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A New ab-Initio Approach for NMR Chemical Shifts in Periodic Systems

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We present a new method for computing NMR chemical shifts and magnetic susceptibilities in extended systems through an ab initio density functional perturbation theory approach. The method is applicable to crystalline and amorphous insulators under periodic boundary conditions, as well as to isolated molecules. The formalism exploits the exponentially decaying nature of localized Wannier orbitals. We have implemented the method in the context of a plane wave pseudopotential approach. The results are in good agreement with experiment and with calculations that use other theoretical methods.

I. Introduction

Nuclear magnetic resonance (NMR) is one of the most powerful experimental methods in structural chemistry. The quantities extracted from NMR spectra, in particular chemical shifts, are widely used to characterize the chemical environment of individual atoms. Coordination numbers, bond types, and even bonding distances and angles can be obtained by analyzing the resonance lines of the nuclear spins. Many empirical rules exist to relate chemical shifts to these properties, but they fail whenever subtle quantum effects are involved.

Thus, the ab initio calculation of chemical shifts has become more and more popular, and over the years, many methods have been developed in the quantum chemistry community to perform such computations. A good review of the various approaches and recent developments in this field is given in ref 1. One major problem that appears in these calculations is the choice of the gauge. While being in principle a cyclic variable, gauge can significantly affect the results in an actual calculation. To minimize this effect, several solutions have been proposed: in the GIAO method (gauge-including atomic orbitals[2]), one transforms the gauge of the basis set functions to the position of their nuclei, whereas in the IGLO method (individual gauges for localized orbitals[3]), the gauges of the final wave functions are transformed to their centers of charge. The CSGT method (continuous set of gauge transformations[4]) finally defines a gauge which depends on the position where the induced current is to be calculated.

However, there is another issue that restricts the applicability of the existing implementations of these methods to isolated systems. The Hamiltonian, which represents the magnetic field, contains the position operator. In an extended system, which would typically be treated under periodic boundary conditions, this operator is ill-defined. In particular, this position operator and therefore the perturbation Hamiltonian operator do not have any periodicity, as would be required for periodic boundary conditions.

Recently, a new formalism has been presented which allows the calculation of chemical shifts and other magnetic properties in extended systems using periodic boundary conditions.[5,6] This formulation is based on a magnetic field which is modulated in space. To return to the experimental situation of a homogeneous field, the limit of infinite modulation wavelength is evaluated numerically. This is done using a small, but finite wavevector.

We propose an alternative method for extended systems in periodic boundary conditions. We take advantage of the exponential decay properties of localized Wannier orbitals[7,8] and treat these localized orbitals as virtually isolated. For the gauge problem, a particular variant of the CSGT method mentioned above[4] is adapted to our situation and applied to these localized orbitals.

The implementation we present is based on density functional theory (DFT)[9−11] in combination with gradient-corrected exchange correlation energy functionals. We use a pseudopotential plane wave representation of the electronic structure in the frozen core approximation. This allows the efficient calculation of large systems and, in combination with molecular dynamics, good statistical sampling.

The results agree well with the existing calculations as well as with experiment.

II. Chemical Shifts and Susceptibilities

When a magnetic field is applied to a medium, it induces a current due to the modification of the electronic ground state. This electronic current distribution induces an additional inhomogeneous magnetic field. The chemical shift tensor is defined as the proportionality factor between the induced and the externally applied magnetic field at the positions of the nuclei:

$$\sigma(\mathbf{R}) = \frac{\partial \mathbf{B}^{\text{ind}}(\mathbf{R})}{\partial \mathbf{B}^{\text{ext}}} \tag{1}$$

The induced field is determined by the total electronic current $\mathbf{j}(\mathbf{r})$ through

$$\mathbf{B}^{\text{ind}}(\mathbf{r}) = \frac{\mu_0}{4\pi}\int d^3r' \, \frac{\mathbf{r}' - \mathbf{r}}{|\mathbf{r}' - \mathbf{r}|^3} \times \mathbf{j}(\mathbf{r}') \tag{2}$$

where μ_0 is the permeability of the vacuum. Since in our

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approach the system is treated under periodic boundary conditions, the current density will be periodic and we can calculate eq 2 in reciprocal space from the Fourier transform of the current:

$$\mathbf{B}^{\text{ind}}(\mathbf{G} \neq 0) = -\mu_0\, i\, \frac{\mathbf{G}}{|\mathbf{G}|^2} \times \mathbf{j}(\mathbf{G}) \tag{3}$$

The $\mathbf{G} = 0$ component of the field depends on the bulk magnetic susceptibility tensor, χ, and the shape of the sample:

$$\mathbf{B}^{\text{ind}}(\mathbf{G} = \mathbf{0}) = \kappa\, \chi\, \mathbf{B}^{\text{ext}} \tag{4}$$

In the case of a spherical system, the prefactor κ is given by $\kappa = 2/3$. The bulk susceptibility χ can also be expressed as a function of the orbital electronic current as

$$\chi = \frac{\mu_0}{2\Omega} \frac{\partial}{\partial \mathbf{B}^{\text{ext}}} \int_\Omega d^3r\, \mathbf{r} \times \mathbf{j}(\mathbf{r}) \tag{5}$$

where the integral is done over one unit cell of volume Ω. A single cell is sufficient since the integral is invariant under translations of any lattice vector $\mathbf{R}_L$ because of

$$\mathbf{j}(\mathbf{r} + \mathbf{R}_L) = \mathbf{j}(\mathbf{r}) \tag{6}$$

and

$$\int_\Omega d^3r\, \mathbf{j}(\mathbf{r}) = 0 \tag{7}$$

Therefore, the integral over the complete sample can be written as the sum of integrals over unit cells, and all these integrals are equal. The molar susceptibility is related to χ through $\chi^m = \Omega N_L \chi$ with the Avogadro number N_L.

