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Accurate hyperfine couplings for $C_{59}N$

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Abstract

We identify the shortcomings of existing ab initio quantum chemistry calculations for the hyperfine couplings in the recently characterized azafullerene, $C_{59}N$. Standard gaussian basis sets in the context of all-electron calculations are insufficient to resolve the spin density near the cores of the atoms. Using the projector augmented wave (PAW) method implemented on top of a standard pseudo-potential plane-wave density-functional framework, we compute significantly more accurate values for the Fermi contact interaction. © 2002 Elsevier Science B.V. All rights reserved.

Electron spin resonance (ESR) is one of the key tools for structural studies of defects and radicals. The hyperfine splitting of the resonance line by magnetic nuclei is used to identify particular peaks with various sites in the system. To make such identifications, a theoretical prediction of the hyperfine splitting is necessary. The performance of such predictions has been historically relatively difficult, because the values of the spin density, which is the required observable, are very small and thus hard to resolve. This problem is much more pronounced in the cases where the electronic states associated with the unpaired electron are p-like, which further contributes to the reduction of the absolute spin density values near the ionic cores.

In this Letter, we investigate the cause of the especially poor performance of the electronic structure calculation for the case of the azafullerene, $C_{59}N$, and provide a method that predicts significantly more accurate values for the hyperfine splittings.

The study of doped fullerenes and nanotubes is a very active area, because dopants can make fullerenes chemically and electronically active. The potential applications range from novel semiconductors to nanomechanical devices and even biologically active agents. A general review of heterofullerenes is in [1].

In particular, azafullerene, the nitrogen substituted version of C_{60} has received considerable attention. The structural and electronic properties of the $C_{59}N$ monomer have been studied before [2], and it was found that there is significant delocalization of the unpaired electron over the molecular cage. The degree of delocalization over the $C_{59}N$ cage has a significant bearing on the electrical

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properties of the material. However, until recently, $C_{59}N$ was only available in dimerized, inactive form. It is now possible to make solid solutions of the azafullerene monomer in conventional C_{60} in macroscopic quantities [3], and thus direct comparisons with the experiments can be made. The structure of the molecule is shown in Fig. 1. The molecule has a mirror plane, containing the atoms N and C2.

A calculation of the electronic structure of $C_{59}N$ was published in [3] along with the experimental results for the hyperfine splittings. The calculated relative values of the hyperfine coupling were showing the same trends as the experimental data, but the absolute values were off by more than a factor of 2.

At room temperature, due to the rapid reorientation of the molecules in the crystal, only the isotropic hyperfine term is observable. Also called the Fermi contact interaction, it can be expressed for a particular nucleus by the effective Hamiltonian

$$H_{\text{hf}} = A_{\text{hf}} \mathbf{S}_I \cdot \mathbf{S}_e \delta(\mathbf{r} - \mathbf{R}_I), \quad (1)$$

where the subscript I refers to the nucleus, and A_{hf} is the isotropic hyperfine coupling constant and \mathbf{S} is the spin operator. Because of the Dirac delta function, the hyperfine splitting then only depends on the electronic spin density at the position of the nucleus and the nuclear and electronic magnetic moments

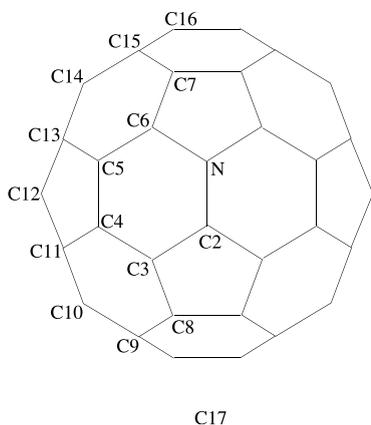


Fig. 1. Structure of azafullerene $C_{59}N$.

$$A_{\text{hf}} = \frac{2\mu_B}{3} \gamma_e \gamma_I \tilde{n}(\mathbf{R}_I),$$

where μ_B is the Bohr magneton, γ_e and γ_I are the electronic and nuclear magnetic moments, respectively, and $\tilde{n}(R)$ is the electronic spin density at the nucleus. The isotropic hyperfine coupling is thus very sensitive to the values of the wavefunctions near the atomic cores, which in this case, similarly to other conjugated systems, can be very small. There are two sources of error: the inaccuracy of the density functional used to describe electronic correlations and the incompleteness of the basis set. Due to the aforementioned small numerical value of the spin density at the nuclear positions, this latter error can be particularly severe. A distinct disadvantage of traditional quantum chemistry methods, such as the one used in [3] is the uncontrolled nature of the standard basis sets with which the wavefunctions and the density is expanded.

