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Hyperfine Electron-Nuclear Interactions in the Frame of the Density Functional and of the Density Matrix Methods

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Abstract.

The matrix elements and expectation values of the hyperfine interaction operators are presented in a form suitable for numerical implementation in density matrix methods. The electron-nuclear spin-spin (dipolar and contact) interactions are considered, as well as the interaction between nuclear-spin and electron-orbital motions. These interactions from the effective Breit-Pauli Hamiltonian determine the hyperfine structure in ESR spectra and contribute to chemical shifts in NMR. Applying the Wigner-Eckart theorem in the irreducible tensor-operator technique and the spin-space separation scheme, the matrix elements and expectation values of these relativistic corrections are expressed in analytical form. The final results are presented as products, or sums of products, of factors determined by the spin and (or) angular momentum symmetry and a spatial part determined by the action of the symmetrized tensor-operators on the normalized matrix or function of the spin or charge distribution.

1 Introduction

In the formalism of reduced density matrices and functions (RDM & RDF) [1-3], the matrix elements and expectation values of the various types of spin-involving operators take the form of products of space and spin factors [1, 4]. The spin part is determined by the spin symmetry and reduces to 3j-symbols while the spatial part is determined by the action of space operators on the spin distribution or correlation matrices or functions [1,4,5]. The spin distribution and correlation matrices and functions are built from the spatial parts of the RDMs and RDFs of first and second order, respectively. In this approach the space-spin separation results from the possibility of separating the space and spin variables in RDMs [6-9] and from the use of split RDMs to represent the matrix elements of the perturbation terms in the Hamiltonian [1,4,10].

In terms of RDMs and RDFs and in the scheme of space-spin separation there are presented in Refs [1,4] the matrix elements and expectation values of the various spin-involving operators, which are relativistic corrections in the Breit-Pauli Hamiltonian [5]. The matrix elements and expectation values of the operators corresponding to the different types of relativistic corrections are reduced to products of a factor determined by the spin symmetry, which characterizes a spin state or a transition between two states in a given spin multiplet, and a space part, that depends neither on the spin state nor on a transition between two states. This space part is generally expressed by the action of the considered space operator on the space part of the relevant spin distribution or correlation matrices or functions.

In Refs [11,12] we took a further step in the treatment of the matrix elements and expectation values of some of the main relativistic corrections, the spin-orbit and spin-spin, electron-electron interactions terms, in a form that is convenient for numerical implementation in density matrix methods. In the present work we shall consider the matrix elements and expectation values of another type of spin-involving relativistic corrections, the electron-nuclear spin-spin (dipolar and contact) interactions, as well as the interaction between nuclear-spin and electron-orbital motions. These terms from the effective Breit-Pauli Hamiltonian determine the hyperfine structure in ESR spectra and contribute to chemical shifts in NMR.

Using the technique of irreducible tensor operators and applying the Wigner-Eckart theorem, the matrix elements and expectation values of these relativistic corrections are expressed as products, or sums of products, of factors determined by the spin symmetry and (or) orbital momentum symmetry and a spatial part determined by the action of the symmetrized tensor-operators on the normalized matrix or function of the spin or charge distribution. The action of the space tensor-operators is the same for a given spin multiplet and does not depend on the splitting or transition case. The expectation values of these relativistic corrections, which give the amount of splitting of energy levels, are expressed in an analytical form suitable for numerical implementation. We also consider the transition matrix elements of the electron-nuclear operators, which are involved in the corresponding transitions.

In Section 2 the main concepts of the reduced density matrix formalism are recalled. The structure of the spin distribution matrix for a given spin state and a transition between two states is presented. In Section 3 the Hamiltonian of nuclear-spin interactions is displayed, and the matrix elements and expectation values of the electron-nuclear dipolar and contact interactions are expressed using the spin distribution matrix, and those for the interactions between nuclear-spin and electron-orbital motions are expressed using the first-order density matrix. In the last section we discuss the results obtained.

