NUCLEAR MOMENTS AND ELECTRON DENSITY FUNCTIONALS IN ATOMS

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ABSTRACT: An electron density functional approach for the calculation of the nuclear multipole moments is presented. The electronic matrix elements entering the experimentally observed hyperfine electron-nucleus interaction constants in atoms are expressed in terms of the electron density functionals of the charge or spin distributions. In principle, the construction of the charge or spin distribution density functionals can be obtained by means of every relativistic or non-relativistic quantum-mechanical or DFT method. The electronic matrix elements for all the electronic operators of the existing Hamiltonians of hyperfine electron-nucleus interactions are considered.

Key words: Electronic structure; Electron-nuclear hyperfine interactions; Nuclear spin interactions and quadrupole effects; Density functionals.
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1 INTRODUCTION

The hyperfine structure in the spectra of the many-electron systems is a result of the interaction of the electronic and nuclear multipole (electric and magnetic) moments. This interaction leads to the superfine splitting of the electronic spectrum, the rotational spectrum of molecules and the electron paramagnetic resonance lines as well [1, 2]. The energy of the hyperfine electron-nucleus interaction is determined by the finite nuclear size, the nuclear spin orientation and the nuclear magnetic moments space distribution. This energy is much smaller than the energy of the interactions in an electronic system and must be considered separately and independently for each fine structure component.

The transitions between neighbouring levels of the fine and hyperfine structures can be measured by means of highly sensitive radioscopic methods, for ex-
ample, microwave absorption, electron-spin resonance (ESR), nuclear magnetic resonance (NMR), atomic and molecular beams.

These experimental methods [1, 2] can give us information about many properties and effects of nuclei connected with nuclear magnetism, for example: the mechanism and time of spin relaxation, the width of the nuclear spin resonance lines and the indirect interaction between nuclear spins. Using the methods of NMR we can experimentally determine the magnetic nuclear moments. There is no any experimental method for direct measurement of the electric nuclear moments and especially the quadrupole momentum. They can be determined with great accuracy from the hyperfine splitting in electronic and molecular spectra [3]-[5]. For some heavy elements there are some good muonic values of the quadrupole momentum.

In the analysis of the multipole electron-nuclear interactions the Hamiltonian is represented as a sum of products of the electronic and nuclear operators. These operators can be written down explicitly and can be obtained by using the perturbation approach by expressing the interaction Hamiltonian in series in powers of the ratio of nuclear and electronic coordinates [3, 6, 7], as well as by a direct introduction of all the multipole interactions [8, 9].

The operators of the magnetic electron-nuclear multipole interactions can be determined also by expanding the Hamiltonian in series in powers of the constant of the fine structure which leads to some relativistic corrections in the main Hamiltonian [10]-[12].

Usually the experimental hyperfine multipole interaction constants are represented as a product of the matrix elements of the corresponding electronic and nuclear operators [1, 3, 6, 7]. The diagonal matrix elements of the nuclear operators correspond to the multipole moments (magnetic dipole, electric quadrupole, magnetic octopole nuclear moments)[1, 6, 13]. In addition to the diagonal electronic matrix elements, the non-diagonal matrix elements must be considered as well, because of some important second order effects. The non-diagonal matrix elements are also important in the analysis of the magnetic transitions induced by the external magnetic fields [3]-[5]. Using the theoretical interpretation of the multipole electric and magnetic moments through the experimental values of the hyperfine interaction constants and the calculated multipole electronic operators matrix elements, one can obtain the values of the electric and magnetic nuclear moments. The calculation of the matrix elements of the multipole magnetic operators is essential in determining the relative contribution of the magnetic interactions and gives us the possibility to estimate the role of the quadrupole interaction in a hyperfine structure. Different transitions in the resonance spectra make it possible to extract the quadrupole interaction constant by means of the analysis of the magnetic hyperfine sub-term or by means of the analysis of the deviation from the interval rules produced by a magnetic dipole electron-nuclear interaction. The correct description of the hyperfine constants needs the inclusion of the relativistic corrections [14].
In this paper we present the electronic matrix elements for all electronic operators and express them in terms of the density functional of charge or spin distributions. Thus for including the relativistic effects one must take the corresponding density functional of relativistic corrections, for instance, the functional given in paper [15, 16].

2 ELECTRON-NUCLEAR OPERATORS OF THE HYPERFINE INTERACTIONS

2.1 Multipole Interaction Operators

The operators of electron-nuclear multipole interactions can be written down \[\hat{H} = \sum_k \hat{H}_k = \sum_k \hat{Q}^k \cdot \hat{F}^k = \sum_k \sum_q (-1)^q Q^k F^k_q,\] (1)

where \(\hat{H}_k\) is the Hamiltonians of the electric (\(k\)-even) and of the magnetic (\(k\)-odd) interactions of the nuclei with the electronic shell. Here \(\hat{Q}^k\) and \(\hat{F}^k\) are irreducible tensor operators of \(k\) rank with components \(Q^k_q\) and \(F^k_q\). These operators act in the spaces of the total nuclear moment \(I\) and of the total electronic moment \(J\) correspondingly.

