowledge, the only approach available for the calculation of all-electron NMR chemical shifts in solids, a truly independent validation is not possible. However, by constructing a suitable pseudopotential and taking a high enough plane-wave cut-off energy we are able to compare with essentially all-electron results—in which all the electrons in the chosen system are considered to be valence electrons. In this way we can check the corrections to the conventional pseudopotential results. Obviously, such calculations are computationally intensive due to the extremely large number of plane waves

TABLE III. The NMR chemical shift for carbon in methane using Troullier-Martins potentials with a range of core radii. These LDA calculations were performed using a plane-wave cutoff of 180 Ry (converged to 0.01 ppm for the hardest potential) and in a simulation cell of 1000 Bohr^3. With ''bare,'' ''Δd,'' and ''Δp,'' we indicate the valence GIPAW contributions to the chemical shifts, given by the bare field $B_{bare}^{(1)}(R)$ and the two correction fields $B_{\Delta d}^{(1)}(R)$ and $B_{\Delta p}^{(1)}(R)$, respectively.

Core radius (Bohr)	σ_{GIPAW}				
	Core	Bare	Δd	Δp	Total
1.2	198.88	7.30	3.96	−19.14	191.00
1.4	198.88	12.22	3.99	−24.08	191.01
1.6	198.88	17.03	3.98	−28.64	191.25
1.8	198.88	21.65	3.92	−32.86	191.59

required to reach convergence. We therefore choose diamond as our example periodic system. Carbon is sufficiently light that an all-electron plane-wave calculation is possible, and the diamond structure has a very small primitive unit cell and a high degree of symmetry. The $1s$, $2s$, and $2p$ electrons are all considered to be valence electrons and we construct a purely local Troullier-Martin[30] pseudopotential with a core radius of 0.4 Bohr radii.

Table IV compares the results of a GIPAW pseudopotential calculation (the $1s$ electrons are treated as core electrons, and a core radius of 1.6 Bohr radii used) and the all-electron plane-wave calculation obtained with the purely local Troullier-Martin pseudopotential. The contributions can be separated into core and valence terms in a gauge-invariant way, as shown in Ref. 17. Thus, in the case of the all-electron result we performed two calculations of the chemical shift after achieving self-consistency, once taking into account all the electrons, and a second time excluding the valence electrons from the calculation of the chemical shift. The valence term presented is the difference between these two results. We present the all-electron results at two plane-wave cutoffs—800 and 1400 Rydbergs and a $10\times10\times10$ Monkhorst-Pack **k**-point grid. All the contributions to the chemical shifts are converged to within a part per million. The valence contributions of the GIPAW and all-electron results differ by only 1.39 ppm which may be attributed to the slight uncorrected pseudization error that remains in the all-electron result. We have confidence that if the core radius were reduced to less than 0.4 Bohr radii the difference between the results of the two approaches would decrease. The GIPAW pseudopotential result is expected to be closer to the true all-electron NMR chemical shift.

TABLE IV. The valence contribution to the isotropic chemical shift of crystalline diamond (ppm).

Method	Valence contribution to σ
GIPAW	−65.85
All-electron at 800 Ry	−64.89
All-electron at 1400 Ry	−64.46

X. CONCLUSIONS

We have presented an *ab initio* theory for the evaluation of NMR chemical shifts in both finite and infinitely periodic systems. We have correctly treated the complications introduced due to the use of pseudopotentials, and so, in contrast to the original implementation of the MPL approach,[7] we are not restricted to the calculation of the chemical shifts for light elements. We introduced an extension to the projector augmented-wave method which is valid for systems in non-zero uniform magnetic fields, the gauge-including projector augmented-wave method.

Our implementation of GIPAW into a parallelized plane-wave pseudopotential code allows the calculation of NMR chemical shifts in large, low-symmetry extended systems. We expect that the methodology will prove useful in the calculation of other magnetic properties. Our work also suggests that the implementation of GIPAW into quantum chemical approaches would lead to a considerable improvement in their efficiency for the calculation of NMR chemical shifts for heavy elements.

