

# A comparison of methods for the calculation of NMR chemical shifts

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A theory (MPL) to compute the NMR chemical shifts in condensed matter systems using periodic boundary conditions was presented by F. Mauri, B. Pfommer, and S. G. Louie [Phys. Rev. Lett. **77**, 5300 (1996)]. The MPL method has been implemented so far within a pseudopotential formulation in which the wave functions are expanded in plane waves. In this paper, we compare analytically the MPL approach within the density functional theory to existing methods for the calculation of the chemical shifts such as GIAO (gauge-including atomic orbitals), CSGT (continuous set of gauge transformations), and IGAIM (individual gauges for atoms in molecules). To this end we apply the MPL approach to molecules since the latter methods are conceived only for finite systems. We show theoretically the equivalence between a variant of the CSGT and the MPL method applied to finite systems. Moreover, we analyze numerically the efficiency of the different methods when atomic orbital basis sets are employed, by comparing the basis-set convergence properties. We find that the CSGT and IGAIM approaches have the same convergence properties as GIAO, whereas their computational time is significantly smaller. In the MPL method, the contribution of the valence electrons to the chemical shift converges rapidly with respect to the size of the basis set, whereas the convergence properties of the core contribution are poor. We improve the convergence by separating the core and the valence contributions in a gauge-invariant manner, by applying the MPL method only to the valence contribution, and by treating the core contribution with IGAIM. The performances of the resulting approach compare favorably with those of the other methods. Finally we find that the core contribution to the chemical shift is independent of the chemical environment, in contrast to what is sometimes found in the literature. In conclusion, our results indicate that, to compute the chemical shifts in both molecules and solids, using atomic orbital basis sets, one could use the MPL method to evaluate the valence contribution and add to it a rigid core contribution as obtained, for instance, from an atomic calculation. © 1999 American Institute of Physics.

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## I. INTRODUCTION

Nuclear magnetic resonance (NMR) is one of the most powerful and extensively used experimental methods to probe the electronic structure and the molecular geometry of materials.<sup>1</sup> A significant part of the NMR spectral information are the chemical shifts, which describe the interaction between an external magnetic field and the magnetic moment of an atomic nucleus. Numerical *ab initio* calculations of the chemical shifts have proved to be a useful tool to interpret experimental data. Indeed, in certain cases the measured

NMR spectra in combination with *ab initio* calculations lead to an unequivocal determination of the microscopic structure of the system under study. Moreover, the degree of agreement between calculated and measured chemical shifts is a benchmark of the theoretical modeling of the underlying electronic structure.

In quantum chemistry, *ab initio* calculations of the chemical shift exist since the 70's. In these calculations the electronic wave functions are expanded in terms of atomic orbitals.<sup>2</sup> The use of atomic basis sets of finite size yields a dependence of the chemical shift upon the chosen gauge origin of the vector potential that describes the external magnetic field. Many different approaches exist to deal with this so-called gauge origin problem, such as the gauge-including atomic orbital (GIAO) method,<sup>3</sup> the individual gauge for lo-

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calized orbitals (IGLO) method,<sup>4</sup> or the set of gauge transformation (SGT) class of methods, which includes the individual gauges for atoms in molecules (IGAIM) method<sup>5</sup> and the continuous set of gauge transformation (CSGT) approaches.<sup>6,7</sup> All these methods are restricted to *finite* systems such as molecules and clusters that are isolated in free space. Recently Mauri, Pfrommer, and Louie (MPL)<sup>8</sup> developed a method to compute the chemical shift in extended condensed matter systems using periodic boundary conditions. These allow us to perform calculations on truly *infinite* systems formed by the unit cell and all its periodic replicas. The MPL approach has been applied to periodic systems, such as crystals<sup>8,9</sup> and, with a super-cell technique, to disordered systems such as liquids<sup>10</sup> and amorphous materials.<sup>11</sup>

So far, the MPL method has been used only in calculations based on pseudopotentials and plane waves. The use of pseudopotentials introduces errors which are negligible only for first- and second-period elements of the periodic table.<sup>8,11</sup> A necessary condition to compute chemical shifts of heavier elements with a pseudopotential approach is that the core electron contribution to the chemical shifts be rigid, i.e., independent from the chemical environment. Finally, the efficiency of the MPL method when atomic orbital basis sets are employed still has to be verified.

In this paper, we compare analytically the MPL approach to the quantum chemistry methods for the calculation of the chemical shift within the density functional theory (DFT). We find that the MPL approach, when applied to molecules, is equivalent to a variant of the SGT approach. Moreover, we analyze numerically the efficiency of the MPL method when atomic orbital basis sets are employed, by comparing the basis-set convergence properties of the MPL method to those of the well established GIAO and IGAIM methods. Finally we separate the contributions to the chemical shift of core and valence electrons in a gauge-invariant manner to study the validity of a frozen-core approximation in chemical shift calculations.

The paper is divided in two parts. In the first, a short overview of the SGT class of methods is given, the MPL approach is applied to molecular systems, and finally a hybrid method for the calculation of the chemical shift is presented, where we separate core and valence states gauge-invariantly. In the second part we discuss our numerical results. Different methods are checked for their convergence properties with respect to the size of several basis sets, and we present an investigation of the core contribution to the chemical shift, studying its dependence on the chemical environment.

## II. THEORY

### A. Magnetic response within DFT

The chemical shift tensor  $\vec{\sigma}$  is defined by the linear response of a sample to an external uniform magnetic field  $\mathbf{B}_{\text{ext}}$  at the nuclear position  $\mathbf{r}_N$ :

$$\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r}_N) = -\vec{\sigma}(\mathbf{r}_N)\mathbf{B}_{\text{ext}} = \frac{1}{c} \int d^3\mathbf{r} \mathbf{J}^{(1)}(\mathbf{r}) \times \frac{\mathbf{r}_N - \mathbf{r}}{|\mathbf{r}_N - \mathbf{r}|^3}, \quad (1)$$

where  $\mathbf{B}_{\text{in}}^{(1)}(\mathbf{r}_N)$  is the induced first-order magnetic field in the sample and  $\mathbf{J}^{(1)}(\mathbf{r})$  is the induced first-order quantum electric current.