The standard procedure to obtain the orbital electronic current density $\mathbf{j}$ is perturbation theory. The field $\mathbf{B}$ is represented by a vector potential $\mathbf{A}$ satisfying $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})$. A typical choice for $\mathbf{A}$ in the case of a homogeneous magnetic field is

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}(\mathbf{r} - \mathbf{R}) \times \mathbf{B} \tag{8}$$

with a cyclic variable $\mathbf{R}$, the gauge origin. The effect of this additional degree of freedom will be discussed in Section III. The perturbation Hamiltonians at first and second order in the field strength are given by

$$H^{(1)} = \frac{e}{m}\, \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) \tag{9}$$

$$H^{(2)} = \frac{e^2}{2m}\, \mathbf{A}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}) \tag{10}$$

with the momentum operator $\mathbf{p}$ and the charge e and mass m of the electron. The first-order perturbation gives rise to a correction in the electronic ground state with respect to the unperturbed system:

$$\varphi = \varphi^{(0)} + B\varphi^{(1)} \tag{11}$$

This correction $\varphi^{(1)}$ is responsible for the induced current, which can be obtained as

$$\mathbf{j}(\mathbf{r}') = \frac{e^2}{m} \mathbf{A}(\mathbf{r}')|\varphi^{(0)}(\mathbf{r}')|^2 + \frac{e}{m} \langle \varphi^{(0)}|[\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}]|\varphi^{(1)}\rangle \tag{12}$$

III. The Gauge Origin Problem

The current density, eq 12, written in terms of the orbital contributions $\mathbf{j}_k$, can be separated into the so-called dia- and paramagnetic terms:

$$\mathbf{j}(\mathbf{r}') = \sum_k \mathbf{j}_k(\mathbf{r}') = \sum_k \mathbf{j}_k^{\text{d}}(\mathbf{r}') + \mathbf{j}_k^{\text{p}}(\mathbf{r}')$$

$$\mathbf{j}_k^{\text{d}}(\mathbf{r}') = \frac{e^2}{m} \mathbf{A}(\mathbf{r}')|\varphi_k^{(0)}(\mathbf{r}')|^2$$

$$\mathbf{j}_k^{\text{p}}(\mathbf{r}') = \frac{e}{m} \langle \varphi_k^{(0)}|[\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p}]|\varphi_k^{(1)}\rangle \tag{13}$$

Both contributions individually depend on the gauge, whereas the total current $\mathbf{j}$ is gauge-independent. However, the two contributions are large numbers and have opposite signs. For our choice of the vector potential, eq 8, $\mathbf{A}(\mathbf{r})$ is linear in the gauge origin $\mathbf{R}$. Therefore, the diamagnetic current $\mathbf{j}_k^{\text{d}}$ grows linearly in $\mathbf{R}$, and $\mathbf{j}_k^{\text{p}}$ must compensate for this in order to fulfill the invariance of the total current.

Thus, for large distances $|\mathbf{r} - \mathbf{R}|$, the current density $\mathbf{j}$ results from the cancellation of two large terms, making the actual calculation rather challenging. In a computer simulation using a finite basis set, the gauge invariance of $\mathbf{j}$ is no longer numerically verified.

Over the years, many techniques have been developed to minimize this problem for isolated molecules.[2-4] Our goal is to calculate magnetic properties in a periodic system. In this context, the probably most natural approach is the so-called "$\mathbf{R} = \mathbf{r}$" variant of the CSGT method.[4] For each point $\mathbf{r}'$ in space, the current density is calculated with the gauge origin $\mathbf{R}$ being set equal to $\mathbf{r}'$. This method makes the diamagnetic part vanish analytically:

$$\mathbf{j}_k^{\text{d}}(\mathbf{r}') = 0 \tag{14}$$

such that cancellations of large numbers no longer occur.

In practice, the current is computed as

$$\mathbf{j}_k(\mathbf{r}') = \frac{e}{m} \langle \varphi_k^{(0)}|(\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p})[|\varphi_k^{\mathbf{r}\times\mathbf{p}}\rangle - \mathbf{r}' \times |\varphi_k^{\mathbf{p}}\rangle] \cdot \mathbf{B} \tag{15}$$

Here, $|\varphi_k^{\mathbf{r}\times\mathbf{p}}\rangle$ and $|\varphi_k^{\mathbf{p}}\rangle$ are the first-order perturbation wave functions for the special perturbation Hamiltonians:

$$|\varphi_k^{\mathbf{r}\times\mathbf{p}}\rangle \rightarrow H^{(1)} = \mathbf{r} \times \mathbf{p} \tag{16}$$

$$|\varphi_k^{\mathbf{p}}\rangle \rightarrow H^{(1)} = \mathbf{p} \tag{17}$$

This formulation avoids actually calculating distinct wave functions $\varphi^{(1)}$ for each point $\mathbf{r}'$ in space. Denoting the perturbation theory Green's function (see also Section V for details):

$$G_{lk} = -(H^{(0)}\,\delta_{kl} - \langle \varphi_k^{(0)}|H^{(0)}|\varphi_l^{(0)}\rangle)^{-1} \tag{18}$$

we can formally express the first-order perturbation wave functions for an arbitrary perturbation operator O as

$$|\varphi_k^{O}\rangle = \sum_l G_{kl}\, O\, |\varphi_l^{(0)}\rangle \tag{19}$$

where O is either $\mathbf{p}$ or $\mathbf{r} \times \mathbf{p}$. By expanding eq 19 in the basis of the unperturbed unoccupied orbitals, one would obtain the well-known sum-over-states expression for the first-order perturbation wave function.

