Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Materials of "Hydrogen bonding and chemical shift assignments in carbazole functionalized isocyanides from Solid-State NMR and First-Principles calculations."

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1 Introduction

In this document, we present some details of the converse approach for chemical shielding tensor calculations as now implemented in the Vienna *Ab-initio* Simulation Package (VASP) [1, 2, 3, 4] using Density Functional Theory (DFT). After a brief description of the theory and the PAW data sets used for this work, we provide some test calculations on finite (molecular) systems using both VASP and the quantum chemistry package DALTON [5] and on extended (crystalline) systems using the well-established direct approach from Mauri *et al.* [6, 7] as implemented in QUANTUM-ESPRESSO[8].

2 Overview of the converse approach

2.1 Theory

In the converse approach the shielding tensor $\boldsymbol{\sigma}_s$, of a given nucleus s, is related to the macroscopic orbital magnetisation $\boldsymbol{M}^{\text{ind}}$ induced by a magnetic dipole $\boldsymbol{m}_s$ placed at the nuclear position [9]. One can formalize this relation via:

$$\sigma_{s,\alpha\beta} = -\Omega \frac{\partial M_\beta^{ind}}{\partial m_{s,\alpha}} \tag{1}$$

where Ω is the volume of the cell and $\alpha, \beta = \{x, y, z\}$ are the Cartesian components of the respective vectors and tensor.

The isotropic chemical shielding (σ_{iso}) is given by the trace of the chemical shielding tensor $\sigma_{\text{iso}} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. Therefore, in general three calculations are needed (one for each direction of the applied magnetic dipole) to obtain the isotropic contribution. The calculation gives access to the shielding (or shifts which is the opposite sign quantity) in an absolute scale. Here we only calculated the valence contribution to the absolute shift. The experimental isotropic chemical shifts (δ_{iso}) and this absolute isotropic chemical shielding are related through the definition of a shielding reference (σ_{ref}) as $\delta_{\text{iso}} = \sigma_{ref} - \sigma_{\text{iso}}$. Experimentally the reference is set according to an external compound, in a theoretical approach it is more convenient to use a well defined internal reference site to compare with experimental values.

The central quantity in the converse approach for NMR shift calculations is the total orbital magnetization induced by the local magnetic moment. If this quantity is easily evaluated for finite systems, for periodic systems the problem was only recently solved in the context of the Modern Theory of Magnetization (MTM) [10]. Indeed, from the former, which found its foundation on the geometric phase approach (Berry phase), the total orbital magnetization can be defined using only bulk properties:

$$\mathbf{M}^{\text{orb}} = -\frac{1}{2c}\text{Im}\sum_{n\mathbf{k}} \langle \partial_{\mathbf{k}} u_{n\mathbf{k}} | \times (\mathcal{H}_{\mathbf{k}} + \epsilon_{n\mathbf{k}}) | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle \tag{2}$$

where $|u_{n\mathbf{k}}\rangle$ are the cell-periodic part of the Bloch states, $\mathcal{H}_{\mathbf{k}} = e^{-i\mathbf{kr}}\mathcal{H}e^{+i\mathbf{kr}}$ is an effective Hamiltonian and $\epsilon_{n\mathbf{k}}$ its eigenvalues.

The determination of the ground state of the perturbed Hamiltonian, which includes the vector potential due to the magnetic dipole, is then sufficient to calculate the resulting change in orbital magnetization as derived by Ceresoli et al. [10]. However, as for the linear response methods, the pseudopotential response need to be corrected to obtain accurate shifts. The orbital magnetization is then obtained as:

$$\mathbf{M}^{ind} = \mathbf{M}^{orb} + \Delta\mathbf{M}_{ONE} \tag{3}$$

Atom	configuration	r(s)	r(p)	r(d)
H	$1s^1$	0.950	1.100	1.100
C	$[He]2s^2 2p^2$	1.200	1.500	1.500
O	$[He]2s^2 2p^4$	1.200	1.520	1.500
N	$[Ne]2s^2 2p^3$	1.200	1.500	1.500

Table 1: Electronic configuration and cutoff radii for the norm-conserving PAW data set used in the current work.

where the first right-hand term corresponds to the orbital magnetization which can be calculated by the MTM and the second is the term arising from the GIPAW one-center correction. More details about this derivation can be found in Ref. [11]. At the moment only the norm-conserving PAW method can be used for chemical shielding (tensor) calculations with VASP.

2.2 Norm-conserving PAW data sets

Table 1 brings together the principal parameters used to generate the PAW data sets which we used in the present work. The data sets were constructed using the PBE functional.

For C, O and N the d-channel is treated as local pseudopotential, so only an explicit PAW reconstruction is done for the s and p channels. For each angular momentum channel only one reference energy is used (chosen to be the bound state).