Using the symmetric gauge for the vector potential that describes the external magnetic field

$$\mathbf{A}(\mathbf{r}') = \frac{1}{2} \mathbf{B}_{\text{ext}} \times (\mathbf{r}' - \mathbf{d}), \quad (2)$$

with the gauge origin  $\mathbf{d}$ , we get within DFT:<sup>12-14</sup>

$$\begin{aligned} \mathbf{J}^{(1)}(\mathbf{r}) = & -\frac{1}{c} \sum_{o,e} \langle \psi_o^{(0)} | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}| \mathbf{p}] \frac{|\psi_e^{(0)}\rangle\langle\psi_e^{(0)}|}{\epsilon_o - \epsilon_e} \\ & \times [(\mathbf{r} - \mathbf{d}) \times \mathbf{p}] \cdot \mathbf{B}_{\text{ext}} |\psi_o^{(0)}\rangle \\ & - \frac{1}{2c} \rho(\mathbf{r}) \mathbf{B}_{\text{ext}} \times (\mathbf{r} - \mathbf{d}). \end{aligned} \quad (3)$$

Here,  $|\psi_i^{(0)}\rangle$  are the eigenfunctions of the unperturbed Hamiltonian with eigenvalues  $\epsilon_i$  and the summation is over occupied states  $o$  and empty states  $e$ ,  $\rho(\mathbf{r}) = 2 \sum_o \langle \psi_o^{(0)} | \mathbf{r} \rangle \times \langle \mathbf{r} | \psi_o^{(0)} \rangle$  is the electron density, and a factor 2 for the spin is included.<sup>15</sup> In Eq. (3) the term containing the sum over occupied and empty states gives the first-order paramagnetic contribution and the term containing  $\rho(\mathbf{r})$  gives the first-order diamagnetic contribution.

If Eq. (3) is evaluated exactly,  $\mathbf{J}^{(1)}(\mathbf{r})$  is independent of the choice of the gauge origin  $\mathbf{d}$ . As a consequence we have

$$\begin{aligned} 0 = & \frac{1}{c} \sum_{o,e} \langle \psi_o^{(0)} | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}| \mathbf{p}] \frac{|\psi_e^{(0)}\rangle\langle\psi_e^{(0)}|}{\epsilon_o - \epsilon_e} \\ & \times [\mathbf{d} \times \mathbf{p}] \cdot \mathbf{B}_{\text{ext}} |\psi_o^{(0)}\rangle + \frac{1}{2c} \rho(\mathbf{r}) \mathbf{B}_{\text{ext}} \times \mathbf{d}. \end{aligned} \quad (4)$$

Since  $\mathbf{d}$  and  $\mathbf{B}_{\text{ext}}$  are arbitrary, it turns out that

$$\begin{aligned} -\delta_{\alpha\beta} \rho(\mathbf{r}) = & 2 \sum_{o,e} \langle \psi_o^{(0)} | [p_\alpha |\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}| p_\alpha] \\ & \times \frac{|\psi_e^{(0)}\rangle\langle\psi_e^{(0)}|}{\epsilon_o - \epsilon_e} p_\beta |\psi_o^{(0)}\rangle, \end{aligned} \quad (5)$$

where  $\alpha$  and  $\beta$  are any two of the Cartesian coordinates. Equation (5) is the generalized  $f$ -sum rule.<sup>16</sup>

In numerical calculations based on atomic orbitals, finite Hilbert spaces are used. In this case, the generalized  $f$ -sum rule no longer holds. In particular, the left-hand side of Eq. (5) contains the electron ground-state density, which converges faster with respect to the basis set size than the right-hand side, which depends on transitions from occupied to empty states. Hence  $\mathbf{J}^{(1)}(\mathbf{r})$  computed using Eq. (3) is no longer invariant for a variation of the gauge origin  $\mathbf{d}$ , or equivalently for a rigid translation of the system. This constitutes the so-called gauge origin problem in the calculation of  $\vec{\sigma}$ . The deviations of the calculated values from the converged  $\vec{\sigma}$  results depend sensitively on the gauge origin. For example, if the current is computed at a point  $\mathbf{r}$  far from the gauge origin  $\mathbf{d}$ , both, para- and diamagnetic parts of  $\mathbf{J}^{(1)}(\mathbf{r})$  become large and the sum of the two parts converges slowly with respect to the basis set.

This problem is addressed in the set of gauge transformations (SGT) methods by redefining the gauge origin  $\mathbf{d}$  as a

parametric function that depends on the position  $\mathbf{r}$  at which  $\mathbf{J}^{(1)}(\mathbf{r})$  is evaluated.<sup>6</sup> In this case the vector potential is:

$$\mathbf{A}(\mathbf{r}') = \frac{1}{2} \mathbf{B}_{\text{ext}} \times (\mathbf{r}' - \mathbf{d}(\mathbf{r})), \quad (6)$$

and the current becomes

$$\begin{aligned} \mathbf{J}^{(1)}(\mathbf{r}) = & -\frac{1}{c} \sum_{o,e} \langle \psi_o^{(0)} | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}] \frac{|\psi_e^{(0)}\rangle\langle\psi_e^{(0)}|}{\epsilon_o - \epsilon_e} \\ & \times \{ [\mathbf{r} \times \mathbf{p}] \cdot \mathbf{B}_{\text{ext}} | \psi_o^{(0)}\rangle - \mathbf{p} | \psi_o^{(0)}\rangle \cdot [\mathbf{B}_{\text{ext}} \times \mathbf{d}(\mathbf{r})] \} \\ & - \frac{1}{2c} \rho(\mathbf{r}) \mathbf{B}_{\text{ext}} \times [\mathbf{r} - \mathbf{d}(\mathbf{r})]. \end{aligned} \quad (7)$$