We do not use this Green's function formulation in the actual calculation, but rather perform a variational energy minimization (see Section V). Equation 19 serves only as a compact notation to obtain a closed expression for the current density:

$$\mathbf{j}_k(\mathbf{r}') = \frac{e}{m}\sum_l \langle \varphi_k^{(0)}|(\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p})[G_{kl}\,\mathbf{r}\times\mathbf{p}|\varphi_l^{(0)}\rangle - G_{kl}\,\mathbf{r}'\times\mathbf{p}|\varphi_l^{(0)}\rangle]\cdot\mathbf{B} \quad (20)$$

In this formulation, it becomes apparent that any simultaneous translation of the relative origin for the operator **r** and the gauge $\mathbf{R} = \mathbf{r}'$ automatically cancel each other out. In particular, the current is invariant under arbitrary orbital-specific translations $\mathbf{d}_l$:

$$\mathbf{j}_k(\mathbf{r}') = \frac{e}{m}\sum_l \langle \varphi_k^{(0)}|(\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p})[G_{kl}\,(\mathbf{r}-\mathbf{d}_l)\times\mathbf{p}|\varphi_l^{(0)}\rangle - G_{kl}\,(\mathbf{r}'-\mathbf{d}_l)\times\mathbf{p}|\varphi_l^{(0)}\rangle]\cdot\mathbf{B} \quad (21)$$

This formulation looks somewhat similar to the well-known IGLO gauge transformation (individual gauges for localized orbitals[3]), but it is not the same. Our physical gauge is always the $\mathbf{R} = \mathbf{r}'$ version of the CSGT method. However, this gauge still leaves the freedom to translate the coordinate system individually for each orbital, according to eq 21. This will turn out to be useful in the following section.

A straightforward application of eq 21 would be too expensive. In fact, it would require one inversion of the Hamiltonian per real space mesh point $\mathbf{r}'$. Such an operation has approximately the cost of a total energy calculation, which leads to a prohibitive computational effort.

We note however, that the second term of $\mathbf{j}_k$ can be rewritten as

$$-\frac{e}{m}\sum_l \langle \varphi_k^{(0)}|(\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p})G_{kl}\,(\mathbf{r}'-\mathbf{d}_l)\times\mathbf{p}|\varphi_l^{(0)}\rangle\cdot\mathbf{B} = -\frac{e}{m}\sum_l \langle \varphi_k^{(0)}|(\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p})(\mathbf{r}'-\mathbf{d}_k)\times G_{kl}\mathbf{p}|\varphi_l^{(0)}\rangle\cdot\mathbf{B} + \Delta\mathbf{j}_k(\mathbf{r}') \quad (22)$$

where

$$\Delta\mathbf{j}_k(\mathbf{r}') = -\frac{e}{m}\sum_l \langle \varphi_k^{(0)}|(\mathbf{p}|\mathbf{r}'\rangle\langle\mathbf{r}'| + |\mathbf{r}'\rangle\langle\mathbf{r}'|\mathbf{p})G_{kl}\,(\mathbf{d}_k-\mathbf{d}_l)\times\mathbf{p}|\varphi_l^{(0)}\rangle\cdot\mathbf{B} \quad (23)$$

The evaluation of the first term of eq 22 can be done at the computational cost of one total energy calculation, while $\Delta\mathbf{j}_k$ requires one such calculation per electronic state *k*.

At first sight, the sum $\Delta\mathbf{j} = \sum_k \Delta\mathbf{j}_k$ seems to be equal to zero, since the inner operator is antisymmetric in *k*, *l*. But since the momentum operators in eq 23 do not commute with the Green's function, $\Delta\mathbf{j}$ does not vanish unless all $\mathbf{d}_l$ are equal. However, we shall show that in most circumstances, $\Delta\mathbf{j}$ can be neglected.

IV. The Position Operator Problem

The formalism described so far is straightforward to use in isolated systems, whereas the extension to periodic systems is problematic. The position operator which figures in the perturbation Hamiltonian, eq 9, is not well defined for an infinite system.

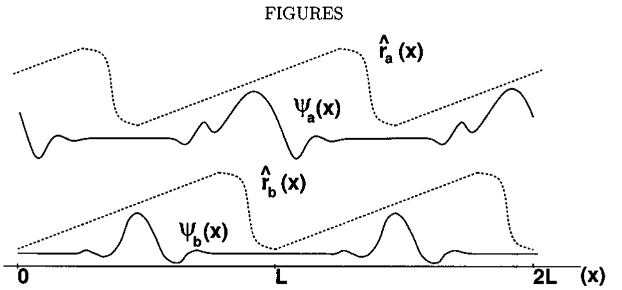

Figure 1. Two localized orbitals $\Psi_a(x)$, $\Psi_b(x)$ with specific position operators $r_a(x)$, $r_b(x)$.

A possible solution to this problem has been proposed and applied by Mauri et al.[5,6,15−18] (MPL). They replace the homogeneous magnetic field **B** by a modulated one, $\mathbf{B}(\mathbf{r}) = \mathbf{B}_0 \cos \mathbf{q}\cdot\mathbf{r}$, with a finite wavevector **q**. Consequently, also the perturbation Hamiltonian becomes **q**-periodic and therefore well-defined for an extended system. The physically relevant case $\mathbf{B}(\mathbf{r}) = \mathbf{B}_0$ is obtained by doing a numerical differentiation with a small, but nonzero value for **q** and $-\mathbf{q}$, and the response wave functions have to be complex even in the Γ only sampling of the Brillouin zone.

However, the method shows that it is feasible to compute NMR chemical shifts of periodic and amorphous systems with good accuracy using a pseudopotential plane-wave approach.

We propose a different approach. Instead of transforming the homogeneous magnetic field to a periodic one, we define a new periodic position operator.