The diagonal matrix elements of the \(Q^k_0\) component of the nuclear operator \(\hat{Q}^k\) in the state \(I, M_I = I\), is the \(2^k\) total nuclear electric (even \(k\)) or the nuclear magnetic (odd \(k\)) moments

\[\langle I I | Q^k_0 | I I \rangle = \frac{1}{\sqrt{2I+1}} C_{I I 0}^{k I} < I \| \hat{Q}^k \| I >= \]

\[= \begin{cases} M_k & (k - \text{odd}) \\ Q_k & (k - \text{even}) \end{cases}, \] (3)

where \(C_{I I 0}^{k I}\) are the Clebsch-Gordon coefficients and \(< I \| \hat{Q}^k \| I >\) is the reduced matrix element of the operator \(\hat{Q}^k\). The matrix elements with \(k = 1, 2, 3\)
correspond to the nuclear moments \([6, 13]\)

\[
M_1 = \mu, \quad Q_2 = \frac{Q}{2}, \quad M_3 = -\Omega,
\]

where \(\mu\) is the magnetic dipole, \(Q\) is the electric quadrupole, and \(\Omega\) is the magnetic octopole nuclear moments.

Let us consider the case when the external field can be neglected. Then in the first approximation of the perturbation theory the energy of the hyperfine interactions is determined by the matrix elements of the Hamiltonian \(\hat{H}\) Eq.(1) which are diagonal with respect to \(J, I\) and total moment \(F = I + J\)

\[
E^{(1)}_J(F) = < \beta I \alpha J F M_F | \hat{H} | \beta I \alpha J F M_F >.
\]  

(4)

Here \(M_F\) is the value of the \(z\)-projection of the total atomic moment, \(\alpha\) and \(\beta\) are the additional quantum numbers of the electronic and nuclear systems correspondingly.

Using Racah formalism [17] we can rewrite the expression \(E^{(1)}_F\) in the form

\[
E^{(1)}_J(F) = \sum_k (-1)^{I+J-F} W(IIJJ; kF) < \alpha J || \hat{F}^k || \alpha J > < \beta I || \hat{Q}^k || \beta I >
\]

\[
= \sum_k A_k M(II; F; k),
\]  

(5)

where

\[
A_k = < \alpha JJ | F_0^k | \alpha JJ > < \beta II | Q_0^k | \beta II >;
\]

\[
M(II; F; k) = (-1)^{I+J-F} \frac{1}{\alpha_k} W(IIJJ; kF),
\]

\[
a_k = \frac{1}{\sqrt{(2J+1)(2I+1)}} C_J^I 0 0 J C_I^I 0 0 1,
\]

and \(W(IIJJ; kF)\) are the Racah coefficients.

The first three hyperfine interaction constants \(A_k\) are connected with the experimental values of the dipole magnetic \((A)\), the quadrupole electric \((B)\) and the octopole magnetic \((C)\) interaction constants as follow

\[
A_1 = IJA, \quad A_2 = 1/4B, \quad A_3 = C
\]

Calculating the electronic matrix elements in Eq.(5) and using the experimental values for \(E^{(1)}_J(F)\) and \(A_k\) we may obtain the nuclear moments \(\mu, Q\) and \(\Omega\).

The second order perturbation term

\[
E^{(2)}_J(F) = \sum_{J'} \frac{|< \beta I \alpha J F M_F | \hat{H} | \beta I \alpha J' F M_F |^2 |}{E_J - E_{J'}}.
\]  

(6)
where $E_J$ is the energy of the fine structure level $J$, becomes important in the case when the distance between hyperfine structure levels is of the same order as the energy intervals of the fine structure.

In this case the constant corresponding to $E_J^{(2)}(F)$ in Eq.(5) must be added, as a correction to the hyperfine interaction constant $A_k$.

2.2 Breit-Pauli Electron-Nucleus Operators

The Hamiltonian $\hat{H}_{en}$ of the electron-nuclear interactions obtained by means of the expansion of the electronic system Hamiltonian in series in powers of the fine structure constant includes three operators of the effective Breit-Pauli Hamiltonian \[10\]-\[12\]

$$\hat{H}_{en} = \hat{H}_{LI}^{en} + \hat{H}_{dip}^{SI} + \hat{H}_{cont}^{SI}. \quad (7)$$

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

$$\hat{H}_{dip}^{SI} = g_0 \alpha g \alpha_p \sum_i \left\{ 3[S(i) \cdot r_i][I \cdot r_i] - r_i^2 S(i) \cdot I \right\} r_i^{-5}. \quad (8)$$