Building on the formal work of Hohenberg, Kohn and Sham [4,5], and the later algorithmic work of Car and Parrinello [6] and others [7], it is now practical to study large systems with near quantum chemical accuracy using a plane-wave basis set. Below, we use the traditional density-functional plane-wave pseudo-potential method and the local spin density approximation (LSDA) to relax the molecular geometry, then apply the projector augmented wave (PAW) method [8], to calculate all-electron spin densities at the nuclear sites, from which the hyperfine couplings may be computed. A key aspect of this approach is that PAW is used as a *post processing* step, thus already existing standard plane-wave codes can be used to carry out the computationally intensive geometrical optimization steps. After that, the hyperfine constants can be simply and efficiently computed, even using standard numerical packages. The *ab initio* calculations were carried out with the DFT++ package [9], using periodic supercell technique in a 24 bohr cubic cell; the plane-wave cutoff was 20 hartrees. The convergence of the results with respect to the plane-wave cutoff were checked by repeating the calculations at 35 hartrees; the hyperfine couplings only changed by less than 10%. We used

optimized norm conserving pseudo-potentials developed by Rappe [10].

The PAW method was introduced by Blöchl in 1994. It allows the reconstruction of all-electron properties from pseudo-potential calculations. Originally, PAW was presented as a fully self-consistent all-electron method, where the reconstructed wavefunctions are used to compute the total energy. Here, we just use the method of reconstruction. Accordingly, we define angular momentum projector functions $|p\rangle$ for every atomic species, which have the property

$$\langle p_i | \phi_j^{\text{ps}} \rangle = \delta_{ij},$$

where $\phi_j^{\text{ps}}(\mathbf{r})$ are atomic pseudo-wavefunctions and i, j are composite indices of the usual angular momentum channels $[nlm]$. The projectors $|p\rangle$ are localized near the nucleus, and they vanish outside the cutoff radius of the pseudo-potential. The reconstruction formula is

$$|\Psi^{\text{rec}}\rangle = |\Psi^{\text{ps}}\rangle + \sum_R \sum_i \left(|\phi_{R,i}^{\text{ae}}\rangle - |\phi_{R,i}^{\text{ps}}\rangle \right) \times \langle p_{R,i} | \Psi^{\text{ps}} \rangle, \quad (2)$$

where $|\Psi^{\text{ps}}\rangle$ is an extended pseudo-wavefunction, ϕ^{ae} are the orbitals from an all-electron atomic calculation, and R runs through the position of the nuclei. Note that because the atomic pseudo-wavefunctions are identical with the all-electron atomic wavefunctions outside the cutoff radius, the reconstructed wavefunction $|\Psi^{\text{rec}}\rangle$ is identical to the pseudo-wavefunction $|\Psi^{\text{ps}}\rangle$ in the inter-atomic region. The reconstruction is exact within the frozen core approximation if we take a complete set of angular momentum projectors. In practice, it is often enough to take just one projector for every pair l and m .