The choice of the parametric function  $\mathbf{d}(\mathbf{r})$  determines different methods within the SGT class. A possible choice is setting  $\mathbf{d}(\mathbf{r}) = \mathbf{r}$ . We call this approach the “ $d(r) = r$ ” method. In this case, Eq. (7) becomes

$$\begin{aligned} \mathbf{J}^{(1)}(\mathbf{r}) = & -\frac{1}{c} \sum_{o,e} \langle \psi_o^{(0)} | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}] \frac{|\psi_e^{(0)}\rangle\langle\psi_e^{(0)}|}{\epsilon_o - \epsilon_e} \\ & \times \{ [\mathbf{r} \times \mathbf{p}] \cdot \mathbf{B}_{\text{ext}} | \psi_o^{(0)}\rangle - \mathbf{p} | \psi_o^{(0)}\rangle \cdot [\mathbf{B}_{\text{ext}} \times \mathbf{r}] \}. \end{aligned} \quad (8)$$

In this formulation only terms containing a sum over both occupied and empty states appear; each term in this double summation, as well as the total current, is independent of a rigid translation of the system and hence invariant for gauge origin transformations. Notice that Eq. (8) can also be derived using the generalized  $f$ -sum rule, by replacing  $-\rho(\mathbf{r})\delta_{\alpha\beta}$  in Eq. (3) by the left-hand side of Eq. (5). Similarly the MPL method has been derived in Ref. 8 using the generalized  $f$ -sum rule for periodic systems.

One of the main results of this paper is that the MPL method, which has been developed to deal with extended periodic systems, reduces precisely to Eq. (8) when it is applied to isolated molecules. The analytical derivation of this result is given in the Appendix. To apply the MPL method to an isolated molecule, we consider a periodic system with one molecule per unit cell in the limit when the volume of the cell tends to infinity. In this limit the interaction between the molecule and its periodic replicas is removed.

Another method of the SGT class is the IGAIM method,<sup>5</sup> where the gauge origin is chosen to be the position of the nearest atomic nucleus to the point  $\mathbf{r}$  at which  $\mathbf{J}^{(1)}(\mathbf{r})$  is evaluated. Also in this case,  $\mathbf{J}^{(1)}(\mathbf{r})$  is independent of a rigid translation of the system and hence invariant for gauge origin transformations.

The last proposed method of the SGT class is the CSGT method.<sup>7</sup> In the regions close to the nuclei the function  $\mathbf{d}(\mathbf{r})$  is chosen as in the IGAIM method. In the regions between two nuclei a smooth interpolation replaces the step function of IGAIM. However, the results for  $\sigma$  obtained with GAUSSIAN 94 (Ref. 17) using CSGT and IGAIM differ by less than  $10^{-3}$  ppm. Therefore in the following we will just present IGAIM results.

Finally, notice that Eqs. (7) and (8) cannot be used to compute  $\mathbf{J}^{(1)}(\mathbf{r})$  in an extended system described by periodic boundary conditions. Indeed, in a periodic system the expectation values of the angular momentum  $\langle \psi_e^{(0)} | \mathbf{r} \times \mathbf{p} | \psi_o^{(0)} \rangle$  are ill defined, since  $|\psi_i^{(0)}\rangle$  are Bloch wavefunctions delocalized

on the whole space. In contrast, the MPL method in its general formulation, Ref. 8, can be applied both to extended systems and to isolated molecules, where it reduces to Eq. (8).

## B. IGCV method

In this section we separate  $\vec{\sigma}$  into the contributions due to core and valence electrons in a gauge-invariant manner. This allows us to consider two different gauges for core and valence electrons.

The complete set of all states  $\{a\}$  is given by the distinct union of the core states  $\{c\}$ , the valence states  $\{v\}$ , and the empty states  $\{e\}$ . Then we rewrite the induced first-order electronic current  $\mathbf{J}^{(1)}$  as a sum of its core and valence contributions

$$\mathbf{J}^{(1)} = \mathbf{J}_c^{(1)} + \mathbf{J}_v^{(1)}, \quad (9)$$

by dividing the set of occupied states  $\{o\}$  in Eq. (7) into the  $\{c\}$  and  $\{v\}$  subsets. In this way, however, neither  $\mathbf{J}_c^{(1)}$  nor  $\mathbf{J}_v^{(1)}$  would be separately gauge-invariant because by doing so, the basis wave function sets would be  $\{c\} \oplus \{e\}$  for  $\mathbf{J}_c^{(1)}$  and  $\{v\} \oplus \{e\}$  for  $\mathbf{J}_v^{(1)}$ . In a gauge-invariant separation of  $\mathbf{J}_c^{(1)}$  and  $\mathbf{J}_v^{(1)}$  the same complete basis set has to be used in both cases. Formally, this is achieved by redefining the sets of occupied and empty states in Eq. (7) [or in Eq. (5)] in the following way for  $\mathbf{J}_c^{(1)}$

$$\{o\} \rightarrow \{c\}, \quad \{e\} \rightarrow \{v\} \oplus \{e\}; \quad (10)$$

and for  $\mathbf{J}_v^{(1)}$

$$\{o\} \rightarrow \{v\}, \quad \{e\} \rightarrow \{c\} \oplus \{e\}. \quad (11)$$

In other words, the correct separation is achieved by including also  $\{c\}$  to  $\{v\}$  transitions in addition to  $\{c\}$  to  $\{e\}$  transitions for  $\mathbf{J}_c^{(1)}$  and by including also  $\{v\}$  to  $\{c\}$  transitions in addition to  $\{v\}$  to  $\{e\}$  transitions for  $\mathbf{J}_v^{(1)}$ .<sup>18</sup> In this way  $\mathbf{J}_c^{(1)}$  and  $\mathbf{J}_v^{(1)}$  are described independently within the full basis set and are gauge-invariant for a complete Hilbert space. Notice that our separation is independent of the method used to cope with the gauge origin problem.

We can now define the individual gauge for core and valence states (IGCV) method in which we use two different gauges for  $\mathbf{J}_c^{(1)}$  and  $\mathbf{J}_v^{(1)}$ . We use IGAIM for  $\mathbf{J}_c^{(1)}$  as the core is well approximated by a spherical closed shell system. Indeed, in such a system the paramagnetic part vanishes within IGAIM and the current is just given by its diamagnetic part, which depends on the charge density and converges quickly with respect to the basis set size. For the valence electrons this argument does not apply because they describe the bond region between the atoms. Therefore we use  $d(r) = r$  for  $\mathbf{J}_v^{(1)}$ , since taking the gauge origin close to the point at which the current is evaluated avoids large para- and diamagnetic contributions that do not cancel out if a finite basis set is used, as we mentioned before.

