A converse approach to the calculation of NMR shielding tensors

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We introduce an alternative approach to the first-principles calculation of NMR shielding tensors. These are obtained from the derivative of the orbital magnetization with respect to the application of a microscopic, localized magnetic dipole. The approach is simple, general, and can be applied to either isolated or periodic systems. Calculated results show very good agreement with established methods and experimental results.

Nuclear magnetic resonance (NMR) measures the transition frequencies for the reorientation of nuclear magnetic moments in an applied magnetic field. Since the local magnetic field differs from the external one as a result of electronic screening, NMR spectroscopy [1] has been recognized since 1938 [2] to be a powerful experimental probe of local chemical environments, including structural and functional information on molecules, liquids, and increasingly, on solid-state systems.

First-principles calculations of NMR spectra were first developed in the quantum chemistry community [3] and applied to molecules and clusters, but applications to extended crystalline systems were hindered by the difficulty of including macroscopic magnetic fields, which require a non-periodic vector potential and therefore destroy Bloch symmetry. In 1996, Mauri *et al.* developed a linear-response approach for calculating NMR shieldings in periodic crystals based on the long-wavelength limit of a periodic modulation of the applied magnetic field [4], while in 2001 Sebastiani and Parrinello used the Wannier representation to derive an alternative linear-response approach based on the application of an infinitesimal uniform magnetic field [5]. More recently, attention has focused on the development of these approaches in the context of pseudopotential and projector-augmented wave (PAW) descriptions [6–8], leading to a growing use of these methods in combination with modern plane-wave pseudopotential codes [9, 10]. Despite these advances, existing methods for computing NMR shifts in crystalline systems remain complex, in that they require a linear-response implementation with significant extra coding. In principle, the long-wavelength approach [4] could be implemented using standard ground-state calculations, but only at the cost of introducing prohibitively large supercells. Furthermore, constant magnetic fields can be dealt with in supercell calculations—such as e.g. in Ref. [11]—provided they are commensurate, with an integer number of flux quanta per supercell. The drawback is that, even for large supercells, the lower limit of commensurate fields is much larger than the field values actually achievable in a laboratory.

In this Letter, we reformulate the problem of computing NMR shielding tensors in such a way that the need for a linear-response framework is circumvented. For clarity, the previous formulations shall be referred to here as *direct* approaches, in that a magnetic field is applied and the local field at the nucleus is computed. Our alternative, *converse* approach obtains the NMR shifts instead from the macroscopic magnetization induced by magnetic point dipoles placed at the nuclear sites of interest. We demonstrate the method by a first application to small molecules, finding excellent agreement with experiment and with calculations using the direct approach. Our new method is both simple and general, provides a straightforward alternative avenue to the computation of NMR shifts in complex materials that requires very little coding, and can be extended to electronic-structure methods where a linear-response formulation is impractical.

Let us start by considering a sample to which a constant external magnetic field $\mathbf{B}^{\text{ext}}$ is applied. The field induces a current that, in turn, induces a magnetic field $\mathbf{B}^{\text{ind}}(\mathbf{r})$ such that the total magnetic field is $\mathbf{B}(\mathbf{r}) = \mathbf{B}^{\text{ext}} + \mathbf{B}^{\text{ind}}(\mathbf{r})$. In NMR experiments the applied fields are small compared to the typical electronic scales; the absolute chemical shielding tensor $\overleftrightarrow{\sigma}$ is then defined via the linear relationship

$$\mathbf{B}_s^{\text{ind}} = -\overleftrightarrow{\sigma}_s \cdot \mathbf{B}^{\text{ext}} \ , \quad \sigma_{s,\alpha\beta} = -\frac{\partial B_{s,\alpha}^{\text{ind}}}{\partial B_\beta^{\text{ext}}} \ . \qquad (1)$$

The index s indicates that the corresponding quantity is to be taken at position $\mathbf{r}_s$, i.e., the site of nucleus s. NMR experiments usually report the isotropic shielding $\sigma_s = \frac{1}{3}\text{Tr}[\overleftrightarrow{\sigma}_s]$ via a chemical shift that is defined by convention as $-[\sigma_s - \sigma_{\text{ref}}]$. Here σ_{ref} is the isotropic shielding of a reference compound, e.g., tetramethylsilane for ^{1}H and ^{13}C NMR.