For hydrogen two reference energies are used for the s (one at the $1s$ bound state, and the other 0.5 Ry above the vacuum level) and the p (-0.3 and 8.0 Ry relative to vacuum) channels, whereas only one is used for the d channel (6 Ry above vacuum).

3 Test results

3.1 Finite systems (small molecules)

As a first test, we compared chemical shifts for hydrogen and carbon (^{1}H, ^{13}C) obtained on a small molecule set[1] by the converse approach and by all-electron calculations using the DALTON package. For this benchmark test, we only considered the Local Density Approximation (LDA) to DFT. For the plane-wave calculation we used a kinetic energy cut-off of 1000 eV and only one Γ centered **k**-point in a supercell of 14×14×14 Å^3 (16×16×16 Å^3 for the benzene molecule). The all-electron chemical shifts values were obtained with the aug-cc-pCV5Z basis set. Only benzene shifts were obtained with a smaller basis set (see Table 2 for details). For the converse values, the carbon absolute chemical shifts were obtained adding a fixed core contribution of 200.333 ppm (obtained from QUANTUM-ESPRESSO[8]).

For comparison the VASP (i.e. plane-wave PAW) and DALTON (i.e. localized all-electron) results are brought together in Figure 1 and in detail in Table 2. This results show that the VASP converse approach implementation is in the accuracy range of the all-electron calculation. Indeed, most of the relative errors are under 1%. Bigger differences (e.g. benzene) can be attributed to the difficulty to control the basis set convergence for the localized basis set and to the finite size of the supercell of the plane-wave calculations.

[1]Systems: H_2, H_2O, C_6H_6, C_2H_2, C_2H_4, C_2H_6, CH_4, CO_2, CO

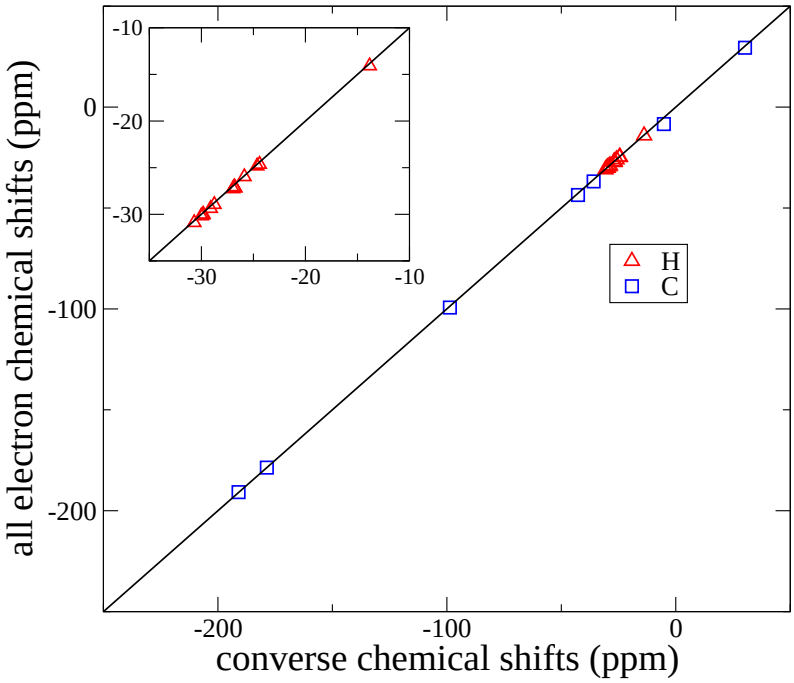

Figure 1: Absolute isotropic chemical shifts for a set of small molecules (see text). The figure compares chemical shifts obtained by the converse calculation in a PAW framework with a all-electron calculation. The inset provide an expansion on the hydrogens shift range. For the converse results, the carbon absolute chemical shifts are obtained adding the fixed core contribution (200.33 ppm). All calculations are DFT-LDA .

	H atom		C atom	
Molecule	converse	all-electron	converse	all-electron
H_2	-25.87	-25.97		
H_2O	-30.00	-30.16		
C_2H_2	-29.93	-30.09	-98.67	-99.33
C_2H_4	-24.41	-24.64	-35.88	-36.84
C_2H_6	-29.81	-29.98	-178.64	-178.61
CH_4	-30.69	-30.89	-190.99	-190.8
C_6H_6	-23.08	-23.24*	-36.55	-39.3*
CO			30.23	29.42
CO_2			-42.71	-43.56

*aug-cc-pCVQZ basis set

Table 2: Comparison between absolute chemical shifts calculated by the converse approach and an all-electron calculation for a set of small molecules. All all-electron calculations are aug-cc-pCV5Z except when indicated otherwise. For the converse calculations we used cut-off kinetic energy of 1000 eV and only one k-point in a supercell of 14×14×14 Å^3 (except benzene: 16×16×16 Å^3). For the converse results, the carbon absolute chemical shifts are obtained adding the fixed core contribution (200.33 ppm). All calculations are DFT-LDA