### III. NUMERICAL RESULTS

In this part we present the results for the isotropic chemical shift  $\sigma$ , as obtained by performing numerical calculations on small molecules. We use the quantum chemical code GAUSSIAN 94<sup>17</sup> to compute geometries and wave functions of the molecules within DFT in the local density approximation (LDA). The  $\sigma$  are calculated for various gauge origin methods. The GIAO and IGAIM approaches are already available in the code.<sup>7</sup> With a straightforward modification of the code we implement  $d(r)=r$  and IGCV. We can now compare numerically four different methods, namely GIAO, IGAIM,  $d(r)=r$ , and IGCV, by checking their convergence properties with respect to the quality of the basis set. In the following sections we present results for molecules containing H, C, N, O, F, Si, and P atoms. For C, N, O, and F we take the  $1s$  orbitals as core, and for Si and P we take the  $1s$ ,  $2s$ ,  $2p$  orbitals as core.

#### A. Basis sets

All our calculations of  $\sigma$  are done with standardized basis sets constructed from the correlation consistent polarized core/valence (cc-pCVxZ) basis sets, developed in Ref. 19. These basis sets extend the ideas of the cc-pVxZ sets<sup>20</sup> by including extra functions designed for core-core and core-valence correlation. We label the basis sets from I to V in order of increasing completeness, with the size of the basis set increasing with increasing number. Basis sets I and II are double zeta, cc-pCVDZ and aug-cc-pCVDZ respectively, basis sets III and IV are triple zeta, cc-pCVTZ and aug-cc-pCVTZ respectively, and basis set V is the quadruple zeta cc-pCVQZ basis set (see EMSL Gaussian Basis Set Order Form<sup>21</sup> for more information). For hydrogen atoms we use the corresponding cc-pVxZ and aug-cc-pVxZ basis sets for sets I to V.

Molecular geometries are optimized with B3LYP (Ref. 22) and with the 6-311+G(2d,p) basis set.<sup>23</sup>

A good test of the quality of a basis set is given by the generalized  $f$ -sum rule, whose connection to the gauge invariance of magnetic properties we pointed out previously. Integrating the generalized  $f$ -sum rule [Eq. (5)] with respect to  $\mathbf{r}$ , we get the simple  $f$ -sum rule

$$4 \sum_{\alpha, e} \langle \psi_o | p_\alpha \frac{|\psi_e\rangle \langle \psi_e|}{\epsilon_o - \epsilon_e} p_\beta | \psi_o \rangle = -\delta_{\alpha\beta} N_{el}, \quad (12)$$

where  $N_{el}$  is the number of electrons in the system.

For sets I to V we evaluate the left-hand side of Eq. (12) for all the occupied states in the system, as well as for the core and the valence contributions to the  $f$ -sum rule, which are separated as described in Eqs. (10)–(11). The results are shown in Table I, where we present the averaged value of the three diagonal elements of the  $f$ -sum rule with  $\alpha = \beta = x, y, z$ . The values are compared in the same table to the expected number of electrons in the considered system. The accuracy increases with respect to the basis sets and we notice that passing from cc-pCVxZ to aug-cc-pCVxZ has almost no effect on the core contribution but increases the valence part, whereas going from double to triple zeta as

TABLE I. Convergence of DFT-LDA  $f$ -sum rule with respect to basis sets (I–V).

	I	II	III	IV	V	$N_{el}$ <sup>a</sup>
<b>C<sub>5</sub>H<sub>5</sub>N</b>						
Total	35.7	38.0	40.9	41.5	41.8	42
Core	9.7	9.9	11.7	11.8	12.0	12
Valence	26.0	28.1	29.2	29.8	29.8	30
<b>C<sub>6</sub>H<sub>6</sub></b>						
Total	35.8	38.1	40.9	41.5	41.8	42
Core	9.7	9.9	11.7	11.8	12.0	12
Valence	26.1	28.2	29.1	29.8	29.8	30
<b>CO</b>						
Total	11.2	12.4	13.5	13.8	13.9	14
Core	3.2	3.2	3.9	3.9	4.0	4
Valence	8.0	9.1	9.6	9.9	9.9	10
<b>Si<sub>2</sub>H<sub>4</sub></b>						
Total	23.4	24.9	30.4	30.8	31.7	32
Core	13.1	13.2	18.8	18.9	19.8	20
Valence	10.3	11.7	11.6	12.0	11.8	12
<b>SiH<sub>3</sub>F</b>						
Total	18.9	21.4	24.6	25.3	25.7	26
Core	8.2	8.2	11.4	11.4	11.9	12
Valence	10.7	13.2	13.3	13.9	13.8	14
<b>PF<sub>3</sub></b>						
Total	29.4	35.3	39.2	41.2	41.2	42
Core	11.5	11.6	15.3	15.3	15.9	16
Valence	17.9	23.6	23.9	25.8	25.3	26

<sup>a</sup> $N_{el}$  is the number of electrons.

well as going from triple to quadruple zeta has the opposite effect.

#### B. Methods

The convergence of the GIAO, IGAIM, IGCV, and  $d(r)=r$  methods with respect to basis sets is investigated on a large set of molecules. We use NH<sub>3</sub>, NF<sub>3</sub>, N<sub>2</sub>, and all molecules listed in Table II except tetramethyl silane (TMS). In Fig. 1 we present the convergence of  $\sigma$  with respect to the basis set sizes for all mentioned methods in the C<sub>6</sub>H<sub>6</sub> and SiF<sub>4</sub> molecules. The  $d(r)=r$  method shows a slower convergence than the other methods, especially for  $\sigma$  of third-period atoms. Nevertheless the values of the  $d(r)=r$  method are approaching those of the others for basis sets of large enough size.