For our purposes here, we also need the notion of a *pseudo-operator*, which arises naturally within the PAW formalism. Using the definition (2), the matrix elements of an operator O between reconstructed wavefunctions are given by

$$\begin{aligned} \langle \Psi_1^{\text{rec}} | O | \Psi_2^{\text{rec}} \rangle &= \langle \Psi_1^{\text{ps}} | O | \Psi_2^{\text{ps}} \rangle + \sum_{RR',ij} \langle \Psi_1^{\text{ps}} | p_{R',j} \rangle \\ &\times \left(\langle \phi_{R',j}^{\text{ae}} | O | \phi_{R,i}^{\text{ae}} \rangle - \langle \phi_{R',j}^{\text{ps}} | O | \phi_{R,i}^{\text{ps}} \rangle \right) \langle p_{R,i} | \Psi_2^{\text{ps}} \rangle. \end{aligned} \quad (3)$$

Note that for local and semi-local operators, only on-site terms contribute, where $R = R'$. Thus we can define a pseudo-operator O^{ps} ,

$$O^{\text{ps}} = O + \sum_{R,ij} |p_{R,j}\rangle \left(\langle \phi_{R,j}^{\text{ae}} | O | \phi_{R,i}^{\text{ae}} \rangle - \langle \phi_{R,j}^{\text{ps}} | O | \phi_{R,i}^{\text{ps}} \rangle \right) \langle p_{R,i}|.$$

This pseudo-operator, when acting on pseudo-wavefunctions, by construction will give the same matrix elements as the corresponding all-electron operator acting on all-electron wavefunctions.

To extract the hyperfine splitting from an ab initio calculation, we need the all-electron spin density at the nuclear positions,

$$\tilde{n}(R) = n_{\uparrow}(R) - n_{\downarrow}(R).$$

The simplicity of the delta function operator in (1) made this one of the first applications of the above reconstruction ideas. If the angular momentum expansion were complete, the first and third terms of Eq. (3) would cancel exactly, and only the term involving the all-electron atomic states would need to be calculated. Also, only the s states have a non-vanishing density at the nucleus of an atom, thus (3) reduces to

$$n^{\text{rec}}(R) = \sum_i n^{\text{ps}}(R) w_i(R), \quad (4)$$

where i is the index of the projectors for the s channels, and the weighting factors w_i are

$$w_i(R) = \frac{n_{i,\text{at}}^{\text{ae}}(0)}{n_{i,\text{at}}^{\text{ps}}(0)},$$

where the subscript “at” refers to densities in isolated atoms. Blöchl calculated hyperfine constants for a variety doped semiconductor systems [11] using Eq. (4) and obtained satisfactory results by just taking a single projector,

$$n^{\text{rec}}(R) = n^{\text{ps}}(R) w_0(R). \quad (5)$$

Eq. (5) amounts to a simple rescaling of the pseudo-spin density by a constant factor.

The problem with the C_{59}N molecule, as mentioned above, is that the unpaired electron is in an orbital which has almost p-like symmetry near the nuclei. The unpaired spin density at the nucleus is therefore very small and its value becomes very

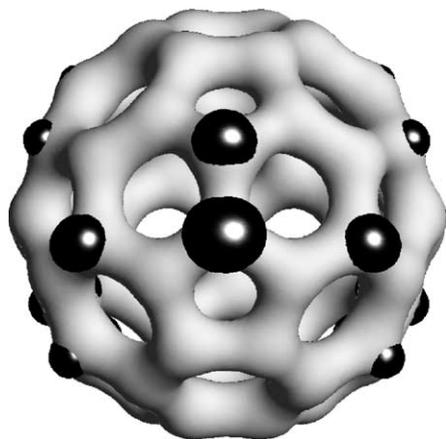


Fig. 2. Contour of the charge density (gray) and the spin density (black) of the $C_{59}N$ molecule.

sensitive to how well the charge density is resolved near the nucleus. We find that a more robust approach is to retain the projector form from Eq. (3) and use the formula

$$n^{\text{rec}}(R) = n_{\text{at}}^{\text{ac}}(R) |\langle \Psi^{\text{ps}} | p_{R,s} \rangle|^2. \quad (6)$$

Apart from the issue of resolution near the ionic core, the truncation of the angular momentum expansion in (3) implies that the projector form (6) is expected to underestimate the spin density, while the simple scaling method (5) overestimates it by assuming that each s channel has the same scaling factor $w_i \equiv w_0$ for a given nucleus. Note that this error is in addition to those resulting from an incomplete spatial resolution of the wavefunction near the core.