2 Matrix Elements of Spin Operators

2.1 Matrix Elements in the RDM Formalism

The RDM of order s (s-RDM) of an N-electron system $(1 \leq s \leq N)$ in state K described by a wave function $\Psi_K(\tau_1, ..., \tau_N)$, eigenfunction of the operators $\mathbf{S}^2$ and S_z, has the form [1-3, 13-18]:

$$\begin{aligned}\rho(KK|\tau_1, ..., \tau_s; \tau_1', ..., \tau_s') &= N(N-1)...(N-s+1) \\ &\times \int \Psi_K(\tau_1, ..., \tau_s; \tau_{s+1}, ..., \tau_N)\Psi_K^*(\tau_1', ..., \tau_s'; \tau_{s+1}, ..., \tau_N)\, d\tau_{s+1} ... \, d\tau_N,\end{aligned} \tag{1}$$

where $\tau_i = (\mathbf{r}_i, \sigma_i)$, $\mathbf{r}_i$ being the position vector and σ_i the spin variable of the i-th electron, and $d\tau_i = d\mathbf{r}_i d\sigma_i$.

The corresponding RDF of order s (s-RDF) is defined by the expression:

$$\begin{aligned}\rho(KK|\tau_1, ..., \tau_s) &= \rho(KK|\tau_1, ..., \tau_s; \tau_1', ..., \tau_s')|_{\tau_{\{i\}}'=\tau_{\{i\}}} \\ &= \rho(KK|\tau_1, ..., \tau_s; \tau_1, ..., \tau_s).\end{aligned} \tag{2}$$

The generalized transition s-RDM between states K and K' described by Ψ_K and $\Psi_{K'}$ has the form [1-3]:

$$\begin{aligned}\rho(KK'|\tau_1, ..., \tau_s; \tau_1', ..., \tau_s') &= N(N-1)...(N-s+1) \\ &\times \int \Psi_K(\tau_1, ..., \tau_s; \tau_{s+1}, ..., \tau_N)\Psi_{K'}^*(\tau_1', ..., \tau_s'; \tau_{s+1}, ..., \tau_N)\, d\tau_{s+1} ... \, d\tau_N.\end{aligned} \tag{3}$$

For the transition s-RDF we have a similar expression, which follows by analogy with Eqn (2).

The expectation value of an *s*-particle operator, $\mathbf{F}(i_1, i_2, ..., i_s)$, can be written as:

$$\langle \mathbf{F}(i_1, i_2, ...i_s) \rangle = Sp_{i_1 i_2 ... i_s} \mathbf{F}(i_1, i_2, ..., i_s)\rho(\tau_1, ..., \tau_s; \tau_1', ..., \tau_s').$$

In Eqn (4), $Sp_{i_1 i_2 ... i_s}$ denotes the operator of the integration over particle coordinates labeled with the corresponding numbers after identification of the primed and unprimed coordinates.

In many-electron theory, the expectation values and matrix elements of symmetric sums of identical operators are of major importance. Then, for the expectation values of a symmetrized sum of identical s-particle operators, $\mathbf{F}(i_1, i_2, ..., i_s)$ (assuming the numbers i_k are ordered as: $1 \leq i_1 < i_2 < ... < i_s \leq N$), we obtain:

$$\begin{aligned} \langle \sum_{\{i_s\}} \mathbf{F}(i_1, i_2, ..., i_s) \rangle \equiv & \langle \Psi_K(\tau_1, ..., \tau_N) | \sum_{\{i_s\}} \mathbf{F}(i_1, i_2, ..., i_s) | \Psi_K(\tau_1, ..., \tau_N) \rangle \\ = & \frac{1}{s!} Sp\, \mathbf{F}(i_1, i_2, ..., i_s) \rho(K | \tau_{i_1}, ..., \tau_{i_s}; \tau'_{i_1}, ..., \tau'_{i_s}), \end{aligned} \tag{4}$$

where $\sum_{\{i_s\}}$ means a summation over all possible sets $(i_1, i_2 ..., i_N)$. Usually, only RDMs and RDFs of 1st and 2nd order are relevent. Higher-order matrices and functions are used in very specific cases.

After separation of the space and spin variables [1,2,6], the 1-RDM takes the form:

$$\rho(\tau_1; \tau'_1) = \sum_{\gamma, \gamma' = \alpha, \beta} \rho^{\gamma, \gamma'}(\mathbf{r}_1; \mathbf{r'}_1) \gamma(\sigma_1) \gamma'^*(\sigma'_1), \tag{5}$$

where the $\rho^{\gamma, \gamma'}(\mathbf{r}_1; \mathbf{r}'_1)$ are the space components and the $\gamma(\sigma)$ $(\gamma = \alpha, \beta)$ are the spin wave-functions. The space components yield the charge matrix:

$$\rho(\mathbf{r}_1; \mathbf{r}'_1) = \rho^{\alpha, \alpha}(\mathbf{r}_1; \mathbf{r}'_1) + \rho^{\beta, \beta}(\mathbf{r}_1; \mathbf{r}'_1) \tag{6}$$

and spin distribution matrix (Section 2.2).

