A Sum-Over-States Formulation of the Diamagnetic Contribution to the Indirect Nuclear Spin Spin Coupling Constant

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The classical expressions for the indirect nuclear spin–spin coupling tensor $\mathbf{J}_{K,L}$ were derived about 40 years ago by Ramsey[1] using second-order perturbation theory. He obtained four terms, all of which had the form required by the empirical NMR energy expression. Three terms (Fermi contact, spin dipole, and paramagnetic spin–orbit) involve the first order wave function and can thus be written as a sum over excited states

$$\mathbf{J}_{K,L}^{FC}=\left(\frac{eg_e\mu_0}{3m_e}\right)^2\frac{\gamma_K\gamma_L}{h}\sum_{n\neq 0}\frac{\langle 0|\delta(\mathbf{r}-\mathbf{R}_K)\mathbf{s}|n\rangle\langle n|\delta(\mathbf{r}-\mathbf{R}_L)\mathbf{s}|0\rangle}{E_0-E_n}, \tag{1}$$

$$\mathbf{J}_{K,L}^{SD}=\left(\frac{eg_e\mu_0}{8\pi m_e}\right)^2\frac{\gamma_K\gamma_L}{h}\sum_{n\neq 0}\frac{\langle 0|\frac{\mathbf{s}}{|\mathbf{r}-\mathbf{R}_K|^3}-3\frac{[\mathbf{s}\cdot(\mathbf{r}-\mathbf{R}_K)](\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^5}|n\rangle\langle n|\frac{\mathbf{s}}{|\mathbf{r}-\mathbf{R}_L|^3}-3\frac{[\mathbf{s}\cdot(\mathbf{r}-\mathbf{R}_L)](\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^5}|0\rangle}{E_0-E_n}, \tag{2}$$

$$\mathbf{J}_{K,L}^{PSO}=\left(\frac{e\mu_0}{4\pi m_e}\right)^2\frac{\gamma_K\gamma_L}{h}\sum_{n\neq 0}\frac{\langle 0|\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\times\mathbf{p}|n\rangle\langle n|\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\times\mathbf{p}|0\rangle}{E_0-E_n}, \tag{3}$$

whereas the so called diamagnetic spin–orbit term involves only the zero-order wave function

$$\mathbf{J}_{K,L}^{DSO}=\frac{e^2}{2m_e}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma_K\gamma_L}{h}\langle 0|\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\cdot\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\mathbf{1}-\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}|0\rangle. \tag{4}$$

Here, $\mathbf{s}$ is the electron spin operator, $\mathbf{R}_K$, $\mathbf{R}_L$ are the position vectors, and γ_K, γ_L are the magnetogyric ratios of the two magnetic nuclei. All other symbols conform to the IUPAC standard[2] and the unit of $\mathbf{J}_{K,L}$ is Hz. The operators are given in their second quantization form.

Sum-over-states expressions, like in Eqs. (1)–(3), may be calculated efficiently as the zero-energy limit of a corresponding polarization propagator[3] or linear response function,[4] whose spectral representation for two arbitrary operators $\mathbf{P}$ and $\mathbf{Q}$ is

$$\langle\langle \mathbf{P};\mathbf{Q}\rangle\rangle_E=\sum_{n\neq 0}\left\{\frac{\langle 0|\mathbf{P}|n\rangle\langle n|\mathbf{Q}|0\rangle}{E+E_0-E_n}-\frac{\langle 0|\mathbf{Q}|n\rangle\langle n|\mathbf{P}|0\rangle}{E+E_n-E_0}\right\}. \tag{7}$$

Correlated calculations of the Fermi contact, spin dipole, and paramagnetic spin–orbit term are thus possible within the second-order polarization propagator approximation (SOPPA),[3] the coupled-cluster doubles (CCDPPA), or the coupled-cluster singles and doubles polarization propagator approximations (CCSDPPA).[5] As there does not exist, however, an unperturbed wave function, that corresponds to the correlated propagator approximations (SOPPA, CCDPPA, and CCSDPPA), it is not possible to calculate the diamagnetic spin–orbit term from Eq. (4) at the same level of approximation. That is only possible at the Hartree–Fock (coupled Hartree–Fock) level of approximation.