The ionic positions in the $C_{59}N$ molecule were relaxed until all forces are less than 0.03 eV/\AA . Fig. 2 shows the contours of the charge density in gray, and the spin density in black; Fig. 3 shows just the spin density. The significant delocalization of the unpaired electron is clearly visible, as well as the oscillations of the spin density as the distance increases away from the nitrogen atom. Table 1 shows our computed hyperfine coupling constants for selected atoms and the results using the GAUSSIAN all-electron program [12] which were published along with the experiment in [3]. It is clear that the full projection formula (6) is much more accurate; the error is at most 20% compared to experi-

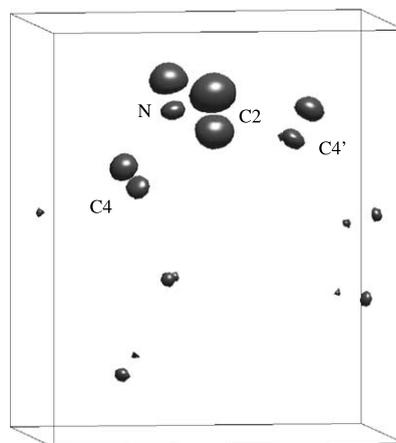
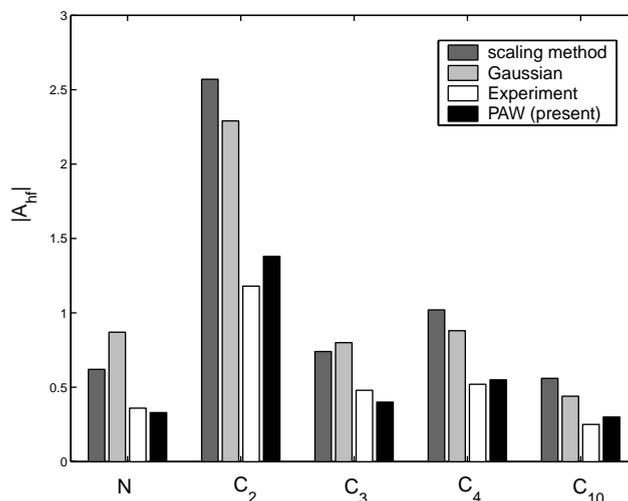


Fig. 3. Contour of the spin density in the $C_{59}N$ molecule.

ment. It is interesting that the values obtained by simply rescaling the pseudo-density are relatively close in agreement with the values from the GAUSSIAN calculation. Both traditional approaches overestimate the hyperfine coupling by over a factor of two. Note that the experiment only measures the absolute value of the hyperfine coupling and that the identification of the experimental values with particular sites is actually inferred from the calculated values. Recently, defects in silica were investigated by Blöchl [13], where PAW was used as an all-electron method. There, the conclusion was similar to ours: much accuracy can be gained by using the full projection method.

In conclusion, we have computed isotropic hyperfine coupling constants for the azafullerene $C_{59}N$ and obtained a much better agreement with recently published experimental data than other calculations. We showed that the hyperfine parameters are very sensitive observables in this system because the unpaired electron is more or less in a p -like state with relatively small spin density at the nuclear sites. Thus, a full projection-based formula of the PAW method was needed to obtain reasonable values for the hyperfine coupling, as opposed to the currently accepted method of simply rescaling of the pseudo-density. This underscores the significance of basis set convergence and related numerical issues regarding the traditional quantum chemistry basis sets.

Table 1
Hyperfine coupling constants in mT



Atom	Expt.	PAW projector method	$n^{ps}(R)$ scaling method	GAUSSIAN B3LYP
N	0.36	0.33	0.62	0.87
C ₂	1.18	1.38	2.57	2.29
C ₃	0.48	-0.40	-0.74	-0.80
C ₄	0.52	0.55	1.02	0.88
C ₁₀	0.25	0.30	0.56	0.44

The present work is in the second and third column. The ‘PAW projector method’ uses Eq. (6), the ‘scaling method’ uses Eq. (5). Note that the experiment only measures the absolute value, so this is what is presented in the bar graph. The GAUSSIAN and experimental values are from [3].

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