We compare the IGCV method with GIAO and IGAIM in more detail in Figs. 2, 3 and 4, where we present, respectively, the mean, mean absolute, and maximum error of C, F,

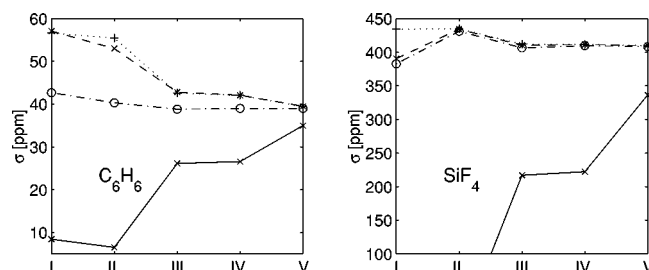


FIG. 1. Total isotropic chemical shift of C<sub>6</sub>H<sub>6</sub> on C nucleus and of SiF<sub>4</sub> on Si nucleus with respect to basis sets I to V for different gauge methods (dotted line: GIAO, dashed line: IGAIM, dash-dotted line: IGCV and solid line:  $d(r)=r$ ).

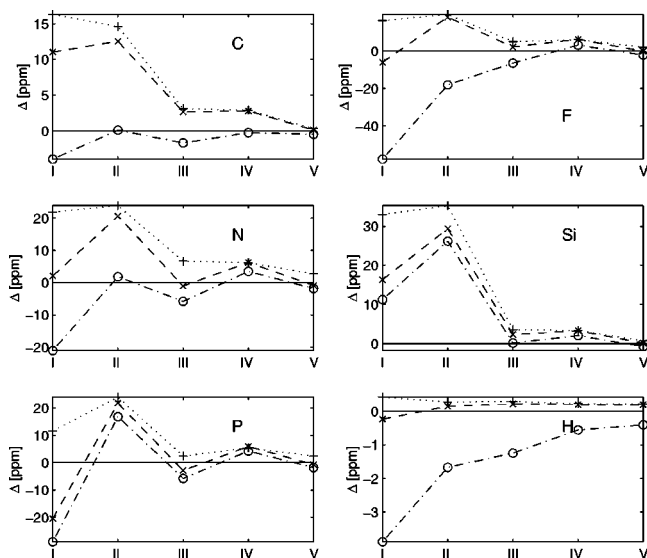


FIG. 2. Mean error to the converged DFT-LDA isotropic chemical shift (in ppm) on different elements with respect to basis sets for different gauge methods (dotted line: GIAO, dashed line: IGAIM, dash-dotted line: IGCV).

N, Si, P, and H chemical shifts as a function of the basis sets. The errors are computed with respect to the arithmetic mean of the converged values (basis V) of GIAO, IGAIM, and IGCV methods. In each molecule all atoms of the same element but with different chemical shifts are taken into consideration. We recall that for an infinite set of basis functions all the methods converge to the same limit. We remark that within our basis sets the convergence behavior of GIAO is comparable to that of IGAIM. Furthermore we find that the convergence behavior of the IGCV method is also comparable to these methods for all atoms but C, where the IGCV convergence is slightly faster and for H atoms where the IGCV method is less performant. For all atoms the  $\sigma$  error

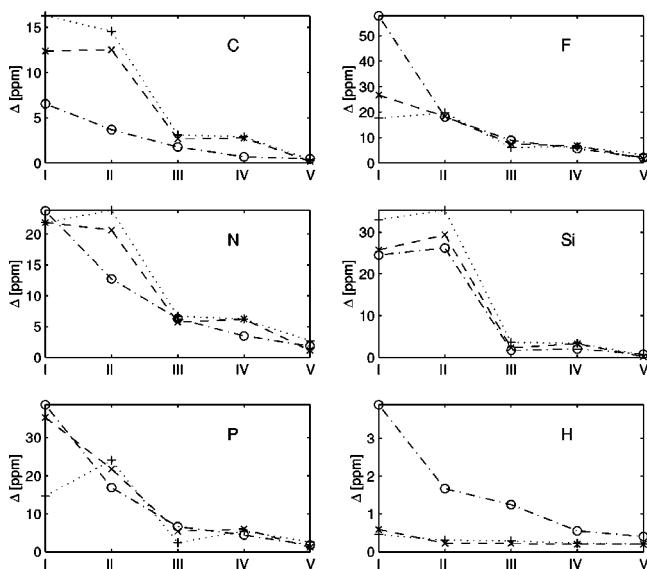


FIG. 3. Mean absolute error to the converged DFT-LDA isotropic chemical shift (in ppm) on different elements with respect to basis sets for different gauge methods (dotted line: GIAO, dashed line: IGAIM, dash-dotted line: IGCV).

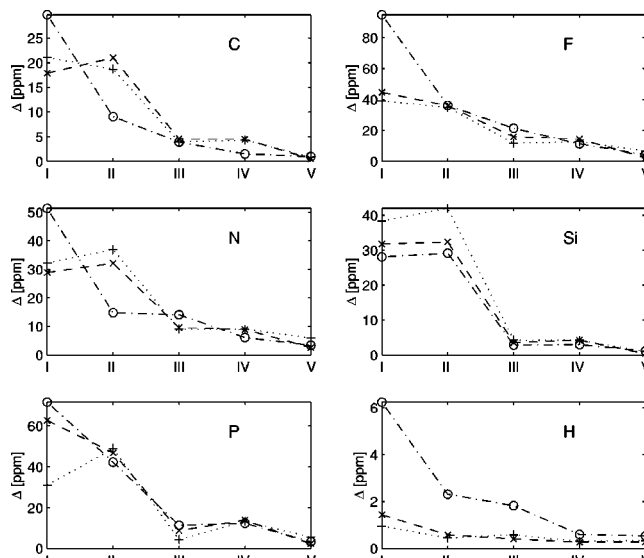


FIG. 4. Maximum error to the converged DFT-LDA isotropic chemical shift (in ppm) on different elements with respect to basis sets for different gauge methods (dotted line: GIAO, dashed line: IGAIM, dash-dotted line: IGCV).

found to converge to the same value at sufficiently large basis sets (for basis set V the methods differ by less than 1 ppm).

Finally we mention that the calculation time of IGCV is of the order of IGAIM, which is considerably faster than GIAO. For the considered molecules, the GIAO calculation is considerably more expensive than the IGAIM calculation if basis set V is used. In addition GAUSSIAN 94 provides parallel calculations for the SGT class of methods, and hence for IGAIM and IGCV, but not for GIAO, which makes the choice of the former methods even more favorable.