For the expectation value of a sum of identical one-particle operators, making use of Eq. (4) one obtains:

$$\begin{aligned} \langle \sum_i \mathbf{F}(i) \rangle \equiv & \langle \Psi_K(\tau_1, ..., \tau_N) | \sum_i \mathbf{F}(i) | \Psi_K(\tau_1, ..., \tau_N) \rangle \\ = & Sp\, \mathbf{F}(1) \rho(K | \tau_1; \tau'_1). \end{aligned} \tag{7}$$

2.2 Spin Distribution Matrices and Functions

In a spin eigenstate (with eigenvalues $S(S+1)$ and M of operators $\mathbf{S}^2$ and S_z, respectively) the spin distribution matrix can be written in the following form [1,2,4,5]:

$$q(\mathbf{r}_1; \mathbf{r}'_1) = 1/2[\rho^{\alpha, \alpha}(\mathbf{r}_1; \mathbf{r}'_1) - \rho^{\beta, \beta}(\mathbf{r}_1; \mathbf{r}'_1)]. \tag{8}$$

The spin distribution matrices $q^{(M)}(\mathbf{r}_1; \mathbf{r}'_1)$ for different spin eigenstates (with $M = S, S-1, ..., -S$) can be expressed in terms of the normalized spin distribution matrices $D_S(\mathbf{r}_1; \mathbf{r}'_1)$, which are independent of M [19,20]:

$$q^{(M)}(\mathbf{r}_1; \mathbf{r}'_1) \equiv q(KK | \mathbf{r}_1; \mathbf{r}'_1) = \frac{M}{S} q(\overline{K}\, \overline{K} | \mathbf{r}_1; \mathbf{r}'_1) \equiv M D_S(\mathbf{r}_1; \mathbf{r}'_1), \tag{9}$$

with:

$$D_S(\mathbf{r}_1;\mathbf{r}'_1) = \frac{1}{S} q(\overline{K}\,\overline{K}|\mathbf{r}_1;\mathbf{r}'_1). \tag{10}$$

Here K is the index of the spin state corresponding to $\langle Sz\rangle = M$, $\overline{K}$ is that corresponding to the maximal value $M = S$, and $q(KK|\mathbf{r}_1;\mathbf{r}'_1)$ can be written as in Eqn (8) using the general definition [1,4]:

$$q(KK'|\mathbf{r}_1;\mathbf{r}'_1)^1_m = \int\limits_{\sigma'_1=\sigma_1} S^1_m(1)\rho(KK'|\tau_1;\tau'_1)d\sigma_1, \tag{11}$$

where the $S^1_m(i)$ ($m = 0, \pm 1$) are symmetrized components of the i-electron spin operator $\mathbf{S}(i)$. Similar formulas can be written for the spin-distribution functions when $\mathbf{r}_1 = \mathbf{r}'_1$.

The spin-distribution matrices for transitions between states $K(SM_S)$ and $K'(S'M_{S'})$ satisfy the relation [1,4]

$$q(KK'|\,\mathbf{r}_1;\mathbf{r}'_1)^1_m = \left\{C^{S\;1\;S'}_{M_S\,m\,M_{S'}}/C^{S\;1\;S'}_{S\;\overline{m}\;S'}\right\} q(\overline{KK}'|\,\mathbf{r}_1;\mathbf{r}'_1)^1_{\overline{m}}, \tag{12}$$

where $C^{S\;1\;S'}_{M_S\,m\,M_{S'}}$ are Clebsch-Gordon coefficients. From their properties it follows that $m = M_{S'} - M_S$ and $\overline{m} = S' - S$. By analogy with (11) one obtains:

$$q(\overline{KK}'|\mathbf{r}_1;\mathbf{r}'_1)^1_m = \int\limits_{\sigma'_1=\sigma_1} S^1_m(1)\rho(\overline{KK}'|\tau_1;\tau'_1)d\sigma_1.$$

Applying the Wigner-Eckart theorem yields

$$\begin{aligned} q(KK'|\,\mathbf{r}_1;\mathbf{r}'_1)^1_m &= \left\{C^{S\;1\;S}_{M_S\,m\,M'_S}\,/\,C^{S\;1\;S}_{S\;0\;S}\right\} q(\overline{KK}'|\,\mathbf{r}_1;\mathbf{r}'_1) \\ &= < SM_S|S^1_m|SM'_S > D_S(\mathbf{r}_1;\mathbf{r}'_1), \end{aligned} \tag{13}$$

where the S^1_m ($m = 0, \pm 1$) are symmetrized components of the total spin $\mathbf{S}$. Eqn (12) is a generalization of Eqn (9) for a transition between different spin states.