Here $g_0$ is the $g$-factor of the free electron, $\alpha = 1/2c$ is a half of the fine structure constant (in atomic units), $g$ is the $g$-factor of the nucleus and $\alpha_p = 1/2m_pc$. The magnetic interaction between the electron angular momentum and the nuclear moment has the form

$$\hat{H}_{LI}^{en} = 2\alpha g \alpha_p \sum_i r_i^{-3} L(i) \cdot I. \quad (9)$$

The operator of the electron-nuclear contact interaction is

$$\hat{H}_{cont}^{SI} = \frac{8\pi}{3} g_0 \alpha g \alpha_p \sum_i \delta(r_i)S(i) \cdot I. \quad (10)$$

It is straightforward to point out that the direct inclusion of the hyperfine interactions of the nuclear momenta and the electronic system leads to the same results as the Hamiltonian $\hat{H}_{en}$ in Eq.(7) \[8, 9\].

3 MATRIX ELEMENTS OF THE ELECTRON OPERATORS

In order to make the matrix elements of the electronic operators suitable for calculations we have to recouple them from the $LM_LSM_SJM_J$ coupling scheme to the $LM_LSM_S$ coupling scheme. Since we consider the hyperfine splitting separately for each level of the fine structure, applying Racah techniques \[17\] we express the matrix elements $\langle \alpha LSJ | \hat{F}^k | \alpha LSJ' \rangle$ and $\langle \alpha LSJ | \hat{H}_{en} | \alpha LSJ' \rangle$ directly through the diagonal matrix elements of $\hat{F}^k$ and $\hat{H}_{en}$ in the $LM_LSM_S$
coupling scheme. Thus, along with the diagonal in $J$ matrix elements determining the $A_k$ constants, we have to calculate the non-diagonal in $J$ matrix elements determining $A_k^{(2)}$ values. It must be pointed out that the non-diagonal in $J$ matrix elements are very important in the estimation of the transition probabilities between the hyperfine levels [2, 4].

3.1 Electric Multipole Operators

The symmetrical tensor operators $(\mathbf{F}^{\text{el}})^k$ Eq.(2) with the components

$$(F^{\text{el}})^k_q = \sum_i -r_i^{-(k+1)}C^k_q(\theta_i, \varphi_i)$$

act only on the space variables, assuming the coupling scheme corresponding to $J = L + S$. Then following the Racah technique [17], and using the diagonal matrix elements $(\mathbf{F}^{\text{el}})^k$ in the $LM_LS$ coupling scheme we may express the electronic matrix elements of Eq.(6) as

$$<\alpha LS|F^k_q|\alpha LS'> = (-1)^{S-L-J+k+1}\sqrt{(2J+1)(2J'+1)}$$

$$\times W(LLJJ'; kS) <\alpha LS|\sum_i -r_i^{-(k+1)}C^k_q(\theta_i, \varphi_i)|\alpha LS > .$$

(11)

Taking into account that the operators $r_i^{-(k+1)}C^k_q(\theta_i, \varphi_i)$ are operators of multiplication the diagonal matrix elements can be expressed by means of the local density functional of charge distribution $\rho(K|\mathbf{r}) = \rho(K|r)$ in state $K \equiv |\alpha LM_LS >$ in the form

$$<\alpha LS|\sum_i r_i^{-(k+1)}C^k_q(\theta_i, \varphi_i)|\alpha LS > = \int \rho^{-k+1}C^k_q(\theta, \varphi)\rho(K|\mathbf{r})d\mathbf{r}. \quad (12)$$

Up to now there is no evidence of the existence of the electric electron-nucleus interactions with $k > 2$. The quadrupole interactions ($k = 2$) can be observed only in the case of degenerate nuclear states and nuclear spin $I \geq 1$ [1]. In our approach in the case of the quadrupole interaction the electronic system may possess an arbitrary total moment. As a matter of fact in the case under consideration the density charge distribution does not depend on the electronic system degeneration. Calculation of the matrix elements of the electronic operator of the quadrupole interaction is equivalent [??] to the calculation the matrix elements of the gradient of the electrostatic field created from the electrons placed in the centre of the nucleus [1], [3]-[5], [7].