As mentioned above, direct approaches [4–8] calculate the chemical shielding from the current response of the system to an external magnetic field using perturbation theory. We propose a fundamentally different approach that circumvents the need to apply an external magnetic field, relying instead on a thermodynamic relation-

ship between mixed partial derivatives. Using $B_{s,\alpha} = B_\alpha^{\mathrm{ext}} + B_{s,\alpha}^{\mathrm{ind}}$, Eq. (1) becomes $\delta_{\alpha\beta} - \sigma_{s,\alpha\beta} = \partial B_{s,\alpha}/\partial B_\beta^{\mathrm{ext}}$. For the moment, we assume that $\mathbf{B}^{\mathrm{ext}}$ can be replaced by the total macroscopic B-field in the denominator of this equation, thus neglecting the *macroscopic* induced field. (This restriction, appropriate for normal components in a slab geometry, will be relaxed shortly.) The numerator may be written as $B_{s,\alpha} = -\partial E/\partial m_{s,\alpha}$, where E is interpreted either as the energy of a virtual magnetic dipole $\mathbf{m}_s$ at one nuclear center $\mathbf{r}_s$ in the field $\mathbf{B}$ for a finite system, or as the energy per cell of a periodic lattice of such dipoles; we adopt the latter view. Then, writing the macroscopic magnetization as $M_\beta = -\Omega^{-1}\,\partial E/\partial B_\beta$ (where Ω is the cell volume),

$$\delta_{\alpha\beta} - \sigma_{s,\alpha\beta} = -\frac{\partial}{\partial B_\beta}\frac{\partial E}{\partial m_{s,\alpha}} = -\frac{\partial}{\partial m_{s,\alpha}}\frac{\partial E}{\partial B_\beta} = \Omega\frac{\partial M_\beta}{\partial m_{s,\alpha}}\ . \tag{2}$$

Thus, $\overleftrightarrow{\sigma}_s$ accounts for the shielding contribution to the macroscopic magnetization induced by a magnetic point dipole $\mathbf{m}_s$ sitting at nucleus $\mathbf{r}_s$ and all of its periodic replicas. In other words, instead of applying a constant (or long-wavelength) field $\mathbf{B}^{\mathrm{ext}}$ to an infinite periodic system and calculating the induced field at all equivalent s nuclei, we apply an infinite array of magnetic dipoles to all equivalent sites s, and calculate the change in magnetization. Since the perturbation is now periodic, it can simply be computed using finite differences of ground-state calculations; isolated system can be handled straightforwardly in the spirit of the supercell approximation. This is our principal result, and it is viable for periodic systems only because of the availability of the recently introduced modern theory of magnetization [12–15]. Note that $\mathbf{M} = \mathbf{m}_s/\Omega + \mathbf{M}^{\mathrm{ind}}$, where the first term is present merely because we have included magnetic dipoles by hand. It follows that the shielding is related to the true induced magnetization via $\sigma_{s,\alpha\beta} = -\Omega\,\partial M_\beta^{\mathrm{ind}}/\partial m_{s,\alpha}$.

It is useful to pause here and consider the analogy of the Born [16] (or dynamical) effective charge tensor $Z_{s,\alpha\beta}^*$, which may be regarded as (i) the component of the force $\mathbf{F}_s$ in direction α on site $\mathbf{r}_s$ by a unit macroscopic electric field $\boldsymbol{\mathcal{E}}$ in direction β (at zero nuclear displacement), or alternatively as (ii) the β-component of the macroscopic electric polarization $\mathbf{P}$ linearly induced by a unit displacement of nucleus s and its periodic replicas in direction α in vanishing macroscopic electric field. Since the force on nucleus s is given by $F_{s,\alpha} = -\partial E/\partial r_{s,\alpha}$, (i) and (ii) are related by

$$Z_{s,\alpha\beta}^* = -\frac{\partial}{\partial \mathcal{E}_\beta}\frac{\partial E}{\partial r_{s,\alpha}} = -\frac{\partial}{\partial r_{s,\alpha}}\frac{\partial E}{\partial \mathcal{E}_\beta} = \Omega\frac{\partial P_\beta}{\partial r_{s,\alpha}}\ , \tag{3}$$