We first localize the wave functions by means of a unitary rotation in the occupied subspace. This is a technique well-known in quantum chemistry, where it is used to determine the location and the nature of chemical bonds. The rotation is chosen such that the spatial extension of the wave functions is minimal, yielding so-called maximally localized Wannier functions.[7] The extension is characterized by the second moment Δ_2 of the orbitals:

$$\Delta_2 = \sum_k \langle\varphi_k|\mathbf{r}^2|\varphi_k\rangle - \langle\varphi_k|\mathbf{r}|\varphi_k\rangle^2 \quad (24)$$

In a periodic system, special care is required to define the position operator properly. A solution to this problem in terms of a Berry phase approach[19] has been given by Mazari et al.[20] A practical scheme to calculate maximally localized Wannier orbitals has recently been presented by Berghold et al.[21] It can be shown that in an insulator, the resulting localized wave functions decay exponentially.[8] If the unit cell is chosen such that the lattice parameter is larger than the decay length, the orbital is significantly different from zero only within a limited region of the cell, and it practically vanishes everywhere else.

The next step is to assign individual virtual cells to these Wannier orbitals. The virtual cells are chosen such that for the corresponding wave function, the cell walls are located in that region of space where the orbital density is close to zero over a certain range. Then, the position operator is defined normally running from $-L/2$ to $+L/2$ inside the virtual cell. At the walls, it makes a smooth transition back from $+L/2$ to $-L/2$, yielding a saw-tooth shape (see Figure 1). This jump is not sharp in order to avoid components of very high frequency in the operator. As a consequence of this definition, the position operator now matches the periodic boundary conditions, since it is identical in every virtual cell and all its replica.

Again, we wish to stress that we have not transformed the orbital's gauge. Had we done so, we would have found additional terms in the perturbation Hamiltonian and the wave function orthonormality relations, as in the IGLO method. The crucial difference is that we do not use individual orbital gauge origins; the gauge is always "$\mathbf{R} = \mathbf{r}'$". Instead, we define an individual reference system for both **r** and **R** simultaneously, as described by the relative origins $\mathbf{d_k}$ in eq 21.

The problem that arises for this construction is that the new operator has a completely unphysical shape around the borders of the virtual cell, where it makes its jump (at $x = nL$). But by choosing the virtual cells as described above, the unphysical transitions lie in those regions of space where the wave function vanishes. As a consequence, the problematic part of the operator is only applied where it has no effect anyway.

Hence, the saw-tooth shape of the position operator as indicated by Figure 1 is a reasonable approximation as long as the wave functions are sufficiently localized.

However, this represents a certain restriction for this method. We require that the decay length be significantly smaller than the lattice constant of the simulation box, as mentioned above. Only in such a case can the virtual cell be chosen with its borders in a region of vanishing density. It follows that for a system with truly delocalized orbitals, like a metal, our approach is not applicable. In such a system, the decay of the Wannier orbitals is only algebraic, and the necessary cell size would far exceed the computationally tractable volume. One would have to resort to the MPL approach, using a k-point sampling of the Brillouin zone.

V. Density Functional Perturbation Theory

We have implemented our method in the framework of density functional perturbation theory (DFPT) using a recently published variational approach.[12] The derivation has strong analogies with other variational schemes used in quantum chemistry. In particular, we note the similarity of our approach to the stationary perturbation theory by Kutzelnigg[13] which is used in the IGLO implementation. We start from a functional for the second-order energy of the system which is variational in the first-order perturbation wave functions $\varphi^{(1)}$:

$$E^{(2)} = \sum_k \langle\varphi_k^{(1)}|H^{(0)} - \epsilon_k^{(0)}|\varphi_k^{(1)}\rangle + \sum_k [\langle\varphi_k^{(1)}|H^{(1)}|\varphi_k^{(0)}\rangle + \langle\varphi_k^{(0)}|H^{(1)}|\varphi_k^{(1)}\rangle] + \frac{1}{2}\int d^3r\, d^3r'\, \frac{\delta^2 E_{\mathrm{Hxc}}[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}') \tag{25}$$

In this expression, the operator $H^{(0)}$ is the traditional KS ground-state Hamiltonian with its eigenvalues $\epsilon_k^{(0)}$. $H^{(1)}$ is the first-order perturbation Hamiltonian and E_{Hxc} is the Hartree, exchange and correlation energy functional.

The wave functions $\varphi^{(0)}$ and $\varphi^{(1)}$ are the zero and first-order expansions of the KS orbitals in powers of the perturbation parameter, respectively. They also define the first-order density:

$$n^{(1)}(\mathbf{r}) = \sum_k \varphi_k^{*(0)}(\mathbf{r})\varphi_k^{(1)}(\mathbf{r}) + \varphi_k^{*(1)}(\mathbf{r})\varphi_k^{(0)}(\mathbf{r}) \tag{26}$$

The orthonormality of the total wave functions, expanded to first order in the perturbation, yields

$$\langle\varphi_k^{(0)}|\varphi_k^{(1)}\rangle + \langle\varphi_k^{(1)}|\varphi_k^{(0)}\rangle = 0\ \forall\ k \tag{27}$$

This is achieved by imposing a general orthogonality condition on the first-order perturbation wave functions:

$$\langle\varphi_k^{(0)}|\varphi_l^{(1)}\rangle = 0\ \forall\ k,l \tag{28}$$

The variational energy expression, eq 25, is valid for canonical orbitals, i.e., eigenfunctions of the KS Hamiltonian. The generalization to an arbitrary set of wave functions spanning the occupied subspace is straightforward. The only modification is that the KS energies ϵ_k must be replaced by the matrix elements of the KS–Hamiltonian:

$$\epsilon_k \rightarrow \lambda_{kl} = \langle\varphi_l^{(0)}|H^{(0)}|\varphi_k^{(0)}\rangle \tag{29}$$

Then, eq 25 becomes

$$E^{(2)} = \sum_{kl} \langle\varphi_k^{(1)}|H^{(0)}\delta_{kl} - \lambda_{kl}|\varphi_l^{(1)}\rangle + \sum_k [\langle\varphi_k^{(1)}|H^{(1)}|\varphi_k^{(0)}\rangle + \langle\varphi_k^{(0)}|H^{(1)}|\varphi_k^{(1)}\rangle] + \frac{1}{2}\int d^3r\, d^3r'\, \frac{\delta^2 E_{\mathrm{Hxc}}[n^{(0)}]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}') \tag{30}$$