3 Interactions Involving Nuclear Spins

The Hamiltonian $\hat{\mathbf{H}}_N$ of the interactions involving nuclear spins, for a many-electron system in the clamped-nuclei approximation, includes a number of operators from the effective Breit-Pauli Hamiltonian [1,4,7], which describe first and second order effects:

$$\hat{\mathbf{H}}_N = \hat{\mathbf{H}}^Z_N + \hat{\mathbf{H}}^{LI}_{en} + \hat{\mathbf{H}}^{SI}_{dip} + \hat{\mathbf{H}}^{SI}_{cont} + \hat{\mathbf{H}}^{II}_{dir} + \hat{\mathbf{H}}^{II}_{ind} \tag{14}$$

The nuclear Zeeman splitting operator has the form:

$$\hat{\mathbf{H}}_N^Z = -\alpha_p \sum_\lambda g_\lambda \mathbf{B} \cdot \mathbf{I}(\lambda), \tag{15}$$

where $\alpha_p = 1/2m_p c$ in atomic units, g_λ is the g-factor of nucleus λ, $\mathbf{I}(\lambda)$ is its momentum operator and $\mathbf{B}$ is the external magnetic field. This interaction is screened by induced currents in the electronic system, which cause chemical shifts in NMR spectra.

The magnetic interaction between the nuclear moment and the electron orbital motion has the following form:

$$\hat{\mathbf{H}}_{en}^{LI} = 2\alpha\alpha_p \sum_{\lambda,i} g_\lambda r_{\lambda i}^{-3} \mathbf{I}(\lambda) \cdot \mathbf{L}_\lambda(i), \tag{16}$$

where $\alpha = 1/2c$ is half the fine structure constant, $\mathbf{r}_{\lambda i} = \mathbf{r}_i - \mathbf{R}_\lambda$ and $\mathbf{L}_\lambda(i)$ is the orbital angular momentum of electron i about nucleus λ:

$$\mathbf{L}_\lambda(i) = \mathbf{r}_{\lambda i} \times \mathbf{p}(i) = \mathbf{r}_i \times \mathbf{p}(i) - \mathbf{R}_\lambda \times \mathbf{p}(i). \tag{17}$$

This interaction contributes to second order to chemical shifts in NMR spectra.

The electron-nuclear dipole-dipole interaction has the following form:

$$\hat{\mathbf{H}}_{dip}^{SI} = g_0\alpha\alpha_p \sum_{\lambda,i} g_\lambda \left\{3[\mathbf{S}(i) \cdot \mathbf{r}_{\lambda i}][\mathbf{I}(\lambda) \cdot \mathbf{r}_{\lambda i}] - r_{\lambda i}^2 \mathbf{S}(i) \cdot \mathbf{I}(\lambda)\right\} r_{\lambda i}^{-5}, \tag{18}$$

where g_0 is the g-factor of the free electron [21], and the electron-nuclear contact interaction has the form:

$$\hat{\mathbf{H}}_{cont}^{SI} = \frac{8\pi}{3} g_0\alpha\alpha_p \sum_{\lambda,i} g_\lambda \delta(\mathbf{r}_{\lambda i}) \mathbf{I}(\lambda) \cdot \mathbf{S}(i). \tag{19}$$

These interactions determine the hyperfine structure in ESR spectra.

The direct interaction $\hat{\mathbf{H}}_{dir}^{II}$ between nuclear spins is of a dipole-dipole type similar to Eqn (18). It is averaged out in high-resolution NMR spectra. The indirect interaction $\hat{\mathbf{H}}_{ind}^{II}$ occurs through the electronic cloud and is proportional to the scalar product of nuclear spins. It is responsible for line splittings in NMR spectra.