in close analogy with Eq. (2). Note that, in order to comply with the Born definition, one must choose the *lattice-periodical* solution of Poisson's equation, corresponding to vanishing macroscopic electric field. Other choices are possible and lead to other kinds of effective charges,

which are all related to each other by means of the dielectric constant [17]. By comparing Eq. (3) to Eq. (2) we notice that the genuine analogue to $\overleftrightarrow{Z}_s^*$ is $1 - \overleftrightarrow{\sigma}_s$ (and *not* $\overleftrightarrow{\sigma}_s$), as indeed the names "effective" vs. "shielding" imply. The analogy between the electric and magnetic cases would be more direct if only the nucleus carried a magnetic monopole charge; the NMR shielding would then be related to the magnetic force on site s induced by a macroscopic magnetic field, just as Z^* is the electric force induced at $\mathbf{r}_s$ by a macroscopic electric field.

As in the electrical case [17], the choice of magnetic boundary conditions corresponds to a choice of the *shape* of a macroscopic finite sample. Following Ref. [18], the shape effects are embedded in the depolarization coefficients n_α (with $\sum_\alpha n_\alpha = 1$), whose special cases are the sphere ($n_x=n_y=n_z=1/3$), the cylinder along z ($n_x=n_y=1/2$, $n_z=0$), and the slab normal to z ($n_x=n_y=0$, $n_z=1$). The main relationship for the macroscopic fields in Gaussian units may be written as $B_\alpha = B_\alpha^{\mathrm{ext}} + 4\pi(1 - n_\alpha)M_\alpha$. It can be seen that for the slab the normal component of $\mathbf{B}$ coincides with the one of $\mathbf{B}^{\mathrm{ext}}$. Hence our computed $\sigma_{s,zz}$ are suitable for direct comparison with measurements of the normal component performed on a slab-shaped sample. Assuming non-magnetic media with small, isotropic susceptibility χ, it can be shown that the shielding for a general shape is related to our calculated one by $\sigma_{s,\alpha\beta}^{\mathrm{shape}} \simeq \sigma_{s,\alpha\beta} - \delta_{\alpha\beta}\,4\pi\chi(1-n_\beta)$. For the special case of a spherical sample we have $\sigma_{s,\alpha\beta}^{\mathrm{sphere}} \simeq \sigma_{s,\alpha\beta} - (8\pi/3)\,\chi\,\delta_{\alpha\beta}$.

In order to calculate the shielding tensor of nucleus s using Eq. (2), it is necessary to calculate the induced orbital magnetization due to the presence of an array of point magnetic dipoles $\mathbf{m}_s$ at all equivalent sites $\mathbf{r}_s$. The vector potential of a single dipole in Gaussian units is given by [19]

$$\mathbf{A}^0(\mathbf{r}) = \frac{\mathbf{m}_s \times (\mathbf{r} - \mathbf{r}_s)}{|\mathbf{r} - \mathbf{r}_s|^3}\ . \tag{4}$$

For an array of magnetic dipoles $\mathbf{A}(\mathbf{r}) = \sum_\mathbf{R} \mathbf{A}^0(\mathbf{r} - \mathbf{R})$, where $\mathbf{R}$ is a lattice vector. Since $\mathbf{A}$ is periodic, the average of its magnetic field $\nabla \times \mathbf{A}$ over the unit cell vanishes; thus, the eigenstates of the Hamiltonian remain Bloch-representable. In the Fourier representation $\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{G}\neq 0} \tilde{\mathbf{A}}(\mathbf{G})\,e^{i\mathbf{G}\cdot\mathbf{r}}$ with

$$\tilde{\mathbf{A}}(\mathbf{G}) = -\frac{4\pi i}{\Omega}\frac{\mathbf{m}_s \times \mathbf{G}}{G^2}\,e^{-i\mathbf{G}\cdot\mathbf{r}_s}, \tag{5}$$