### C. Core contribution to the chemical shift

In this section we present only converged results (basis V) obtained with the IGAIM method. Table II presents the variation of the total and the core  $\sigma$  on C, Si, and P atoms in different molecules. While the variation of  $\sigma$  is highly dependent on the chemical environment, the core contribution appears to be constant. Indeed, the variation on all atoms in our calculations turned out to be less than 0.6 ppm. As the basis sets are quadruple zeta on the core orbitals, we have four degrees of freedom in this region, and thus the core is not chosen to be rigid by default. In most cases only relative  $\sigma$  are required. These can be computed with just the valence contribution, since the core contribution cancels out in the differences.

Furthermore, in Table II we also present the diamagnetic part of the core contribution of the  $\sigma$  computed within the IGAIM method. Comparing these values to the total core contribution, we see that the core is essentially diamagnetic if the gauge origin is chosen to be at the nucleus. This is not true for a different choice of the gauge origin.

Different results concerning the core contribution are found in the quantum chemical literature.<sup>4,24</sup> In Ref. 4 the authors find an important variation between different mol-

TABLE II. Core contribution to IGAIM isotropic absolute chemical shifts (in ppm) for different molecules calculated at the DFT-LDA level of theory.  $\sigma_{\text{total}}$  is the total chemical shift,  $\sigma_{\text{core}}$  is the core contribution to the chemical shift, and  $\sigma_{\text{core-dia}}$  is the diamagnetic part of the core contribution.

Molecule	$\sigma_{\text{total}}$	$\sigma_{\text{core}}$	$\sigma_{\text{core-dia}}$
C atom			
CO	-21.16	198.81	198.72
CH <sub>4</sub>	191.22	198.82	198.60
CH <sub>3</sub> F	99.66	198.87	198.68
CH <sub>3</sub> NH <sub>2</sub>	150.44	198.85	198.67
C <sub>6</sub> H <sub>12</sub>	148.34	198.85	198.70
C <sub>6</sub> H <sub>6</sub>	39.52	198.82	198.71
CF <sub>4</sub>	35.29	199.00	198.92
HCP	6.84	198.83	198.88
C <sub>5</sub> H <sub>5</sub> N <sup>a</sup>	34.14	198.82	198.71
TMS	182.08	198.82	198.65
Si atom			
SiF <sub>4</sub>	409.69	831.86	830.50
SiH <sub>3</sub> F	305.45	832.01	830.03
Si <sub>2</sub> H <sub>4</sub>	202.99	832.06	830.60
SiH <sub>4</sub>	424.37	831.95	829.75
TMS	304.39	831.99	831.60
P atom			
HCP	290.00	902.25	901.76
PF <sub>3</sub>	172.52	902.86	902.19
P <sub>2</sub>	-375.45	902.36	902.23
P <sub>4</sub>	826.62	902.44	902.34

<sup>a</sup>C atom on opposite position to N in the ring is presented.

ecules (up to 60 ppm) for the core contribution to  $\sigma$  on third-row elements such as Si, P, and S. In Ref. 24 the authors find a relatively rigid core contribution in third-period atoms only if the  $2p$  electrons are considered as valence orbitals, contrary to what is done in the present work. We think that these results differ from ours due to a nongauge-invariant separation of core and valence electrons in both references.

#### D. Valence-core transitions in chemical shift calculations

In order to achieve a gauge-invariant separation between core and valence states it is necessary to follow the procedure discussed in Sec. II B. In Table III we report our results for the contribution to  $\mathbf{J}_v^{(1)}$  due to valence-core transitions, when  $\{o\}$  and  $\{e\}$  in Eq. (7) are chosen as specified in Sec. II B. The data shows that these contributions are negligible when the IGAIM gauge is chosen, but they are not if the  $d(r)=r$  gauge is chosen. Interestingly, the valence to core transitions for the  $d(r)=r$  gauge are also basically independent of the chemical environment, and they could be neglected if we only need the relative  $\sigma$ .

The fact that the core and the valence-core contributions to  $\sigma$  are rigid suggests that, in principle, a computation of the relative  $\sigma$  for third-period atoms within a pseudopotential approach should be possible.

#### IV. CONCLUSION

We have shown theoretically the equivalence between a version of the SGT methods and the MPL method applied to finite systems. For a set of molecules we tested the conver-

TABLE III. Contribution to DFT-LDA isotropic absolute chemical shifts ( $\sigma$ , in ppm) due to valence to core state transitions. IGAIM and  $d(r)=r$  gauges are presented on C, F, Si, and P nuclei for different molecules.

Molecule	IGAIM	$d(r)=r$
C atom		
CH <sub>4</sub>	-0.23	-7.02
CH <sub>3</sub> F	-0.04	-6.62
C <sub>6</sub> H <sub>6</sub>	-0.02	-6.85
HCP	-0.04	-6.33
F atom		
CH <sub>3</sub> F	-0.004	-20.11
SiF <sub>4</sub>	-0.21	-20.04
SiH <sub>3</sub> F	-0.17	-20.05
PF <sub>3</sub>	-0.04	-19.93
Si atom		
SiF <sub>4</sub>	-1.83	-1.93
SiH <sub>3</sub> F	-0.65	-2.04
Si <sub>2</sub> H <sub>4</sub>	-0.28	-1.95
SiH <sub>4</sub>	-0.41	-2.06
P atom		
HCP	-0.35	-2.69
PF <sub>3</sub>	-0.22	-2.53
P <sub>2</sub>	-0.14	-2.68
P <sub>4</sub>	-0.001	-2.81

gence properties of different methods with respect to the quality of Gaussian basis sets. We find that the CSGT and IGAIM approaches have the same convergence properties as GIAO, but with a smaller computational cost. In the MPL method, the contribution of the valence electrons to the chemical shift converges rapidly with respect to the size of the basis set, whereas the convergence properties of the core contribution are poor. We improve the convergence by separating the core and the valence contributions in a gauge-invariant manner, by applying the MPL method only to the valence contribution and by treating the core contribution within IGAIM. The performances of the resulting approach compare favorably with the other methods. From our calculations, we find that the core contribution to the chemical shift is independent of the chemical environment, contrary to what is sometimes found in the quantum chemical literature.