3.2 Magnetic Multipole Operators

For each value of $k$ the operators Eq.(2) of the magnetic multipole interactions are the sum of two operators. The first term acts only on the space variables of the electronic system

$$(F^{\text{mg}})^k_1 = \frac{2\mu_e}{k} \sum_i [\nabla_i (r_i^{-(k+1)}C^k(\theta_i, \varphi_i))] \cdot \mathbf{L}(i). \quad (13)$$
In terms of contravariant and covariant cyclic components this operator may be written as

\[ (\tilde{F}^{mg})^k_i = \frac{2\mu_e}{k} \sum_i \sum_{m=-1}^1 [\nabla_i (r_i^{-(k+1)} C^k(\theta_i, \varphi_i))]^m L^1_m(i). \] (14)

The contravariant component of the vector in the middle brackets, corresponding to the component \( C^k_q(\theta_i, \varphi_i) \) of the normalized spherical function \( C^k(\theta_i, \varphi_i) \), can be written as

\[ [\nabla_i (r_i^{-(k+1)} C^k_q(\theta_i, \varphi_i))]^m = \sqrt{\frac{4\pi}{2k+1}} [\nabla_i (r_i^{-(k+1)} Y_{kq}(\theta_i, \varphi_i))]^m \]

\[ = \sqrt{4\pi(k+1)} r_i^{-(k+2)} Y_{kq}^{(k+1)}(\theta_i, \varphi_i)]^m \]

\[ = \sqrt{(k+1)(2k+3)} r_i^{-(k+2)} C^{k+1}_{q-m} 1 \ k C^{k+1}_{q-m}(\theta_i, \varphi_i), \]

where \( Y_{kq}^{(k+1)}(\theta, \varphi) \) are spherical vectors [18], and \( C^{k+1}_{q-m} 1 \ k \) are Clebsch-Gordon coefficients. The scalar product in the right side of the expression Eq.(14), corresponding to the component \( C^k_q(\theta_i, \varphi_i) \) takes the form

\[ \sum_m [\nabla_i (r_i^{-(k+1)} C^k_q(\theta_i, \varphi_i))]^m L^1_m(i) = \frac{\sqrt{(k+1)(2k+3)} r_i^{-(k+2)} [C^{k+1}(\theta_i) \times L(i)]_q^k}, \] (16)

where

\[ [C^{k+1}(\theta_i) \times L(i)]_q^k = \sum_m C^{k+1}_{q-m} 1 \ k C^{k+1}_{q-m}(\theta_i, \varphi) L^1_m(i). \]

Hence, the operator \( (\tilde{F}^{mg})^k_i \) is an irreducible tensor operator of \( k-th \) rank. Since the operators \( (\tilde{F}^{mg})^k_i \) act only on the space part of the electronic system, for the matrix elements of the \( q \) component \( (\tilde{F}^{mg})^k_q \), we obtain

\[ < \alpha LS | (\tilde{F}^{mg})^k_q | \alpha LS' > = (-1)^{S-L-J+k+1} \]

\[ \times \frac{2\mu_e}{k} \sqrt{(2J+1)(2J'+1)(k+1)(2k+3)} W(LLLJ'; kS) \sum_m C^{k+1}_{q-m} 1 \ k \]

\[ \times < \alpha LS | \sum_i r_i^{-(k+2)} [C^{k+1}(\theta_i) \times L(i)]_q^k | \alpha LS >. \] (17)

We can represent the sum in Eq.(17) as

\[ \sum_m C^{k+1}_{q-m} 1 \ k \] \( < \alpha LS | \sum_i r_i^{-(k+2)} C^{k+1}_{q-m}(\theta_i, \varphi) L^1_m(i) | \alpha LS > \]

\[ = \sum_m C^{k+1}_{q-m} 1 \ k \int_{r'_1=r_1} r_i^{-(k+2)} C^{k+1}_{q-m}(\theta_i, \varphi) L^1_m(1) \rho(K | r_1; r'_1) dr_1, \] (18)
where \( \rho(K|r; r') \) is the non-local charge distribution density functional in 
\( K \equiv |\alpha LM_L SM_S > \) state. In Eq.(18) the density functional does not depend on 
the summing indices \( m \) and \( q \).

The second operator of the magnetic multipole interactions acts on the space 
coordinates, as well as on the spin components of the electronic system

\[
(\hat{F}_2^{mg})^k = 2\mu_e \sum_i \nabla_i [r_i^{-1} C^k(\theta_i, \varphi_i)] \cdot S(i).
\]  

(19)

Now we obtain

\[
(\hat{F}_2^{mg})^k = 2\mu_e \sqrt{(k+1)(2k+3)} \sum_i r_i^{-1} [C^{k+1}(i) \times S^1(i)]^k,
\]  

(20)

The \( q \) component of the tensor product in Eq.(20) has the form

\[
[C^{k+1}(i) \times S(i)]^k_q = \sum_m C_{k+1}^{k+1} \left\{ \frac{1}{m} \frac{q}{k} \right\} \sum \frac{1}{m} \frac{q}{k} \frac{S_m^1(i)}{1}
\]  