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APPENDIX: THE GENERALIZED f-SUM RULE

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.,

$$\langle \phi | \mathcal{O} | \phi' \rangle = -\langle \phi' | \mathcal{O} | \phi \rangle \tag{A1}$$

and

$$\langle \phi | \mathcal{E} | \phi' \rangle = \langle \phi' | \mathcal{E} | \phi \rangle \tag{A2}$$

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 $\mathbf{p}$, $\mathbf{L}$, $\mathbf{v}$, $\mathbf{v}_{\mathbf{R}}^{nl}$, $\mathbf{J}^{p}(\mathbf{r}')$, and $\Delta \mathbf{J}_{\mathbf{R}}^{p}(\mathbf{r}')$ 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

$$s = -4 \sum_{o} \text{Re} \left[\langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} \mathcal{G}(\varepsilon_0) \frac{1}{i} [\mathcal{E}, \bar{H}^{(0)}] | \bar{\Psi}_{o}^{(0)} \rangle \right]. \tag{A3}$$

The sums over o and o' (below) run over the occupied orbitals, and those over e' over the empty ones. Using the fact that $\bar{H}^{(0)} | \bar{\Psi}_{k}^{(0)} \rangle = \varepsilon_k | \bar{\Psi}_{k}^{(0)} \rangle$, Eq. (33), and $\Sigma_{e'} |\hat{\Psi}_{e'}\rangle\langle\bar{\Psi}_{e'}| = 1 - \Sigma_{o'} |\bar{\Psi}_{o'}\rangle\langle\bar{\Psi}_{o'}|$, the expression for s may be rewritten as

$$s = -4 \sum_{o} \text{Re} \left[\frac{1}{i} \langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} \mathcal{E} | \bar{\Psi}_{o}^{(0)} \rangle \right]$$

$$+ 4 \sum_{o,o'} \text{Re} \left[\frac{1}{i} \langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} | \bar{\Psi}_{o'}^{(0)} \rangle \langle \bar{\Psi}_{o'}^{(0)} | \mathcal{E} | \bar{\Psi}_{o}^{(0)} \rangle \right]. \tag{A4}$$

Since the eigenstates $|\bar{\Psi}_{k}^{(0)}\rangle$ can be chosen in such a way that $\langle \mathbf{r} | \bar{\Psi}_{k}^{(0)} \rangle$ is a real quantity, $\langle \bar{\Psi}_{k}^{(0)} | \mathcal{O} | \bar{\Psi}_{k'}^{(0)} \rangle = -\langle \bar{\Psi}_{k'}^{(0)} | \mathcal{O} | \bar{\Psi}_{k}^{(0)} \rangle$ and $\langle \bar{\Psi}_{k}^{(0)} | \mathcal{E} | \bar{\Psi}_{k'}^{(0)} \rangle = \langle \bar{\Psi}_{k'}^{(0)} | \mathcal{E} | \bar{\Psi}_{k}^{(0)} \rangle$. Using these relations it follows that

$$\sum_{o,o'} \langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} | \bar{\Psi}_{o'}^{(0)} \rangle \langle \bar{\Psi}_{o'}^{(0)} | \mathcal{E} | \bar{\Psi}_{o}^{(0)} \rangle$$

$$= -\sum_{o,o'} \langle \bar{\Psi}_{o'}^{(0)} | \mathcal{O} | \bar{\Psi}_{o}^{(0)} \rangle \langle \bar{\Psi}_{o}^{(0)} | \mathcal{E} | \bar{\Psi}_{o'}^{(0)} \rangle$$

$$= -\sum_{o,o'} \langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} | \bar{\Psi}_{o'}^{(0)} \rangle \langle \bar{\Psi}_{o'}^{(0)} | \mathcal{E} | \bar{\Psi}_{o}^{(0)} \rangle, \tag{A5}$$

where for the last equality we just interchanged the dummy indexes o and o'. From Eq. (A5) we conclude that the double summation of Eq. (A4) is equal to zero and

$$s = -4 \sum_{o} \text{Re} \left[\frac{1}{i} \langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} \mathcal{E} | \bar{\Psi}_{o}^{(0)} \rangle \right]$$

$$= 2 \sum_{o} \langle \bar{\Psi}_{o}^{(0)} | \frac{1}{i} [\mathcal{E}, \mathcal{O}] | \bar{\Psi}_{o}^{(0)} \rangle. \tag{A6}$$