where the reciprocal lattice vector $\mathbf{G} = 0$ may be excluded from the sum with no loss of generality. Note that we have implicitly chosen the transverse gauge $\nabla\cdot\mathbf{A} = 0$, which is apparent from $\mathbf{G}\cdot(\mathbf{m}_s \times \mathbf{G}) = 0$. The periodic vector potential $\mathbf{A}(\mathbf{r})$ can now be included in the Hamiltonian with the usual substitution for the momentum operator $\mathbf{p} \to \mathbf{p} - \frac{e}{c}\mathbf{A}$. As a result, the kinetic energy

operator becomes

$$\frac{p^2}{2m_e} \longrightarrow \frac{p^2}{2m_e} - \frac{e}{m_e c}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2m_e c^2}A^2 \ , \qquad (6)$$

where m_e is the electronic mass and c is the speed of light. Due to our choice of gauge, $\mathbf{p}$ and $\mathbf{A}$ commute. We can now calculate the shielding according to Eq. (2) by solving for the ground state with the additional terms of Eq. (6) included in the Hamiltonian, and then calculating the resulting change in orbital magnetization [20].

As an initial test, we have applied our converse approach to the calculation of the NMR chemical shifts for small molecules in a supercell geometry, since these can be directly compared with previous results obtained by Mauri *et al.* using the direct method [4]. Because we use a large supercell with vacuum between molecules, the magnetic susceptibility of the system effectively vanishes, and our computed $\overleftrightarrow{\sigma}_s$ can be compared to the experimental one without any shape correction. For the same reason, the recently-developed theory of orbital magnetization for extended systems [12–15] or its single k-point extension [21] is not needed, and we compute the induced magnetization directly from the current distribution (paramagnetic plus diamagnetic), which is

$$\mathbf{j}(\mathbf{r}) = \sum_{n=1}^{occ} \left[\frac{e\hbar}{m_e}\mathrm{Im}\left[\psi_n^*(\mathbf{r})\nabla\psi_n(\mathbf{r})\right] - \frac{e^2}{m_e c^2}\mathbf{A}(\mathbf{r})|\psi_n(\mathbf{r})|^2 \right] \ . \tag{7}$$

We implemented this approach into PWSCF, part of the QUANTUM-ESPRESSO distribution [22]. Here, the simplicity of the converse method becomes obvious—the implementation only required additional coding of the order of 100 lines. We used a local-density exchange-correlation functional as in Ref. [4], and the structural parameters have been taken from footnote [22] therein, in order to allow for a close comparison between the direct and converse methods. We chose a dipole perturbation $|\mathbf{m}_s|$ of $1\mu_B$, although the results are numerically insensitive to dipoles in the range from 10^{-6} to $10^3\mu_B$.

First, we used Coulombic potentials (i.e., a plane-wave all-electron approach) with a high plane-wave energy cutoff of 500 Ry to calculate the ^{1}H NMR chemical shielding of several small molecules. Our results are given in Table I together with experimental and theoretical values. It is immediately obvious that the direct and converse methods give almost identical results, validating our approach.

Second, we performed these calculations in a pseudopotential approximation, since plane-wave codes use pseudopotentials to allow the use of a lower kinetic-energy cutoff and, hence, greater computational efficiency. Two complications need to be taken into account in this case. First, a Blöchl-like PAW reconstruction needs to be performed, as shown by Pickard and Mauri [6], for all elements beyond the first row. Since, at the moment, we are only concerned with hydrogen shielding,

TABLE I: Hydrogen NMR chemical shielding σ in ppm for several different molecules. Values for the direct method are taken from Ref. [4]. The pseudopotential results for the direct method—according to footnote [21] of Ref. [4]—have been corrected by 0.3 ppm in order to allow a better comparison between the direct and converse methods.

	exp.	all-electron		pseudopotential	
		direct	converse	direct	converse
H_2	26.26 [a]	25.9	25.9	25.6	25.6
HF	28.51 [a]	28.4	28.5	28.1	28.1
CH_4	30.61 [a]	30.7	30.7	30.4	30.4
C_2H_2	29.26 [b]	28.6	29.2	28.3	28.2
C_2H_4	25.43 [b]	24.5	25.4	24.2	24.0
C_2H_6	29.86 [b]	29.7	29.7	29.4	29.4

[a] Reference [23].
[b] Reference [24].