(21)

where the spin moment acts on the spin subsystem. Since both operators \( C^{k+1}(i) \) 
and \( S(i) \) act on two different subsystems they commute, and the matrix elements

of the components \( \langle F_2^{mg} \rangle_q^k \) can be expressed as

\[
< \alpha LS J | (\hat{F}_2^{mg})^k_q | \alpha LS J' > = 2\mu_e \sqrt{(k+1)(2k+1)(2k+3)(2J+1)(2J'+1)}
\]

\[ \times \left\{ \begin{array}{ccc}
L & L & k+1 \\
S & S & 1 \\
J & J' & k
\end{array} \right\} \sum_m C_{k+1}^{k+1} \frac{1}{m} \frac{q}{k} \frac{S_m^1(i)}{1} \langle \alpha LS | \sum_i r_i^{-1} C_{k+1}^{k+1} \left\{ \frac{1}{m} \frac{q}{k} \right\} \sum \frac{1}{m} \frac{q}{k} \frac{S_m^1(i)}{1} | \alpha LS >.
\]  

(22)

Applying the equations Eqs.(61)-(64) of the Appendix to the right hand matrix 
elements in Eq.(22) we have

\[
< \alpha LM_L SM_S | \sum_i r_i^{-1} C_{k+1}^{k+1} \left\{ \frac{1}{m} \frac{q}{k} \right\} \sum \frac{1}{m} \frac{q}{k} \frac{S_m^1(i)}{1} | \alpha LM_L SM'_S > = \\
\int r_1^{-1} C_{k+1}^{k+1} \left\{ \frac{1}{m} \frac{q}{k} \right\} \sum \frac{1}{m} \frac{q}{k} \frac{S_m^1(i)}{1} d\mathbf{r}_1 = \\
< SM_S | S_m^1 | SM'_S > \int r_1^{-1} C_{k+1}^{k+1} \left\{ \frac{1}{m} \frac{q}{k} \right\} \sum \frac{1}{m} \frac{q}{k} \frac{S_m^1(i)}{1} D_S(\mathbf{r}_1) d\mathbf{r}_1,
\]  

(23)

where \( D_S(\mathbf{r}_1) = q(\mathbf{K} \mathbf{K} | \mathbf{r}_1; \mathbf{r}_1) \) is the normalized spin distribution density 
functional, \( K' \equiv |\alpha LM_L SM'_S >, \) and \( \mathbf{K} \equiv |\alpha LM_L SS >. \)

The application of the Wigner-Eckart theorem for the matrix elements

\[
< SM_S | S_m^1 | SM'_S > \text{ yields}
\]

\[
< SM_S | S_m^1 | SM'_S > = \sqrt{\frac{3}{2}} \frac{1}{\sqrt{2S+1}} C_{M_S M'_S}^{1 S}. 
\]  

(24)
Finally the contribution of the component \((F_{mg}^2)_q\) of the magnetic operator \(\hat{F}^m_g\) for the hyperfine splitting of any spin multiplet term under consideration \((SM_S)\) has the form

\[
<\alpha LSJ|(F_{mg}^2)_q|\alpha LSJ'> = \sqrt{6}\mu_e \frac{1}{\sqrt{2S+1}} \times \sqrt{(k+1)(2k+1)(2k+3)(2J+1)(2J'+1)} \times \left\{ \begin{array}{ccc}
L & L & k+1 \\
S & S & 1 \\
J & J' & k
\end{array} \right\} \sum_m C^{k+1}_{q-m} \frac{1}{m} C^{S}_{m} \frac{1}{S} C^{S}_{m'} \frac{1}{S'} \times \int r_1^{-(k+2)} C^{k+1}_{q-m}(\vartheta_1, \phi_1) D_S(r_1) dr_1.
\]

(25)

### 3.3 Electron-Nucleus Dipole Operator

The magnetic dipole coupling between electron and nuclear spins Eq.(8) can be written down in a form in which the electronic and nuclear variables are separated

\[
\hat{H}_{SI}^{SI} = g_0\alpha g_{\alpha} \alpha p \sum_i S(i) \cdot \left[ 3 \frac{\mathbf{r}_i \otimes \mathbf{r}_i}{r_i^5} - \frac{\mathbf{n}^2(i)}{r_i^3} \right] \cdot \mathbf{I}.
\]

(26)

Here \(\mathbf{n}^2(i)\) is the unit tensor formed from the unit vector \(\mathbf{n}(i) = \mathbf{r}_i/r_i\).

The sum of the one-electronic operators in Eq.(26) can be written as

\[
\hat{H}_{SI}^{SI} = g_0\alpha g_{\alpha} \alpha p \sum_i r_i^{-3} \mathbf{K}(i) \cdot \mathbf{I},
\]

(27)

where

\[
\mathbf{K}(i) = 3[S(i) \cdot \mathbf{n}(i)]\mathbf{n}(i) - S(i).
\]

(28)

The components \(K^1_q(i)\) of the axial vector \(\mathbf{K}(i)\) can be written in the form

\[
K^1_q(i) = \sum_l D^2_{ql} S^1_l(i),
\]

(29)

where the second-rank, symmetric, traceless tensor

\[
D^2_{ql} = 3n_q(i)n_l(i) - \delta_q n_q(i)n_l(i)
\]

(30)

is proportional to the normalized spherical function \(C^2(\vartheta_i, \phi_i)\).