3.1 Electron-Nuclear Dipolar Interactions

The magnetic dipole coupling between electron and nuclear spins can be written in a form where electron and nuclear variables appear separated:

$$\hat{\mathbf{H}}_{dip}^{SI} = g_0\alpha\alpha_p \sum_{\lambda,i} g_\lambda \mathbf{S}(i) \cdot [3\frac{\mathbf{r}_{\lambda i} \bigotimes \mathbf{r}_{\lambda i}}{r_{\lambda i}^5} - \frac{\mathbf{n}^2}{r_{\lambda i}^3}] \cdot \mathbf{I}(\lambda), \tag{20}$$

where $\mathbf{n}^2$ is the unit tensor formed from the unit vector $\mathbf{n}_\lambda(i) = \mathbf{r}_{\lambda i}/r_{\lambda i}$. For each nucleus λ the sum of one-electron operators in Eqn (20) can be written as:

$$\hat{\mathbf{H}}^{SI}_{dip}(\lambda) = g_0 \alpha g_\lambda \alpha_p \sum_i r^{-3}_{\lambda i} \mathbf{K}_\lambda(i) \cdot \mathbf{I}(\lambda), \tag{21}$$

where

$$\mathbf{K}_\lambda(i) = 3[\mathbf{S}(i) \cdot \mathbf{n}_\lambda(i)]\mathbf{n}_\lambda(i) - \mathbf{S}(i). \tag{22}$$

The components $K_k(i)$ of the axial vector $\mathbf{K}(i)$ for nucleus λ can be written in the form:

$$K_k(i) = \sum_l D_{kl} S^{(1)}_l(i), \tag{23}$$

where the second-rank, symmetric, traceless tensor

$$D_{kl} = 3n_k(i)n_l(i) - \delta_{kl} n_k(i) n_l(i) \tag{24}$$

is proportional to the normalized spherical functions $C^2(\vartheta_i, \varphi_i)$ with components:

$$C^p_q(1) \equiv C^p_q(\vartheta_1, \varphi_1) = [4\pi/(2p+1)]^{1/2} Y^p_q(\vartheta_1, \varphi_1).$$

Then the components of the symmetrized vector $\mathbf{K}^1(i)$ are:

$$K^1_q(i) = C[D^2 \otimes S^1]^1_q = C \sum_{m,m'} C^{2\ 1\ 1}_{m\ m'\ q} C^2_m(\vartheta_i, \varphi_i) S^1_{m'}(i), \tag{25}$$

where the $[D^2 \bigotimes S^1]^1_q$ are the components of an irreducible first-rank tensor built from D^2 and S^1. The constant C can be derived from atomic spectroscopy theory [22,23] and is equal to $10^{1/2}$.

Using the above relations and expressing the scalar product of $\mathbf{K}(i)$ and $\mathbf{I}(\lambda)$ in Eqn (21) as a tensor product of their symmetrized forms $\mathbf{K}^1(i)$ and $\mathbf{I}^1(\lambda)$, one obtains:

$$\begin{aligned} \hat{\mathbf{H}}^{SI}_{dip}(\lambda) &= g_0 \alpha g_\lambda \alpha_p \sum_i r^{-3}_{\lambda i} \sum_q (-1)^q (K)^1_q(i) \cdot I^1_{-q}(\lambda) \\ &= \sqrt{10} g_0 \alpha g_\lambda \alpha_p \sum_q (-1)^q \sum_{m,m'} C^{2\ 1\ 1}_{m\ m'\ q} \sum_i r^{-3}_{\lambda i} C^2_m(\vartheta_i, \varphi_i) S^1_{m'}(i) I^1_{-q}(\lambda). \end{aligned} \tag{26}$$

If one separates the electron and nuclear parts of the wave-function one obtains, for the matrix elements between two states K and K' within an electron spin multiplet and K_λ and K'_λ of nucleus λ:

$$\begin{aligned} \langle KSM_SK_\lambda | \hat{\mathbf{H}}^{SI}_{dip}(\lambda) | K'SM'_SK'_\lambda \rangle &= \sqrt{10} g_0 \alpha g_\lambda \alpha_p \sum_q (-1)^q \sum_{m,m'} C^{2\ 1\ 1}_{m\ m'\ q} \\ &\times \langle KSM_S | \sum_i r^{-3}_{\lambda i} C^2_m(\vartheta_i, \varphi_i) S^1_{m'}(i) | K'SM'_S \rangle \langle K_\lambda | I^1_{-q}(\lambda) | K'_\lambda \rangle. \end{aligned} \tag{27}$$