From this expression we finally obtain the generalized f-sum rule

$$\sum_{o} \langle \bar{\Psi}_{o}^{(0)} | \frac{1}{i} [\mathcal{E}, \mathcal{O}] | \bar{\Psi}_{o}^{(0)} \rangle$$

$$= -4 \sum_{o} \text{Re} \left[\langle \bar{\Psi}_{o}^{(0)} | \mathcal{O} \mathcal{G}(\varepsilon_0) \frac{1}{i} [\mathcal{E}, \bar{H}^{(0)}] | \bar{\Psi}_{o}^{(0)} \rangle \right]. \tag{A7}$$

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[1] *Encyclopedia of NMR*, edited by D.M. Grant and R.K. Harris (Wiley, London, 1996).

[2] See e.g., J.A. Tossell, Phys. Chem. Miner. **27**, 70 (1999); Chem. Phys. Lett. **303**, 435 (1999); G. Valerio, A. Goursot, R. Vetrivel, V. Malkina, and D.R. Salahub, J. Am. Chem. Soc. **120**, 11 426 (1998); G. Valerio and A. Goursot, J. Phys. Chem. **103**, 51 (1999).

[3] W. Kutzelnigg, U. Fleischer, and M. Schindler, *NMR Basic Principles and Progress* (Springer-Verlag, Berlin, 1990), Vol. 23, pp. 165–262.

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

[5] T.A. Keith and R.F.W. Bader, Chem. Phys. Lett. **194**, 1 (1992).

[6] J.R. Cheeseman, G.W. Trucks, T.A. Keith, and M.J. Frisch, J. Chem. Phys. **104**, 5497 (1996).

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

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

[9] F. Mauri, B.G. Pfrommer, and S.G. Louie, Phys. Rev. Lett. **79**, 2340 (1997).

[10] Y.-G. Yoon, B.G. Pfrommer, F. Mauri, and S.G. Louie, Phys. Rev. Lett. **80**, 3388 (1998).

[11] F. Mauri, B.G. Pfrommer, and S.G. Louie, Phys. Rev. B **60**, 2941 (1999).

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

[13] F. Buda, P. Giannozzi, and F. Mauri, J. Phys. Chem. **104**, 9048 (2000).

[14] F. Mauri, A. Pasquarello, B.G. Pfrommer, Y.-G. Yoon, and S.G. Louie, Phys. Rev. B **62**, R4786 (2000).

[15] J. Ridard, B. Levy, and Ph. Millie, Mol. Phys. **36**, 1025 (1978).

[16] M. Kaupp, V.G. Malkin, O.L. Malkina, and D.R. Solahub, Chem. Phys. Lett. **235**, 382 (1995).

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

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

[19] P.E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).

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

[21] N. Holzwarth *et al.*, Phys. Rev. B **55**, 2005 (1997).

[22] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[23] P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).

[24] C.J. Pickard, Ph.D. thesis, Cambridge University, Cavendish Laboratory, 1997.

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

[26] H. Kageshima and K. Shiraishi, Phys. Rev. B **56**, 14 985 (1997).

[27] H.M. Petrilli, P.E. Blöchl, P. Blaha, and K. Schwarz, Phys. Rev. B **57**, 14 690 (1998).

[28] L. Kleinman and D. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[29] D.R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[30] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[31] An operator O is short ranged if $\langle \mathbf{r}' | O | \mathbf{r} \rangle$ tends to zero exponentially, or faster, as $|\mathbf{r}' - \mathbf{r}| \to \infty$.

[32] T.A. Keith and R.F.W. Bader, Chem. Phys. Lett. **210**, 223 (1993).

[33] For a review on the pseudopotential plane-wave approach see, e.g., M.C. Payne *et al.*, Rev. Mod. Phys. **64**, 1045 (1992).

[34] W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, in *Numerical Recipes in Fortran* (Cambridge University Press, Cambridge, 1992), Chap. 10, pp. 413–418.

[35] M.J. Frisch *et al.*, GAUSSIAN '94 (revision A.1), Gaussian Inc., Pittsburgh PA, 1995.

[36] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[37] S.H. Vosko, Can. J. Phys. **58**, 1200 (1980).

[38] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).