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

\[
K^1_q(i) = C[D^2 \otimes \hat{S}^1]_q = C \sum_{m,m'} C^2_{m} \frac{1}{m} C^2_{m'} \frac{1}{m'} \delta_q n_q(i)n_l(i) S^1_{m'}(i),
\]

(31)
where the \([D^2 \otimes S^1]_q\) are the components of an irreducible first-rank tensor product of \(D^2\) and \(S^1\). The constant \(C\) can be derived from atomic spectroscopy theory \([9]\) and is equal to \(10^{1/2}\).

Using the relations given above and expressing the scalar product of \(K(i)\) and \(I\) in Eq.(27) as a tensor product of their symmetrized forms \(K^1(i)\) and \(I^1\), one obtains

\[
\hat{H}_{\text{dip}}^{SI} = (\hat{F}_{\text{dip}})^1 \cdot \hat{Q}^1 = \sum_q (-1)^q (F_{\text{dip}}^1)_q \cdot Q_{-q}^1.
\]

(32)

The \(q\) component of the electronic operator has the form

\[
(F_{\text{dip}}^1)_q = g_0 \alpha \sum_i r_i^{-3} K^1_q(i) = \\
\sqrt{10} g_0 \alpha \sum_{m,m'} C^2_{1,1,1} \sum_i r_i^{-3} C^2_m(\varphi_i) S^1_{m'}(i),
\]

(33)

and the \(q\) component of the nuclear operator is

\[
Q_{-q}^1 = g_\alpha I_{-q}.
\]

The \(Q_{-q}^1\) components can be obtained by means of the Wigner-Eckart theorem. We have

\[
\langle II|Q^1_{q}|II\rangle = g_\alpha \frac{1}{\sqrt{2J+1}} C^I_{q} 1 1 I_I < I\|\hat{Q}^k\|I >
\]

(34)

\[
= g_\alpha \{C^I_{q} 1 1 I_I /C^I_{k} 0 1 F_F\} M_1,
\]

where \(M_1 = \mu\) is the magnetic dipole nuclear moment.

By analogy with Eq.(5), the matrix elements \(< \beta I \alpha JFM_F|\hat{H}_{\text{dip}}^{SI}|\beta I \alpha J'FM_F >\) can be written as

\[
\langle \beta I \alpha JFM_F|\hat{H}_{\text{dip}}^{SI}|\beta I \alpha J'FM_F > = \\
(-1)^{I+J'-F} W(IIJJ'; F) < \alpha J\|\hat{F}_{\text{dip}}^1\|\alpha J' <\beta I\|\hat{Q}^1\|\beta I >.
\]

(35)

In order to calculate the contribution of this interaction to the hyperfine splitting and to the constant of this splitting \(A_{k=1}\), we recouple the matrix elements \(< \alpha LSJ|\hat{F}_{\text{dip}}^1|\alpha LSJ' >\) from the \(LM_LSM_SJM_J\) to the \(LM_LSM_S\) coupling scheme. Since tensor \([C^2(\varphi, \varphi) \otimes S^1]_1\) acts over space and spin subsystems the 9j-symbol technique leads to

\[
< \alpha LSJ|(F_{\text{dip}}^1)_q|\alpha LSJ' > = 10 \sqrt{3} g_0 \alpha \sqrt{(2J+1)(2J'+1)} \\
\times \left\{ \begin{array}{ccc} L & L & 2 \\ S & S & 1 \\ J & J' & 1 \end{array} \right\} \sum_{m,m'} C^2_{m, m'} q \sum_i r_i^{-3} C^2_m(\varphi_i) S^1_{m'}(i)|\alpha LS >.
\]

(36)
Using Eqs.(61)-(64) of the Appendix we express the matrix elements of the electronic factor in the form

\[
\langle \alpha L S M_S | \sum_i r_i^{-3} C_m^2 (\vartheta_i, \varphi_i) S_m^i (i) | \alpha L S M'_S \rangle = \int_{r_1} \int_{r_1'} r_1^{-3} C_m^2 (\vartheta_1, \varphi_1) q(KK'|r_1; r_1') \cdot D_S(r_1) d\mathbf{r}_1, \quad (37)
\]

Finally for the matrix elements of the electronic dipole operator \( \hat{F}_{dip} \) we obtain

\[
< \alpha L S J | (F_{dip})_q^1 | \alpha L S J' >= 15 \sqrt{2g_0 \alpha} \frac{1}{\sqrt{2S + 1}} \sqrt{(2J + 1)(2J' + 1)} \\
\times \left\{ \begin{array}{ccc} L & L & 2 \\ S & S & 1 \\ J & J' & 1 \end{array} \right\} \sum_{mm'} C_m^2 1_{m'}^1 q C_S^S 1_{M'_S}^S \\
\times \int_{r_1} r_1^{-3} C_m^2 (\vartheta_1, \varphi_1) D_S(r_1) d\mathbf{r}_1. \quad (38)
\]

One can easily see that the functional \( < \alpha L S J | (F_{dip})_q^1 | \alpha L S J' > \) coincides, up to the constant, with the functional of the electronic multipole operator \( < \alpha L S J | (F_{mg}^q)^k | \alpha L S J' > \) (Eq.(25)) for \( k = 1 \).