The purpose of this note is to show that it is possible to find a similar sum-over-states expressions for the diamagnetic contribution. The operator in Eq. (4) may be rewritten as a commutator between the new operator

$$\mathbf{O}^J=\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\times\left(\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\times\mathbf{p}\right) \tag{8}$$

and $\mathbf{r}$, that is

$$\left(\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\cdot\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\mathbf{1}-\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\right)=\frac{2\pi}{ih}[\mathbf{O}^J,\mathbf{r}]. \tag{9}$$

Using Eq. (9) in Eq. (4) and inserting twice the resolution of the identity, the diamagnetic spin–orbit term becomes

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$$\mathbf{J}_{K,L}^{DSO}=\frac{e^2}{2m_e}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma_K\gamma_L}{h}\frac{2\pi}{ih}\times\sum_n\left\{\langle 0|\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\times\left(\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\times\mathbf{p}\right)|n\rangle\times\langle n|\mathbf{r}|0\rangle-\langle 0|\mathbf{r}|n\rangle\times\langle n|\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\times\left(\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\times\mathbf{p}\right)|0\rangle\right\}. \quad (10)$$

Using that the excited states $|n\rangle$ are eigenstates together with the hypervirial relation

$$[\mathbf{r},\mathscr{H}]=\frac{ih}{2\pi m_e}\mathbf{p}, \quad (11)$$

one obtains a sum-over-states expression also for the diamagnetic spin–orbit term,

$$\mathbf{J}_{K,L}^{DSO}=\frac{e^2}{2m_e^2}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma_K\gamma_L}{h}\times\sum_{n\neq 0}\left\{\frac{\left\langle 0\right|\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\times\left(\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\times\mathbf{p}\right)\left|n\right\rangle\langle n|\mathbf{p}|0\rangle}{E_0-E_n}+\frac{\langle 0|\mathbf{p}|n\rangle\langle n|\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^3}\times\left(\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\times\mathbf{p}\right)|0\rangle}{E_0-E_n}\right\}. \quad (12)$$

All contributions to the indirect nuclear spin–spin coupling constant can thus be evaluated using the same method, i.e., a consistent correlated calculation of all contributions within, e.g., SOPPA, CCDPPA, or CCSDPPA is possible. The reformulation of the diamagnetic term is valid for the full tensor. However, as it is based on the operator relation Eq. (9) and on the hypervirial theorem, the sum-over-states and ground state average value expression will only give the same numerical result in the limit of a complete basis set.

It can be easily seen from Eq. (8), that the new operator $\mathbf{O}^J$ is not Hermitian. In actual calculations it is advantageous to work with Hermitian operators. A Hermitian operator can be obtained by adding a second operator $\mathbf{O}_H^J$

$$\mathbf{O}_H^J=-\frac{ih}{2\pi}\left\{\left(\frac{4\pi}{3}\delta(\mathbf{r}-\mathbf{R}_K)+\frac{1}{|\mathbf{r}-\mathbf{R}_K|^3}\right)\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}+\frac{3}{2}\frac{(\mathbf{r}-\mathbf{R}_K)}{|\mathbf{r}-\mathbf{R}_K|^5}\times\left((\mathbf{r}-\mathbf{R}_K)\times\frac{(\mathbf{r}-\mathbf{R}_L)}{|\mathbf{r}-\mathbf{R}_L|^3}\right)\right\} \quad (13)$$

to $\mathbf{O}^J$. Since $\mathbf{O}_H^J$ obviously commutes with $\mathbf{r}$, one may use also $\mathbf{O}^J+\mathbf{O}_H^J$ in Eqs. (9), (10), and (12) instead of $\mathbf{O}^J$.

Calculations of the diamagnetic contribution using Eq. (12) can be expected to be more sensitive to the choice of the basis set than calculations using Eq. (4). However, applications of the analogous expressions for the diamagnetic contributions to the magnetizability[6,7] and to the nuclear magnetic shielding tensor[7,8] showed that the basis set dependence of the sum-over-states diamagnetic terms is comparable to or smaller than that of the corresponding paramagnetic terms. Rather large basis sets were necessary anyway in order to obtain converged results for the paramagnetic contributions. The present scheme is thus an attractive method for consistent correlated calculations of all contributions to the indirect nuclear spin–spin coupling tensor.

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