Using Eqs (11)-(13) we can express the matrix elements of the electronic factor in the form:

$$
\begin{aligned}
&\langle KSM_S|\sum_i r_{\lambda i}^{-3}C_m^2(\vartheta i,\varphi_i)S_{m'}^1(i)|K'SM'_S\rangle \\
&\quad= \int\limits_{\mathbf{r}'_1=\mathbf{r}_1} r_{\lambda 1}^{-3}C_m^2(\vartheta_1,\varphi_1)q(KK'|\mathbf{r}_1;\mathbf{r}'_1)^1_{m'}d\mathbf{r}_1 \\
&\quad= < SM_S|S_{m'}^1|SM'_S > \int\limits_{\mathbf{r}_1} r_{\lambda 1}^{-3}C_m^2(\vartheta_1,\varphi_1)D_S(\mathbf{r}_1)d\mathbf{r}_1,
\end{aligned}
\tag{28}
$$

where $D_S(\mathbf{r}_1)=q(\overline{K}\,\overline{K}|\mathbf{r}_1;\mathbf{r}_1)^1_0/S$ is the normalized spin distribution function. Applying the Wigner-Eckart theorem for the matrix element in Eqn (28) yields:

$$
< SM_S|S_{m'}^1|SM'_S >= \sqrt{\frac{3}{2}}\frac{1}{\sqrt{2S+1}}C^{S\ 1\ S}_{M_S\,m'\,M'_S}. \tag{29}
$$

Finally for a given term, the matrix element in Eqn (27) takes the form:

$$
\begin{aligned}
&\langle KSM_SK_\lambda|\hat{\mathbf{H}}^{SI}_{dip}(\lambda)|KSM_SK'_\lambda\rangle = \sqrt{15}g_0\alpha\alpha_p\frac{1}{\sqrt{2S+1}}\sum_\lambda g_\lambda\sum_q(-1)^q \\
&\times\sum_m C^{2\ 1\ 1}_{m\ 0\ q}M_S\int r_{\lambda 1}^{-3}C_m^2(\vartheta_1,\varphi_1)D_S(\mathbf{r}_1)d\mathbf{r}_1\langle K_\lambda|I^1_{-q}(\lambda)|K'_\lambda\rangle.
\end{aligned}
\tag{30}
$$

This expectation value directly relates to the spectral line splitting due to the electron-nucleus dipolar interaction.

3.2 Electron-Nuclear Contact Interactions

Expressing the scalar product of $\mathbf{I}(\lambda)$ and $\mathbf{S}(i)$ in Eqn (19) through their symmetrized components, one obtains:

$$
\hat{\mathbf{H}}^{SI}_{cont} = \frac{8\pi}{3}g_0\alpha\alpha_p\sum_{\lambda,i}g_\lambda\delta(\mathbf{r}_{\lambda i})\sum_m(-1)^mS^1_m(i)I^1_{-m}(\lambda). \tag{31}
$$

Separating the electronic and nuclear parts in the matrix elements of this operator, one obtains:

$$
\begin{aligned}
&\langle KSM_SK_\lambda|\hat{\mathbf{H}}^{SI}_{cont}|K'SM'_SK'_\lambda\rangle = \frac{8\pi}{3}g_0\alpha\alpha_p\sum_\lambda g_\lambda\sum_m(-1)^m \\
&\times\langle KSM_S|\sum_i\delta(\mathbf{r}_{\lambda i})S^1_m(i)|K'SM'_S\rangle\langle K_\lambda|I^1_{-m}(\lambda)|K'_\lambda\rangle.
\end{aligned}
\tag{32}
$$

Using the same procedure as in the previous subsection, one obtains for the first matrix element:

$$
\begin{aligned}
&\langle KSM_S|\sum_i \delta(\mathbf{r}_{\lambda i})S^1_m(i)|K'SM'_S\rangle \\
&\quad=\left\{C^{S\ 1\ S}_{M_S\, m\, M'_S}/C^{S\,1\,S}_{S\,0\,S}\right\}\int\limits_{\mathbf{r}'_1=\mathbf{r}_1}\delta(\mathbf{r}_{\lambda 1})q(KK'|\mathbf{r}_1;\mathbf{r'}_1)^1_0 d\mathbf{r}_1 \\
&\quad=\langle SM_S|S^1_m|SM'_S\rangle\int\limits_{\mathbf{r}_1}\delta(\mathbf{r}_{\lambda 1})D_S(\mathbf{r}_1)d\mathbf{r}_1 \\
&\quad=\sqrt{\frac{3}{2}}\frac{1}{\sqrt{2S+1}}C^{S\ 1\ S}_{M_S\, m\, M'_S}D_S(\mathbf{R}_\lambda),
\end{aligned}
\tag{33}
$$

where $D_S(\mathbf{R}_\lambda)$ is the spin density at the location of nucleus λ.