Our results indicate that the chemical shifts in solids could be calculated by using the MPL method with atomic orbital basis sets for the valence contribution and by adding to it a rigid core contribution as obtained, for instance, from an atomic calculation.

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## APPENDIX MOLECULAR LIMIT OF THE EXTENDED SYSTEM NMR CHEMICAL SHIFT THEORY

In this appendix we apply the equations of the MPL approach to an isolated molecule in free space. To obtain the molecular limit we consider a periodic lattice with a molecule per unit cell and we let the volume of the unit cell tend to infinity.

Writing the electric current in Fourier space

$$\mathbf{J}^{(1)}(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{J}^{(1)}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (\text{A1})$$

where  $\mathbf{G}$  are the reciprocal lattice vectors, we have:

$$\frac{1}{c} \mathbf{J}^{(1)}(\mathbf{G}) = i\mathbf{G} \times \mathbf{M}(\mathbf{G}). \quad (\text{A2})$$

$\mathbf{M}(\mathbf{G})$  is the magnetization, which can be expressed as

$$\mathbf{M}(\mathbf{G}) = \tilde{\chi}(\mathbf{G}, 0) \mathbf{B}_{\text{ext}} \quad \forall \mathbf{G}, \quad (\text{A3})$$

where  $\tilde{\chi}(\mathbf{G}, \mathbf{G}')$  is the magnetic susceptibility matrix. The current is given by

$$\mathbf{J}^{(1)}(\mathbf{G}) = ic\mathbf{G} \times \tilde{\chi}(\mathbf{G}, 0) \mathbf{B}_{\text{ext}} \quad \forall \mathbf{G}. \quad (\text{A4})$$

Notice that since  $\tilde{\chi}(\mathbf{G}, 0)$  is finite, we have  $\mathbf{J}^{(1)}(\mathbf{G}=0) = 0$ . Substituting the MPL expression<sup>8</sup> for  $\tilde{\chi}(\mathbf{G}, 0)$  in Eq. (A4), we get for  $\mathbf{G} \neq 0$

$$\mathbf{J}^{(1)}(\mathbf{G}) = \tilde{\mathbf{J}}^{(1)}(\mathbf{G}) - \frac{1}{G^2} \mathbf{G}(\mathbf{G} \cdot \tilde{\mathbf{J}}^{(1)}(\mathbf{G})), \quad (\text{A5})$$

and

$$\begin{aligned} \tilde{\mathbf{J}}^{(1)}(\mathbf{G}) = & -\frac{i}{c} \frac{\partial}{\partial q} \int d^3\mathbf{r} e^{-i\mathbf{G}\cdot\mathbf{r}} \sum_{o,e} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \left\{ \langle u_{\mathbf{k},o} | [(-i\nabla + \mathbf{k})|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|(-i\nabla + \mathbf{k} + \mathbf{q})] \frac{|u_{\mathbf{k}+\mathbf{q},e}\rangle\langle u_{\mathbf{k}+\mathbf{q},e}|}{\epsilon_{\mathbf{k},o} - \epsilon_{\mathbf{k}+\mathbf{q},e}} \right. \\ & \times [(-i\nabla + \mathbf{k}) \times \hat{\mathbf{q}}] \cdot \mathbf{B}_{\text{ext}} |u_{\mathbf{k},o}\rangle + \langle u_{\mathbf{k},o} | [(-i\nabla + \mathbf{k}) \times \hat{\mathbf{q}}] \cdot \mathbf{B}_{\text{ext}} \frac{|u_{\mathbf{k}-\mathbf{q},e}\rangle\langle u_{\mathbf{k}-\mathbf{q},e}|}{\epsilon_{\mathbf{k},o} - \epsilon_{\mathbf{k}-\mathbf{q},e}} \\ & \left. \times [(-i\nabla + \mathbf{k} - \mathbf{q})|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|(-i\nabla + \mathbf{k})] |u_{\mathbf{k},o}\rangle \right\}_{q=0}. \end{aligned} \quad (\text{A6})$$

Here  $|u_{\mathbf{k},i}\rangle$  is the periodic part of the unperturbed Bloch eigenstate corresponding to eigenvalue  $\epsilon_{\mathbf{k},i}$ , and  $\hat{\mathbf{q}}$  is an arbitrary wave vector of unit length, perpendicular to  $\mathbf{B}_{\text{ext}}$ . For a complete Hilbert space we have  $\mathbf{J}^{(1)}(\mathbf{G}) = \tilde{\mathbf{J}}^{(1)}(\mathbf{G})$  since we can show that  $\nabla \cdot \mathbf{J}^{(1)}(\mathbf{r}) = \nabla \cdot \tilde{\mathbf{J}}^{(1)}(\mathbf{r}) = 0$ . This is not the case for a finite basis set, because we no longer have  $\nabla \cdot \tilde{\mathbf{J}}^{(1)}(\mathbf{r}) = 0$ . However as we compute  $\vec{\sigma}$  using the Biot–Savart law, Eq. (1), it is easy to see that  $\sigma[\mathbf{J}^{(1)}] = \sigma[\tilde{\mathbf{J}}^{(1)}]$  and we can use  $\tilde{\mathbf{J}}^{(1)}(\mathbf{G})$  in the following. Using  $\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')} = \Omega \delta^3(\mathbf{r}-\mathbf{r}')$ , where  $\Omega$  is the volume of a unit cell, we can again rewrite the current in  $\mathbf{r}$ -space