### 3.4 Electron-Nucleus Orbital-Spin Operator

The operator of the interaction between the electronic orbital momentum and the magnetic moment of nucleus Eq.(9) can be written down as a product of electronic and nuclear operators and has the form

\[
\hat{H}_{en}^{LL} = (\hat{F}_L)^1 \cdot \hat{Q}^1 = \sum_q (-1)^q (F_L)_q^1 \cdot Q_{-q}^1. \quad (39)
\]

The \( q \) component of the electronic operator is

\[
(F_L)_q^1 = 2\alpha \sum_i r_i^{-3} L_q^1 (i) \quad (40)
\]

while the \( q \) component of the nuclear operator is

\[
Q_{-q}^1 = g \alpha \nu I_{-q}^1.
\]

Using the Racah technique we obtain

\[
< \beta I \alpha J F M_F | \hat{H}_{en}^{LL} | \beta I \alpha J' F M_F >= (-1)^{I+J'-F} W(IJJ'; F) < \alpha J \| (\hat{F}_L)^1 \| \alpha J' > < \beta I \| \hat{\mathbf{Q}}^1 \| \beta I >. \quad (41)
\]
The matrix elements $\langle I I | Q^I_q | I I \rangle$ of the nuclear operator components $Q^I_q$ are again taken from Eq.(34).

The matrix elements of the components of electronic operator $\hat{F}^I_L$ in the $LM_LSM_S$ coupling scheme are

$$
< \alpha LSJ | (F^I_L)^I_q | \alpha LSJ' > = 2\alpha (-1)^{S-L-J+k+1}\sqrt{(2J+1)(2J'+1)}
\times W(LLJJ'; kS) < \alpha LS | \sum_i r^{-3}_i L^I_q(i) | \alpha LS > .
$$

(42)

And now we may represent the right side matrix elements in Eq.(42) in terms of the charge distribution density functional. Thus we obtain

$$
\langle \alpha LS | \sum_i r^{-3}_i L^I_q(i) | \alpha LS > = \int_{r_1' = r_1} r^{-3}_1 L^I_q(1) \rho(KK | r_1; r_1') dr_1.
$$

(43)

Here $\rho(KK | r_1; r_1') = \rho(K | r_1; r_1')$ is the non-local density functional charge distribution.

3.5 Electron-Nucleus Contact Operator

The operator of the electron-nucleus contact interactions Eq.(10) can be also given as

$$
\hat{H}^{SI}_{cont} = (\hat{F}^{cont})^I \cdot \hat{Q}^I = \sum_q (-1)^q (F^{cont})^I_q \cdot Q^I_{-q}.
$$

(44)

Here the $q$ component of the electronic operator is

$$
(F^{cont})^I_q = \frac{8\pi}{3} g_0 \alpha \sum_i \delta(r_i) S^I_q(i)
$$

(45)

and the $q$ component of the nuclear operator is

$$
Q^I_{-q} = g\alpha_p I^I_{-q}.
$$

By analogy with Eq.(41) we obtain

$$
< \beta I \alpha J F M_F | \hat{H}^{SI}_{cont} | \beta I \alpha J' F M_F > = (-1)^{I'+J'} F W(IIJJ'; F) < \alpha J || (\hat{F}^{cont})^I || \alpha J' > < \beta I || \hat{Q}^I || \beta I > .
$$

(46)

The matrix elements of the components of electronic operator $(\hat{F}^{cont})^I$ in the $LM_LSM_S$ coupling scheme are

$$
< \alpha LSJ | (F^{cont})^I_q | \alpha LSJ' > = \frac{8\pi}{3} g_0 \alpha (-1)^{S-L-J+k+1}\sqrt{(2J+1)(2J'+1)}
\times W(LLJJ'; kS) < \alpha LS | \sum_i \delta(r_i) S^I_q(i) | \alpha LS > .
$$

(47)
Using the procedure described in subsections 3.2 and 3.3 and the Appendix equations, the electronic matrix elements can be represented in terms of the spin distribution density functional

\[
\langle \alpha L S M_S | \sum_i \delta(\mathbf{r}_i) S^1_q(i) | \alpha L S M'_S \rangle = \left\{ C^S_{M_S q M'_S} / C^S_{0 S 0} \right\} 
\times \int_{r'_1=r_1} \delta(\mathbf{r}_1) q(KK'|\mathbf{r}_1; \mathbf{r}'_1)_{0}^{1} d\mathbf{r}_1 = \langle S M_S | S^1_q | S M'_S \rangle 
\times \int_{r_1} \delta(\mathbf{r}_1) D_S(\mathbf{r}_1) d\mathbf{r}_1 = \sqrt{\frac{3}{2}} \frac{1}{\sqrt{2S+1}} C^S_{M_S q M'_S} D_S(\mathbf{r})|_{r=0},
\]

where \( D_S(\mathbf{r})|_{r=0} \) is the spin distribution density functional at the location of the nucleus.