Then, for a given nucleus, the matrix element of $\hat{\mathbf{H}}^{SI}_{cont}(\lambda)$ is given by:

$$
\begin{aligned}
\langle KSM_SK_\lambda|\hat{\mathbf{H}}^{SI}_{cont}(\lambda)|K'SM'_SK'_\lambda\rangle &= \frac{8\pi}{3}\sqrt{\frac{3}{2}}g_0\alpha g_\lambda\alpha_p\frac{1}{\sqrt{2S+1}} \\
\times\sum_m(-1)^m C^{S\ 1\ S}_{M_S\, m\, M'_S}D_S(\mathbf{R}_\lambda)\langle K_\lambda|I^1_{-m}(\lambda)|K'_\lambda\rangle.
\end{aligned}
\tag{34}
$$

For a given term this expression takes the simple form:

$$
\begin{aligned}
&\langle KSM_SK_\lambda|\hat{\mathbf{H}}^{SI}_{cont}(\lambda)|KSM_SK'_\lambda\rangle \\
&\quad=\frac{8\pi}{3}\sqrt{\frac{3}{2}}g_0\alpha g_\lambda\alpha_p\frac{1}{\sqrt{2S+1}}M_SD_S(\mathbf{R}_\lambda)\langle K_\lambda|I^1_{-0}(\lambda)|K'_\lambda\rangle
\end{aligned}
\tag{35}
$$

which is a closed form for the contact hyperfine splitting.

3.3 Electron-Nuclear Orbital-Spin Interactions

The interaction between the magnetic moment of nuclei and the electronic orbital motion Eq. (16), presented by the symmetrized components of the operators $\mathbf{I}(\lambda)$ and $\mathbf{L}(\lambda)$, can be described by the operator $\hat{\mathbf{H}}^{LI}_{en}$ in the form :

$$
\hat{\mathbf{H}}^{LI}_{en}=2\alpha\alpha_p\sum_{\lambda,i}g_\lambda r^{-3}_{\lambda i}\sum_m(-1)^m I^1_{-m}(\lambda)[L_\lambda(i)]^1_m. \tag{36}
$$

If for a given nucleus the origin of coordinates is chosen at the nucleus then the corresponding operator can be written:

$$
\hat{\mathbf{H}}^{LI}_{en}(\lambda)=2\alpha\alpha_p g_\lambda\sum_i r^{-3}_i\sum_m(-1)^m I^1_{-m}(\lambda)L^1_m(i), \tag{37}
$$

where the $L^1_m(i)$ are the spherical components of orbital momentum of the electron i. Using the relations:

$$\mathbf{p}(i) = -i\nabla_i, \qquad \nabla = \mathbf{n}\frac{\partial}{\partial r} + \frac{1}{r}\nabla_\Omega,$$

where $\mathbf{n}$ is the unit vector of $\mathbf{r}$ and ∇_Ω the spherical part of ∇, one can write $\mathbf{L}(i) = -i[\mathbf{n} \times \nabla_{\Omega_i}]$ [23]. After some algebraic manipulation, one obtains:

$$L^1_m(i) = -\sqrt{2}\sum_{p,q} C^{1\,1\,1}_{p\,q\,m} C^1_p(\theta_i, \varphi_i)(\nabla_{\Omega_i})^1_q. \tag{38}$$