The second-order energy is variational in the first-order perturbation wave functions, under the orthogonality constraint of eq 28:

$$\frac{\delta E^{(2)}}{\delta \varphi^{(1)}} = 0 \tag{31}$$

In our case, the perturbation is a magnetic field. The energy functional simplifies considerably because the first-order density analytically vanishes everywhere. The reason is that the perturbation Hamiltonian and the first-order wave functions are purely imaginary, and thus, the two terms in eq 26 cancel each other out. The matrix element of the magnetic perturbation Hamiltonian, eq 9, in the position representation is given by

$$\langle\mathbf{r}|H^{(1)}|\mathbf{r}'\rangle = i\,\frac{\hbar e}{2m}\,\delta^3(\mathbf{r} - \mathbf{r}')\,(\mathbf{r} - \mathbf{R}) \times \mathbf{B}\cdot\nabla \tag{32}$$

It is purely imaginary, so that with real wave functions and a neccessarily real energy, eq 25, the first-order orbitals $\varphi_k^{(1)}$ must be purely imaginary, too. Hence, the first-order density, eq 26, vanishes analytically for magnetic perturbations, and the energy functional, eq 30, simplifies to

$$E^{(2)} = \sum_{kl} \langle\varphi_k^{(1)}|H^{(0)}\,\delta_{kl} - \lambda_{kl}|\varphi_l^{(1)}\rangle + \sum_k [\langle\varphi_k^{(1)}|H^{(1)}|\varphi_k^{(0)}\rangle + \langle\varphi_k^{(0)}|H^{(1)}|\varphi_k^{(1)}\rangle] \tag{33}$$

The stationarity condition on the energy, eq 29, can be written as an inhomogeneous system of coupled equations for the $\varphi_k^{(1)}$:

$$\sum_l (H^{(0)}\,\delta_{kl} - \lambda_{kl})|\varphi_l^{(1)}\rangle = -H^{(1)}|\varphi_k^{(0)}\rangle \tag{34}$$

This equation could be formally inverted using Green's function, eq 18. In our implementation, however, eq 34 is solved directly using a conjugate-gradient minimization algorithm.[12] Its computational cost is essentially equal to that of a total energy

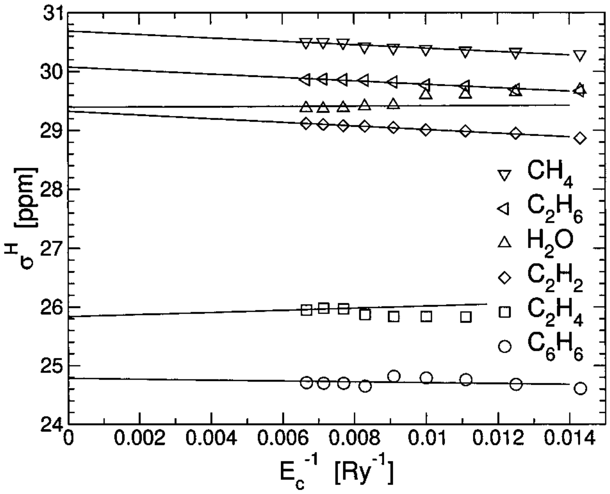

Figure 2. Convergence of ^{1}H shielding with cutoff.

calculation. No wave functions of unoccupied states are required, in contrast to sum-over-states techniques.

VI. Pseudopotential Correction

Our implementation is based on a representation in plane waves. We model the interaction between valence and core electrons by pseudopotentials. Therefore, no core orbital is taken into account, and the valence wave functions have an incorrect shape in the core region. The chemical shift is extremely sensitive to precisely that region of space, because the interaction between nuclear spin and current is proportional to $1/r^2$. Thus, it is not clear a priori whether a pseudopotential implementation can give meaningful results at all.

Often, the contribution of the core orbitals to the chemical shift is almost constant with respect to the chemical environment of the atom. In the recent investigation of Gregor et al.,[22] it has been shown that this property can be exploited to correct for the frozen-core approximation. A simple additive constant is sufficient to reproduce the all-electron shieldings satisfactorily in many cases.

VII. Application to Isolated Molecules

A. Convergence of the Chemical Shift. Our method has been implemented in CPMD,[23] a DFT pseudopotential suite of programs based on a plane-wave (PW) representation. Using a supercell technique, we have applied our method to isolated molecules to validate the approach and the implementation.

For all molecules, the experimental geometries have been used.[24] As discussed in section VI, the carbon shifts need to be corrected for the core contribution through a semiempirical additive constant. The constant was taken to be the difference between our valence-electron shielding and the experimental shielding[29] for tetramethylsilane (TMS). We use pseudopotentials of Goedecker et al.[25] with a BLYP gradient corrected functional,[26,27] and a unit cell of size (20 au)^3.

As a first test, we have investigated the convergence properties of our results with the plane wave cutoff E_c. This cutoff determines the size of the basis set, which is mathematically complete at $E_c \to \infty$. At standard values of 50−70 Ry, this limit is not reached, even within the frozen core approximation. However, the electronic structure is usually well reproduced by that point. The convergence of the chemical shifts with the wave function cutoff is shown in Figures 2 and 3 for a representative set of small organic molecules in the gas phase.

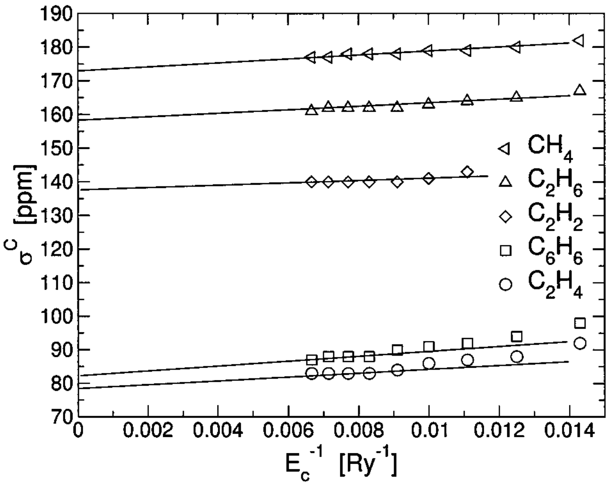

Figure 3. Convergence of ^{13}C shielding with cutoff.

