NMR chemical shifts in periodic systems from first principles

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Abstract

A recently developed ab-initio method for the calculation of NMR chemical shifts and magnetic susceptibilities in systems under periodic boundary conditions is presented and applied to a hydrogen-bonded molecular crystal. The calculations can unambiguously assign the chemical shifts to individual atoms in experimental spectra, and can further serve for the validation of simulated atomic trajectories and geometries. Apart from the example presented, the method can be applied to crystalline and amorphous insulators, as well as to isolated molecules using a supercell technique. The results are in good agreement with experiment. © 2002 Elsevier Science B.V. All rights reserved.
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1. Introduction

Nuclear magnetic resonance (NMR) properties, in particular NMR chemical shifts, provide important insight into the physics and chemistry of microscopic systems. Coordination numbers, bonding distances and other structural information can be extracted from measured resonance lines. Due to this ability, NMR spectroscopy has become one of the most widespread tools for analysis in structural chemistry.

Many empirical rules exist to relate chemical shifts to conformational properties, but they are unable to take into account any but the simplest quantum effects involved in the problem. For several decades, many methods for computing NMR parameters have been developed in quantum chemistry, but they are all restricted to isolated systems in the gas phase. A first generalization to extended systems was developed a few years ago by Mauri et al. [1]. They showed that orbital magnetic response quantities can also be calculated under periodic boundary conditions.

In this paper, a recently developed alternative approach [2] is presented and applied to a strongly hydrogen-bonded molecular crystal. The formalism is based on Kohn–Sham density-functional theory [3], and exploits the exponentially decaying nature of localized Wannier orbitals [4]. It is implemented in a plane-wave pseudopotential scheme [5] and can be applied to crystalline and amorphous insulators under periodic boundary conditions, as well as to isolated molecules using a supercell technique. The new approach is designed for extended disordered systems,
where it is more efficient than previous methods. The method has already been shown to be of great value in the assignment of NMR chemical shifts [2, 9] and is currently being applied to a variety of organic systems.

2. Theory

When an external magnetic field is applied to an insulator, it modifies the electronic orbitals such that local ring currents are induced. This electronic current density creates an additional inhomogeneous magnetic field, superimposed onto the external one. The chemical shift tensor of an atom is defined as the proportionality factor between the induced and the externally applied magnetic field at the position of a nucleus:

\[ \sigma(\mathbf{r}) = -\frac{\partial \mathbf{B}_{\text{ind}}(\mathbf{r})}{\partial \mathbf{B}_{\text{ext}}} \]  

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

\[ \mathbf{B}_{\text{ind}}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int \frac{d^3 r}{|\mathbf{r} - \mathbf{R}|} \times \mathbf{j}(\mathbf{r}), \]  

where \( \mu_0 \) is the permeability of the vacuum. In a system under periodic boundary conditions, the current density is periodic and we can calculate Eq. (2) in reciprocal space from the Fourier transform of the current:

\[ \mathbf{B}_{\text{ind}}(\mathbf{G} \neq 0) = -\mu_0 \frac{\mathbf{G}}{|\mathbf{G}|} \times \mathbf{j}(\mathbf{G}). \]  

The \( \mathbf{G} = 0 \) component of the field depends on the bulk magnetic susceptibility tensor, \( \chi \), and the geometry of the sample:

\[ \mathbf{B}_{\text{ind}}(\mathbf{G} = 0) = \kappa \chi \mathbf{B}_{\text{ext}}. \]  

In the case of a spherical sample, the prefactor \( \kappa \) is given by \( \kappa = 2/3 \). The magnetic susceptibility can also be evaluated from the electronic current [2].

In our approach, the current density \( \mathbf{j} \) is computed through second order perturbation theory [8] on the electronic wavefunctions. We use maximally localized Wannier orbitals [4], which are obtained from the canonical Kohn–Sham states through a unitary transformation:

\[ |\psi_k^{(0)}\rangle = \sum_l U_{kl} |\psi_{\text{KS}}^l\rangle. \]  

The vector potential in the perturbation Hamiltonian of the magnetic field contains a position operator. We have shown previously [2] that, when applied to a spatially localized wavefunction, the use of a sawtooth-shaped, orbital-specific position operator yields a locally correct representation of the perturbation and has furthermore the required periodicity of the system. Using the continuous set of gauge transformations (CSTG) method [6], we obtain the electronic current density as a sum of three contributions:

\[ \mathbf{j}(\mathbf{r}) = \sum_k \langle \psi_k^{(0)} | \mathbf{j}_k (\psi_k^{(a)}) - |\psi_k^{(a)} + \psi_k^{(\Delta)}) \rangle \]  

with the current density operator \( \mathbf{j}_k \) and

\[ |\psi_k^{(a)}\rangle = \sum_l \mathcal{G}_{kl}(\mathbf{r} - \mathbf{d}_k) \times \mathbf{p} |\psi_l^{(0)}\rangle \cdot \mathbf{B}, \]  

\[ |\psi_k^{(\Delta)}\rangle = \sum_l \mathcal{G}_{kl}(\mathbf{r} - \mathbf{d}_k) \times \mathbf{p} |\psi_l^{(0)}\rangle \cdot \mathbf{B}, \]  

where \( \mathcal{G}_{kl} \) denotes the Green’s function and \( \mathbf{d}_k \) are the centers of charge of the localized ground state orbitals \( |\psi_k^{(0)}\rangle \). The Green’s function is given by:

\[ \mathcal{G}_{kl} = \sum_{\alpha, \beta} U_{kl}^\alpha |\psi_\alpha\rangle \langle \psi_\beta| U_{ol}^\beta, \]  

where \( \varepsilon_\alpha \) and \( \varepsilon_\beta \) are the Kohn–Sham energy eigenvalues of the occupied and empty orbitals, respectively. The actual calculation of the perturbation orbitals is done via minimization of a generalized variational second order energy functional [8].