The matrix element between the electronic states K and K' and nuclear states K_λ and K'_λ can then be written:

$$\begin{aligned}\langle KK_\lambda \mid \hat{\mathbf{H}}^{LI}_{en}(\lambda) \mid K'K'_\lambda\rangle &= 2\alpha\alpha_p g_\lambda \sum_m (-1)^m \\ &\times \langle K \mid \sum_i r_i^{-3} L^1_m(i) \mid K'\rangle \langle K_\lambda \mid I^1_{-m}(\lambda) \mid K'_\lambda\rangle,\end{aligned} \tag{39}$$

where the electronic factor takes the form:

$$\begin{aligned}\langle K \mid \sum_i r_i^{-3} L^1_m(i) \mid K'\rangle &= \int\limits_{\mathbf{r}'_1=\mathbf{r}_1} r_1^{-3} L^1_m(1)\rho_1(KK' \mid \mathbf{r}_1; \mathbf{r}'_1) d\mathbf{r}_1 \\ &= -\sqrt{2}\sum_{p,q} C^{1\,1\,1}_{p\,q\,m} \int\limits_{\mathbf{r}'_1=\mathbf{r}_1} r_1^{-3} C^1_p(\theta_1, \varphi_1)(\nabla_{\Omega_1})^1_q \rho(KK' \mid \mathbf{r}_1; \mathbf{r}'_1) d\mathbf{r}_1,\end{aligned} \tag{40}$$

$\rho(KK' \mid \mathbf{r}_1; \mathbf{r}'_1)$ being the charge transition matrix.

For molecules in the clamped-nuclei approximation, the orbital momentum of electron i about nucleus λ is given by Eqn (36). Using the formula for the matrix element of a tensor-operator product:

$$\langle K \mid f \cdot g \mid K\rangle = \sum_{K'} \langle K \mid f \mid K'\rangle \langle K' \mid g \mid K\rangle,$$

it appears that $\mathbf{R}_\lambda \times \mathbf{p}(i) = 0$ since the matrix element of $\mathbf{R}_\lambda$ differs from zero only when $M_L(i) = M'_L(i)$ while that of $\mathbf{p}(i)$ differs from zero only when $M'_L(i) = M_L(i) + 1$. Then, for the matrix element of $\hat{\mathbf{H}}^{LI}_{en}$, one obtains:

$$\begin{aligned}\langle KK_\lambda \mid \hat{\mathbf{H}}^{LI}_{en} \mid K'K'_\lambda\rangle &= 2\alpha\alpha_p \sum_\lambda g_\lambda \sum_m (-1)^m \\ &\times \langle K \mid \sum_i r_{\lambda i}^{-3} [L_\lambda(i)]^1_m \mid K'\rangle \langle K_\lambda \mid I^1_{-m}(\lambda) \mid K'_\lambda\rangle,\end{aligned} \tag{41}$$

where the electronic factor takes a form analogous to Eqn (40).

4 Conclusion

The results presented here give the possibility to include electron-nuclear spin-spin (dipolar and contact) interactions as well as interactions between nuclear-spin and electron-orbital motions in a density matrix theory for spin-polarized systems, even in degenerate or excited states. The procedures used allow not only to include relativistic corrections in a variational approach of density matrix methods but also to perform calculations in terms of vector-model and valence-bond schemes.

The matrix elements and expectation values of operators with a complex form, such as those of electron-nuclear spin-spin interactions, are reduced to simple forms involving well tabulated Clebsch-Gordon coefficients. The only specific component in the matrix elements of operators $\hat{\mathbf{H}}^{SI}_{dip}$ and $\hat{\mathbf{H}}^{SI}_{cont}$ is the normalized spin distribution function $D_S(\mathbf{r}_1)$, which is the same for a given spin multiplet.

The calculation of the matrix elements of $\hat{\mathbf{H}}^{LI}_{en}$ reduces to elementary operations on the first-order density matrix. The same holds true for density functionals built in terms of density matrices. We could use the local-density functional form of the spin distribution function or the average local-density functional approximation for the spin distribution matrix [25] to include these relativistic corrections.

In the Barth-Hedin construction [26], widely used in Kohn-Sham type calculations for spin-polarized systems, the energy functional is defined in terms of the first-order density matrix. This does not allow the description of relativistic corrections, which require a two-particle density matrix. There it is only possible to determine the influence of an external magnetic field and only for the ground state.

The formalism presented here and in [11,12] can be used in density matrix and density functional methods for the determination of relativistic corrections from the Breit-Pauli Hamiltonian, not only for the ground state but also for arbitrary states of a spin multiplet. This formalism can also be used to express the effect of an external magnetic field.

The use of a suitable minimization procedure, e.g. the local-scaling transformation scheme [27-29], more precisely its formulation for spin-polarized systems [30] – that keeps automatically space and spin symmetry, would allow direct minimization of the energy density functional, including relativistic terms.

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