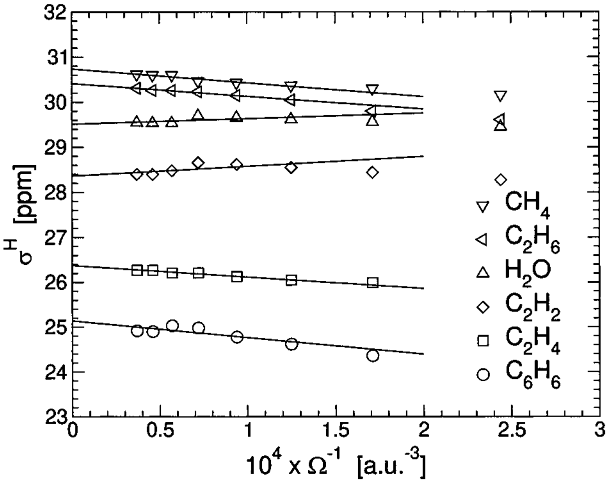

Figure 4. Convergence of ^{1}H shielding with cell volume.

The extrapolation of the chemical shift of the isolated molecules to infinite cutoff ($E_c^{-1} \to 0$) shows that a good convergence is already reached at a typical value of 70−90 Ry. The convergence error is in the range of about 0.2 ppm for hydrogen and a few ppm for carbon.

Another approximation is the finite size of the unit cell in our calculation. To check the influence of the interaction between a molecule and its periodic replica, we have also studied the convergence with the cell volume with a PW cutoff fixed at $E_c = 70$ Ry (Figure 4). Obviously, the standard cell size of (20 au)^3 mentioned above is enough to eliminate the influence of neighboring cells.

B. Comparison with Experiment. We compare our extrapolated results for a representative set of small organic molecules with the values calculated with the Gaussian 94 package,[28] with the MPL results[6] and with experiment (Figures 5and 6). In ref 15, only carbon shifts relative to TMS are given. They were converted to an absolute scale using the experimental value for TMS $\sigma^C_{\mathrm{TMS}} = 188.1$ ppm. Experimental shieldings have been taken from ref 29. The Gaussian calculation was done in DFT using the CSGT method,[4] the BLYP exchange-correlation functiona,l[26,27] and a 6-311G(3df,3pd) basis set.

In the case of an isolated system, we can perform the calculation imposing that the virtual cells are all equal ($\mathbf{d}_k = \mathbf{d}_l$ $\forall$ k, l), which makes $\Delta \mathbf{j}_k = 0$ in eq 23. In Figures 5 and 6, this exact calculation is compared with the approximation $\Delta \mathbf{j}_k = 0$

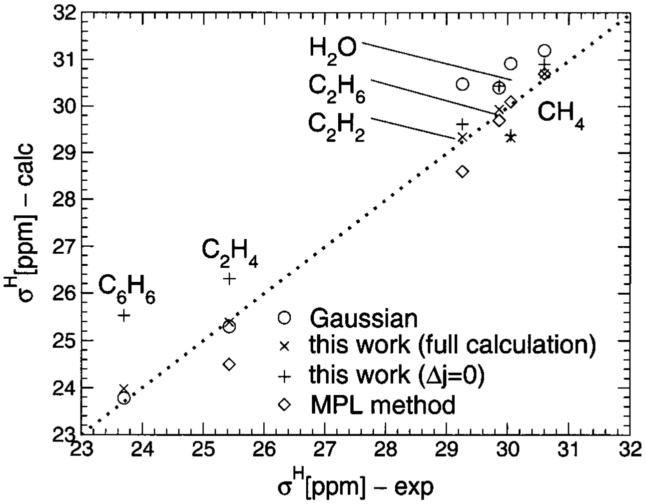

Figure 5. ^{1}H NMR chemical shifts.

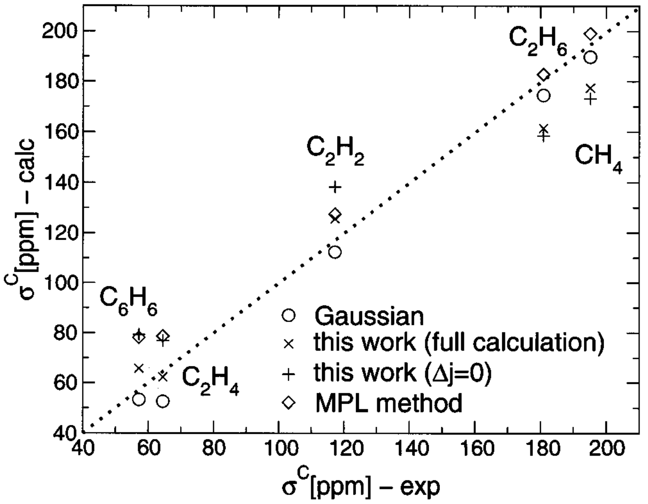

Figure 6. ^{13}C NMR chemical shifts.

in the case of different virtual cells, where $\mathbf{d}_k \neq \mathbf{d}_l$. In both cases, the results are extrapolated to infinite cutoff, as described in the previous section.

For the ^{1}H shifts, the agreement of our values with both Gaussian and experiment is in general very good. Our numbers essentially coincide with the experimental ones up to a maximum difference of about 0.6 ppm which is comparable to the error of Gaussian and that of the MPL approach. The difference between the full and the approximate calculation is negligible except in the presence of strongly overlapping delocalized orbitals, as in C_6H_6. Thus, for a system containing π-electrons, it is a good practice to choose the same virtual cells for all π-orbitals.