3.2 Periodic Systems (crystalline compounds)

To show the ability of the current implementation to reproduce chemical shifts for periodic systems, we present a simple test calculation on crystal diamond in comparison to the direct and the converse approach as implemented in QUANTUM-ESPRESSO. It worth noting that

	VASP	ESPRESSO	
Calculation	converse	direct	converse [9]
2-atoms 12×12×12	-131.43	-131.25	–
8-atoms 8×8×8	-131.48	-131.27	-131.20
64-atoms 4×4×4	-131.56	-131.27	-131.24

Table 3: ^{13}C absolute chemical shift of diamond for different cell size. All calculations are PBE and we used a cutoff kinetic energy of 1360 eV (∼100 Ry as in [9]) . Core contribution (200.333 ppm).

direct approach values presented here were obtained without considering the macroscopic the contribution of shape dependent surface currents that could be calculated from the susceptibility of the compound.

We adopted the same lattice parameters as used in Ref. [9] (e.g. a =3.498Å). The introduction of the magnetic dipole in the periodic system could lead to interactions between periodical images of the perturbed site. Also, to test the convergence with respect to the supercell size, we performed the calculation for three different cells (two-atom fcc cell, eight-atom cubic cell and 64-atom cubic cell). Table 3 includes all these different calculations for the converse and the direct approaches together with converse values as reported in [9]. We add to the VASP results a core contributions of 200.333 ppm (as calculated in QUANTUM-ESPRESSO). We attribute the small differences to different PAW data sets.

As expected the linear response approach (i.e. direct) shows almost no difference when changing the size of the supercell.[2] In case of the converse approach, the convergence with respect to the supercell size is within ∼0.1 ppm. The 2-atom fcc cell value was unexpected as the smallest distance between to perturbed images is only about 2.5Å. However, other test calculation shows that the supercell convergence can be more critical than in this particular case. We assume that the high symmetry of carbon diamond could lead to some well-suited error cancellation.

[2]In the direct approach by Mauri et al. [6], the perturbation is periodic and obtained in a long wavelength limit ($\mathbf{q} \rightarrow 0$). In practice this limit is finite and results should be checked against this parameter. However, a default value of 0.01 is generally sufficient.

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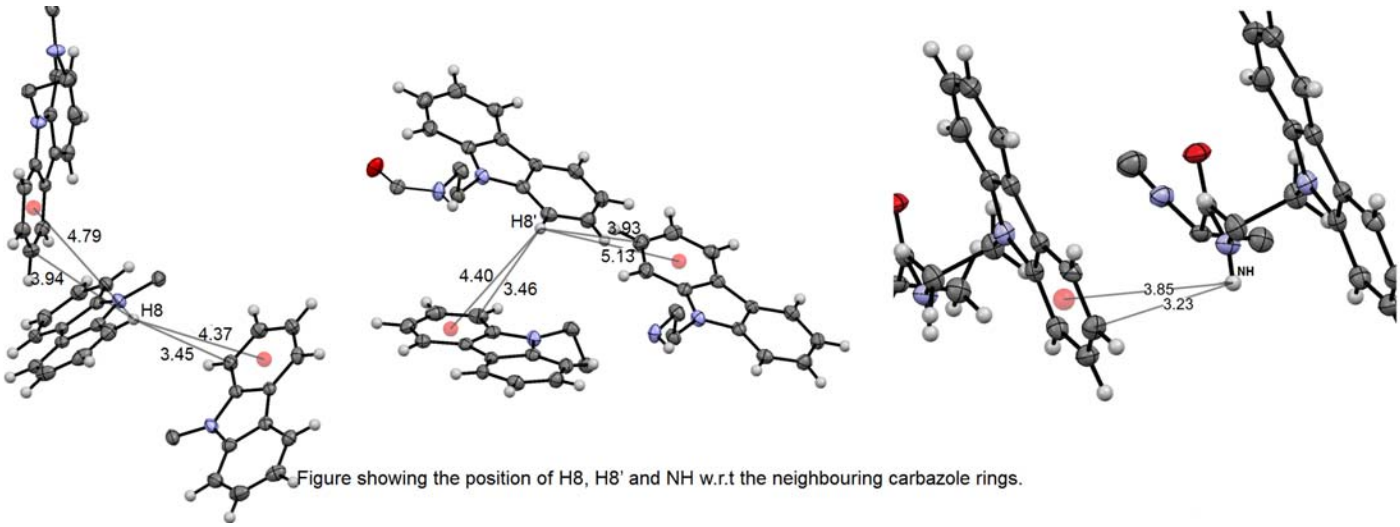

Figure showing the position of H8, H8' and NH w.r.t the neighbouring carbazole rings.