we have neglected this issue. A second and more subtle point concerns pseudopotentials that contain nonlocal projectors (as it is usually the case when the Kleinman-Bylander separable form is used [25]). This becomes apparent if the effect of applying a constant vector potential $\mathbf{A}_0$ is considered. Such a gauge change should not produce any observable effects, and indeed does not because of cancellations between the substitution $\mathbf{p} \to \mathbf{p} - \frac{e}{c}\mathbf{A}_0$ for the momentum operator and $\psi \to \psi e^{(ie/\hbar c)\mathbf{A}_0\cdot\mathbf{r}}$ for all wavefunctions. However, if the pseudopotential is nonlocal, a similar cancellation is ensured only if the nonlocal projectors $|\beta_{lm}\rangle$ are phase-twisted according to [6, 26]

$$\sum_{lm} v_l |\beta_{lm}\rangle\langle\beta_{lm}| \to \sum_{lm} v_l \, e^{\frac{ie}{\hbar c}\mathbf{A}_0\cdot\mathbf{r}}|\beta_{lm}\rangle\langle\beta_{lm}|e^{-\frac{ie}{\hbar c}\mathbf{A}_0\cdot\mathbf{r}} \ , \tag{8}$$

where the indices l and m correspond to orbital and azimuthal angular momenta and v_l is the Kleinman-Bylander coefficient. When the vector potential is not constant, as in Eq. (4), the correct choice of phase twist is generally not obvious. Nevertheless, it is a reasonable first approximation to adopt Eq. (8) with $\mathbf{A}_0$ replaced by $\mathbf{A}(\mathbf{r}_i)$ for all nonlocal projectors located on the atom at $\mathbf{r}_i$. That is, we assume that $\mathbf{A}(\mathbf{r})$ is constant throughout the small core region in which the projector differs from zero. Because this approximation is not perfect, however, the current density $\mathbf{j}(\mathbf{r})$ still has an erroneous contribution $\mathbf{j}_{err}(\mathbf{r})$ inside the core regions. We have found that we can largely correct for this remaining error by identifying $\mathbf{j}_{err}(\mathbf{r})$ through its unphysical property $\nabla\cdot\mathbf{j}_{err}(\mathbf{r}) \neq 0$. More precisely, we calculate the first moment of the current divergence

$$\Delta\mathbf{J}_i = \int_{core\ i} d^3r \ \mathbf{r} \left(\nabla\cdot\mathbf{j}(\mathbf{r})\right) \ , \tag{9}$$

and add to the total current of Eq. (7) a "current δ-function" of strength $-\Delta\mathbf{J}_i$ located at $\mathbf{r}_i$ before computing the magnetization.

Taking all the above into account, we have again calculated the hydrogen NMR chemical shieldings of the same molecules as before. Our pseudopotentials were of the Troullier-Martins type [27]; for H we used a local pseudopotential, and for all other atoms we included a nonlocal s-projector. We find convergence of the shielding for a cutoff of 70 Ry, and our results for the isotropic shielding are reported in Table I. Again, it can be seen that the direct and converse approaches give almost identical results.

We turn now to a discussion of the relative advantages and disadvantages of the converse method compared with the direct method. A potential disadvantage of the converse method is that in order to calculate the shielding tensor for N atoms, we need to perform $3N$ calculations. Using the direct method, on the other hand, one obtains the shieldings of all N atoms at once by only performing three calculations. However, in many cases one is not interested in the shielding of all atoms in the system, but rather only in a few, e.g., near a binding site of a large molecule. In this case, the methods may be competitive. But the main advantage of the converse method is really the simplicity of its implementation, in that it works via finite differences of ground-state calculations and does not require a linear-response implementation. This is likely to be a significant advantage for future applications in conjunction with more complex forms of exchange-correlation functionals such as DFT+U, exact exchange, or hybrid functionals.

In conclusion, we have derived an alternative first-principles method for calculating NMR chemical shielding tensors. The new approach is considerably simpler, since difficulties concerning the choice of the gauge origin are avoided and the need for a linear-response implementation is circumvented. We have demonstrated the correctness and viability of our approach by calculating the shieldings of simple molecular systems and finding excellent agreement with previous theoretical and experimental results. Applications to more complex systems, including crystalline systems for which the orbital magnetization will need to be computed [12–15], are currently in progress.

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