The difference between our results and Gaussian are relatively small, except for C_6H_6 and C_2H_2. Considering the use of different basis sets and the different methodology of the calculation, we find a satisfactory overall agreement.

The differences with respect to the MPL method are mostly due to different computational approximations. Using the same cutoff (70 Ry) and the same level of theory (LDA) as Mauri, our results agree up to 0.3 ppm.

Concerning the ^{13}C-atoms, the agreement is still good but less satisfactory. Here, the limits of the approach become apparent, in particular of the frozen core approximation. The rigid additive correction for the pseudopotential is not able to reproduce the different hybridization states quantitatively. A change in the coordination induces an error of about 20 ppm. The approximation of neglecting $\Delta\mathbf{j}$ in the current density accounts for an error of typically less than 15 ppm. However, the shifts still compare well to experiment, especially between similar chemical environments. There, the relative error is only a few ppm. Again, our method has an accuracy comparable to the other ones.

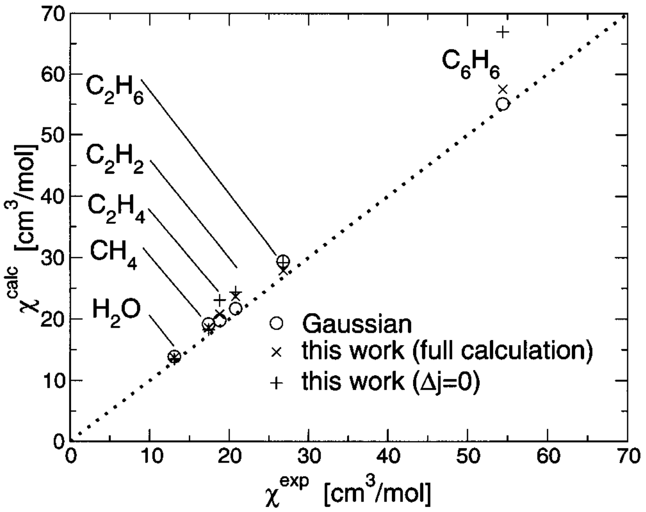

Figure 7. Magnetic susceptibilities in cm^3/mol.

C. Magnetic Susceptibilities. The magnetic susceptibility, eq 5, is a byproduct of our calculation and can be obtained almost for free. The isotropic molar susceptibilities of our test molecules are presented in Figure 7. They have also been extrapolated to infinite cutoff. Experimental values are taken from ref 30.

As in the case of the chemical shifts, we obtain a good agreement with existing theoretical methods and experiment. The only molecule where the susceptibility is not as accurate is benzene. Again, this reflects the difficulties of density functional theory in describing delocalized orbitals with high accuracy.

The calculation of χ also suffers from the use of pseudopotentials. The contribution of the core electrons to the magnetic bulk susceptibility is not considered. This approximation is valid for light elements, but would fail for nuclei with spatially extended core electrons.[5]

The comparison between the full and approximate calculations shows that for the magnetic susceptibility, neglecting $\Delta\mathbf{j}$ has a maximum effect of 2 cm^3/mol, which can safely be ignored. Again, the exception is benzene, where the contribution of eq 23 accounts for a deviation of 10 cm^3/mol.

VIII. Periodic Systems

A. Liquid Water. In simulations of bulk water, periodic boundary conditions are used in order to minimize finite size errors and to eliminate any surface effects. A certain number of water molecules in a large unit cell is periodically repeated in space.

For such a periodic system, there are no quantum chemical calculations, since the conventional IGLO and CSGT implementations cannot be applied to systems under periodic boundary conditions. A comparison is only possible with experiment and with the recently published MPL method. In Figure 8, a direct comparison is presented for a given system. It is a snapshot taken from an ab initio trajectory of liquid water at

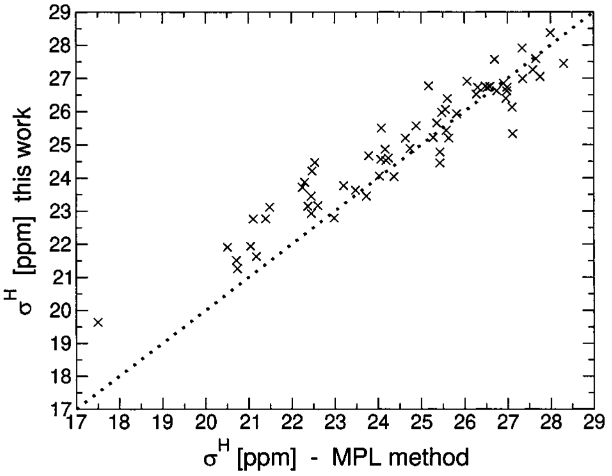

Figure 8. Direct comparison MPL method—this work.

room temperature and consists of 32 water molecules within periodic boundary conditions.

The correlation with the shieldings obtained through the MPL approach shows a satisfactory overall agreement. The distribution of the shift values is very similar, although some of the individual shieldings differ significantly. The maximum discrepancy is about 2 ppm, which can be explained through the different approximations assumed in the two methods.

The gas-to-liquid shift of water resulting from a statistical analysis of a longer trajectory (9ps)[31] of liquid water is shown in Table 1. The experimental values are taken from ref 32.

TABLE 1: ^{1}H and ^{17}O Gas to Liquid Shifts

	$\delta_{\mathrm{liq}}(^{1}\mathrm{H})$ [ppm]	$\delta_{\mathrm{liq}}(^{17}\mathrm{O})$ [ppm]
this work	4.1	30
MPL method	5.8	37
experiment	4.3	36.1

As in the recently published calculation by Pfrommer et al.,[18] the gas-to-liquid shifts $\delta(^{1}\mathrm{H})$ and $\delta(^{17}\mathrm{O})$ of water (Table 1) are well reproduced. The hydrogen shift turns out to be closer to experiment than that of oxygen. This is not surprising, because in the frozen core approximation, our pseudopotentials cannot take into account the changes of the electronic structure in the core region.