$$\begin{aligned} \tilde{\mathbf{J}}^{(1)}(\mathbf{r}) = & -\frac{i}{c} \frac{\partial}{\partial q} \sum_{o,e} \int \Omega \frac{d^3\mathbf{k}}{(2\pi)^3} \left\{ \langle u_{\mathbf{k},o} | [(-i\nabla + \mathbf{k})|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|(-i\nabla + \mathbf{k} + \mathbf{q})] \frac{|u_{\mathbf{k}+\mathbf{q},e}\rangle\langle u_{\mathbf{k}+\mathbf{q},e}|}{\epsilon_{\mathbf{k},o} - \epsilon_{\mathbf{k}+\mathbf{q},e}} \right. \\ & \times [(-i\nabla + \mathbf{k}) \times \hat{\mathbf{q}}] \cdot \mathbf{B}_{\text{ext}} |u_{\mathbf{k},o}\rangle + \langle u_{\mathbf{k},o} | [(-i\nabla + \mathbf{k}) \times \hat{\mathbf{q}}] \cdot \mathbf{B}_{\text{ext}} \frac{|u_{\mathbf{k}-\mathbf{q},e}\rangle\langle u_{\mathbf{k}-\mathbf{q},e}|}{\epsilon_{\mathbf{k},o} - \epsilon_{\mathbf{k}-\mathbf{q},e}} \\ & \left. \times [(-i\nabla + \mathbf{k} - \mathbf{q})|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|(-i\nabla + \mathbf{k})] |u_{\mathbf{k},o}\rangle \right\}_{q=0} + \mathbf{c}, \end{aligned} \quad (\text{A7})$$

where  $\mathbf{c}$  is a constant due to the  $\mathbf{G}=0$  term.

We take the molecular limit by considering a single lattice cell, which contains one molecule and let  $\Omega$  tend to infinity. This implies that  $\tilde{\mathbf{J}}^{(1)}(\mathbf{r}) = 0$  outside of the volume occupied by the molecule and hence  $\mathbf{c} = 0$  in Eq. (A7). As the volume of the cell increases, the coupling between neighboring cells becomes weaker. In this limit, the electronic dispersion relation disappears and the energy eigenvalues  $\epsilon_{\mathbf{k},i}$  lose their  $\mathbf{k}$ -dependence, i.e.,  $\epsilon_{\mathbf{k},i} \rightarrow \epsilon_i$ . Analogously, inside the unit cell the Bloch eigenfunctions  $|\psi_{\mathbf{k},i}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}} |u_{\mathbf{k},i}\rangle$  tend to the canonical molecular orbitals  $|\psi_i\rangle$  for the isolated molecule and hence  $|u_{\mathbf{k},i}\rangle \rightarrow e^{-i\mathbf{k}\cdot\mathbf{r}} |\psi_i\rangle$ .

The current, expressed in terms of molecular orbitals, reads

$$\begin{aligned} \tilde{\mathbf{J}}^{(1)}(\mathbf{r}) = & -\frac{i}{c} \frac{\partial}{\partial q} \sum_{o,e} \int \Omega \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{q}\cdot\mathbf{r}} \\ & \times \left\{ \langle \psi_o | [(-i\nabla)|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|(-i\nabla)] \right. \\ & \times \frac{|\psi_e\rangle\langle\psi_e|}{\epsilon_o - \epsilon_e} e^{i\mathbf{q}\cdot\mathbf{r}} (-i\nabla \times \hat{\mathbf{q}}) \cdot \mathbf{B}_{\text{ext}} |\psi_o\rangle \\ & + \langle \psi_o | (-i\nabla \times \hat{\mathbf{q}}) \cdot \mathbf{B}_{\text{ext}} e^{i\mathbf{q}\cdot\mathbf{r}} \frac{|\psi_e\rangle\langle\psi_e|}{\epsilon_o - \epsilon_e} \\ & \left. \times [(-i\nabla)|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|(-i\nabla)] |\psi_o\rangle \right\}_{q=0}, \end{aligned} \quad (\text{A8})$$

where we used the commutation relation  $[-i\nabla, e^{\pm i\mathbf{k}\cdot\mathbf{r}}] = \pm\mathbf{k}e^{\pm i\mathbf{k}\cdot\mathbf{r}}$ . Notice that the integrand is  $\mathbf{k}$ -independent and  $\int\Omega d^3\mathbf{k}/(2\pi)^3 = 1$ .

Deriving with respect to  $q$  we obtain

$$\begin{aligned} \tilde{\mathcal{J}}^{(1)}(\mathbf{r}) = & \frac{2}{c} \sum_{o,e} \left\{ \langle \psi_o | [\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}| + |\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}] \frac{|\psi_e\rangle\langle\psi_e|}{\epsilon_o - \epsilon_e} \right. \\ & \times [ \hat{\mathbf{q}} \cdot \mathbf{r} ] [ (\mathbf{p} \times \hat{\mathbf{q}}) \cdot \mathbf{B}_{\text{ext}} ] | \psi_o \rangle \\ & - \langle \psi_o | [ (\hat{\mathbf{q}} \cdot \mathbf{r}) \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | + | \mathbf{r} \rangle \langle \mathbf{r} | (\hat{\mathbf{q}} \cdot \mathbf{r}) \mathbf{p} ] \\ & \left. \times \frac{|\psi_e\rangle\langle\psi_e|}{\epsilon_o - \epsilon_e} (\mathbf{p} \times \hat{\mathbf{q}}) \cdot \mathbf{B}_{\text{ext}} | \psi_o \rangle \right\}. \quad (\text{A9}) \end{aligned}$$

We eliminate  $\hat{\mathbf{q}}$  by recalling that it is a vector perpendicular to  $\mathbf{B}_{\text{ext}}$ , but otherwise completely arbitrary. Therefore, taking two mutually perpendicular vectors  $\hat{\mathbf{q}}_1$  and  $\hat{\mathbf{q}}_2$ , both perpendicular to  $\mathbf{B}_{\text{ext}}$ , as in Ref. 8, and calculating

$$\bar{\mathcal{J}}^{(1)}(\mathbf{r}) = \frac{1}{2} [\tilde{\mathcal{J}}^{(1)}(\mathbf{r}, \hat{\mathbf{q}}_1) + \tilde{\mathcal{J}}^{(1)}(\mathbf{r}, \hat{\mathbf{q}}_2)], \quad (\text{A10})$$

we get an expression independent of  $\hat{\mathbf{q}}$ , which is identical to Eq. (8).

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<sup>15</sup> Equation (3) is obtained by the linear variation of the Hamiltonian of the system with respect to an applied magnetic field. Within DFT this linear variation is given by  $\mathcal{H}^{(1)} = (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})/2c$ . Notice that within DFT and contrary to CDFT or Hartree-Fock, there is no linear variation of the self-consistent part of the potential energy since, for magnetic perturbations, the linear variation of the charge density is zero.

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