The separation of the electronic response into three separate parts, Eqs. (7)–(9), makes it possible to use the position operator of an extended system in a well-defined way. Only positions and position operators relative to a local reference point (the center of charge, \( \mathbf{d}_k \)) appear in Eqs. (7)–(9). Thus, the problem of ill-defined absolute positions in an infinite periodic system is circumvented.

Further, the three contributions have a quite different magnitude. As shown in [2], the first and second parts, \( |\psi_k^{(a)}\rangle \) and \( |\psi_k^{(\Delta)}\rangle \), dominate the NMR shieldings, especially for protons. The third contribution, Eq. (9), can therefore often be neglected.
However, when strongly overlapping orbitals or strong hydrogen bonds are present, such as in the example discussed below, $|\psi_k^{(\Lambda)}\rangle$ also has to be taken into account. The calculation of this term is computationally more expensive, but still feasible since it can be done under a much weaker convergence criterion. A systematic study of this term revealed that the necessary number of self-consistent iterations in the perturbative calculation of $|\psi_k^{(\Lambda)}\rangle$ is about ten times smaller compared with the first two terms.

The calculations are done using a pseudopotential plane-wave package [5]. Especially for heavier nuclei, the effect of replacing the core electrons by pseudopotentials is non-trivial. Generally, it has been shown [7] that in many cases, a simple additional constant is enough to account for the core orbitals. The frozen core approximation is thus justified in these cases. However, a pseudopotential does not reproduce the chemical environment of the core region exactly, and the NMR chemical shift is very sensitive to changes in this region. Of course, this introduces an additional source of error. However, in the following we shall apply our method to proton chemical shifts, for which no such problems arise.

3. Crystalline imidazole

We have computed $^1$H NMR parameters of crystalline imidazole, $\text{N}_2\text{C}_3\text{H}_4$. The crystal (depicted in Fig. 1) consists of hydrogen bonded imidazole molecules, whose planes are tilted by 120°.

Imidazole and its derivatives have received much attention due to their potential use as proton conductors in fuel cells. As a step towards the understanding of the transport mechanism, the structure and dynamics of protons in the imidazole single crystal can be investigated by magic angle spinning (MAS) proton NMR spectroscopy.

In Fig. 2(a), the experimental spectrum is shown. It stems from a commercial sample that has been repeatedly melted and cooled down, in order to improve the crystal structure and to eliminate impurities. Graphs (b) and (c) represent the theoretical NMR resonances of a single crystal and an isolated molecule as computed with the method presented above, with eight molecules per unit cell, norm-conserving pseudopotentials of the Martins–Trouiller type [10] and a plane-wave cutoff of 60 Ry. In all calculations the BLYP exchange-correlation functional [11] was used, since this functional is known to reproduce hydrogen bonding reliably. The crystal structure of imidazole was taken from X-ray diffraction data [12]. Geometries of the crystal and the molecule were refined by an $ab$ ini-
tio geometry optimization until the forces on the ions went below $10^{-3}$ atomic units. This was necessary since the X-ray data turned out not to be good enough, especially for the hydrogen positions.

In the experimental spectrum, there is a double peak at 5–7 ppm, and two more at 10 ppm and 14–15 ppm. The double resonance is also found in the calculated spectrum of the crystal and can be assigned to the protons of the three aromatic carbons. The upfield feature at 7 ppm arises from the hydrogen atom at the apical carbon, whereas the larger line at 4–5 ppm stems from the two remaining protons. It is interesting to note that in the isolated molecule, these hydrogen peaks are much less resolved. In the crystal, there is an interaction between the $\pi$-electrons of neighboring rings with the non-apical hydrogens, which creates a downfield shift.

The line at 12 ppm is not found in the theoretical spectra, but its location is essentially equal to that of liquid imidazole, and it is right between the calculated $^1$H lines of the isolated molecule and the crystal. Thus, we assume that it is due to NH protons in a particular glassy or liquid-like configuration that has not yet been considered in our calculations. Simulations of further geometries and also of the liquid state are currently under way in order to investigate the origin of this resonance in more detail.

4. Conclusion

Especially in the solid state, where local quantum effects play a crucial role for the NMR resonance lines, the analysis of experimental spectra is often difficult. In these cases, where the prediction of chemical shifts must be done under periodic boundary conditions, the theoretical approach presented above is a powerful tool for the understanding of local microscopic structure. The calculations presented in this article show that the new method reproduces the experimental NMR chemical shift spectrum of strongly hydrogen bonded periodic systems with a very good accuracy.

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References