B. Diamond under Pressure. In a previous study,[15] Mauri et al. calculated the carbon chemical shifts of diamond in function of pressure. Translating this pressure to molar volumes, they find that the carbon shielding is linear in the volume per atom, with a proportionality factor of 3.44 ppm/a.u.

To check the reliability of our method in a true crystal, we repeat this calculation using a cubic supercell of 64 carbon atoms. The results are shown in Figure 9. The dependence of σ^{C} on the atomic volume yields 3.4 ppm/a.u.^{3}, which is very close to the value found by Mauri.

An analysis of these results is beyond the scope of this work. We refer the reader to the discussion by Mauri et al.[15]

C. Contribution of Δj. In order to estimate the influence the neglected current $\Delta\mathbf{j}$ in the case of a periodically repeated system, we have calculated its contribution to the ^{1}H shift in two infinite polymer chains with different hybridization, $(\mathrm{CH_2})_n$ and $(\mathrm{CH{-}CH{-}O})_n$. The dependence of the orbital corrections $\Delta\sigma_k^{\mathrm{H}}$ on the distance of the orbital's center of charge to the proton is shown in Figure 10. Only the nearest orbitals have a significant contribution, and there is a partial cancellation.

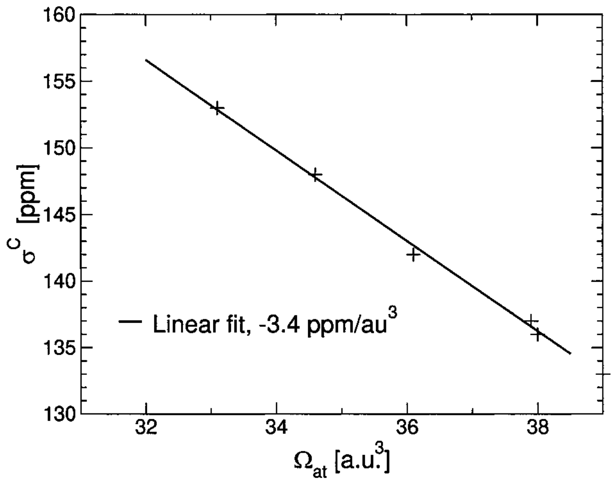

Figure 9. Dependence of σ^{C} on the volume per atom.

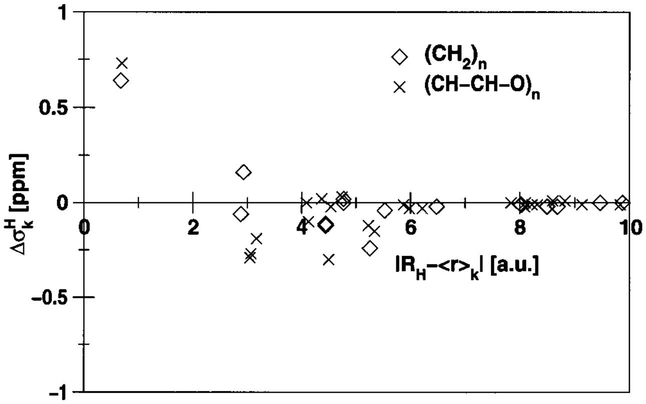

Figure 10. Error in the ^{1}H shift due to the neglected orbital currents $\Delta\mathbf{j}_k$ in infinite linear polymers as a function of the distance between the orbital's center of charge and the proton.

When summing over $\Delta\sigma_k^{\mathrm{H}}$, the total error is about −0.5 ppm for $(\mathrm{CH_2})_n$ and −1.0 ppm for $(\mathrm{CH{-}CH{-}O})_n$. This is about the same as that for the isolated molecules (see Figure 5), and stays within the global accuracy of the calculation.

In the diamond system, the same calculation yields a total error of 28 ppm for the carbon shielding, due to the proximity and the mutual overlap of the orbitals. The correction due to $\Delta\mathbf{j}$ is found to be almost constant with respect to the cell volume, its maximum variation is ±1.5 ppm. This is another case in which relative shieldings are more accurate than absolute ones.

IX. Conclusion

To recapitulate our approach, the perturbation Hamiltonian, eq 9, which contains the new orbital-dependent position operator (Figure 1), is applied to each localized orbital in its own virtual cell. The first-order perturbation wave functions $\varphi^{(1)}$ are then obtained variationally through the minimization of the second-order energy functional, eq 33, following ref 12. The total electronic current density is computed as the periodically repeated sum of all orbital currents obtained from the first-order perturbation wave functions by eq 15. This current leads to the chemical shifts and the magnetic susceptibility through eqs 1 and 5.

The results shown in sections VII and VIII show clearly that the technique presented in this work can be used with good accuracy for amorphous as well as periodic systems.

The practical advantage over the existing formulation for periodic systems by Mauri[6] is the computational effort, which can be significantly smaller. For systems that can be described through a very small primitive cell, like defect-free crystals, we would have to use a supercell technique to obtain sufficiently localized Wannier functions. The MPL approach works with the primitive cell only, making it much more efficient.

However, for systems that in any case require a large unit cell, our computational effort is typically considerably smaller. The computer time needed to calculate a system of 32 water molecules in the liquid state at $\rho = 1$ g/cm^3 is about six times smaller compared to the MPL approach.[33] This becomes especially important in the combination with molecular dynamics. In such a case, to obtain a good statistical average, the NMR chemical shift has to be calculated for a large number of atomic configurations (snapshots) out of the trajectory.

The method presented in this article is currently being applied to a variety of systems, including biologically important molecules, and provides a powerful tool to interpret experimental results.

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