4 CONCLUSION

In this paper we suggest an approach for the calculation of the nuclear multipole moments. In this approach the electronic matrix elements entering the experimentally observed hyperfine interaction constants are expressed in terms of the electron density functionals of the charge or spin distributions. The matrix elements are presented in a form, suitable for numerical implementation. These matrix elements are determined for all the electronic operators entering the Hamiltonians of the different descriptions of hyperfine electron-nuclear interactions. Using the irreducible tensor-operators and the Racah and Fano techniques as well as the density functional and density matrix formalism, we can express these matrix elements as the products of \( 3j \), \( 6j \), or \( 9j \) factors with the space part-charge or spin distribution density functional. In principle, the charge or spin distribution density functionals can be constructed using every relativistic or non-relativistic quantum-mechanical or DFT method.

The matrix elements of the \((\hat{F}_{el})^k\) and \((\hat{F}_{mg})^k\) operators of the Hamiltonians \(\hat{H}_k\) Eq.(1) and the operator \((\hat{F}_{L})^1\) of Hamiltonian \(\hat{H}_{en}\) Eq.(7) are the charge distribution density functionals while the matrix elements of operator \((\hat{F}_{dip})^k\) of the Hamiltonians \(\hat{H}_k\) and two operators \((\hat{F}_{dip})^1\) and \((\hat{F}_{cont})^1\) of the Hamiltonian \(\hat{H}_{en}\) are spin distribution density functionals. It is important to point out that the charge distribution density functional does not depend on the level of the fine structure, this dependence is governed by the \(j\)-symbols. One may notice a similar behaviour in the case of spin distribution density functional. But in this case the normalized functional remains the same within one given spin multiplet. And here, too the fine structure level for which we consider its hyperfine splitting within the spin multiplet is determined by \(3j\), \(6j\) or \(9j\) factors Eq.(25), Eq.(38), Eq.(48). Of course, the hyperfine splitting energy depends on \(j\)-symbols as well as on the corresponding density functional.
It is straightforward to point out that such a representation is valid for the arbitrary degenerate or non-degenerate states of the electronic system and also for arbitrary transitions induced by an external magnetic field. Hence, in the case of the free atoms this approach may be successfully applied to all kinds of experiments determining the nuclear multipole moments.

The charge and spin distribution density functional may be constructed by means of proper relativistic ab-initio results (for instance, the results of paper [19]) or DFT calculations, however of the type which contains more precise relativistic corrections [20]. One also may use the density functional of relativistic corrections given in papers [15, 16]. Of course our approach gives the possibility to make the non-relativistic calculations. The application of this approach in non-relativistic calculations has an advantage because of the density functional methods can be used. We have shown in subsections 3.2 and 3.3 that the the matrix elements Eq.(25) and Eq.(38) of the $\hat{F}_m^2$ and $\hat{F}_{\text{dip}}$ operators written in terms of the spin distribution density functionals have the same analytical form in all cases. Similar results hold for the operators sum $\hat{F}_{\text{dip}} + \hat{F}_L$ and the operators sum $\hat{F}_m^1 = \hat{F}_m^1 + \hat{F}_m^2$ whose matrix elements, however are calculated only numerically, or appear in the special case of one electron above the closed shell [7].

5 APPENDIX

DENSITY FUNCTIONALS OF CHARGE AND SPIN DISTRIBUTIONS

5.1 Charge Distribution Density Functionals

The first order density matrix of a $N$-electronic system in state $K$ described by a wave function $\Psi_K(\tau_1, ..., \tau_N)$, eigenfunction of the operators $S^2$ and $S_z$, has the form [10, 21]

$$\rho(K|\tau_1; \tau'_1) = N \int \Psi_K(\tau_1, \tau_2, ..., \tau_N)\Psi^*_K(\tau'_1, \tau_2, ..., \tau_N) d\tau_2...d\tau_N,$$

(49)

where $\tau_i = (r_i, \sigma_i)$, $r_i$, $(1 \leq i \leq N)$ being the position vector and $\sigma_i$ the spin variable of the $i$-th electron, and $d\tau_i = dr_id\sigma_i$.

The corresponding first order density function is defined by the expression

$$\rho(K|\tau_1) = \rho(K|\tau_1; \tau'_1)|_{\tau'_1=\tau_1} = \rho(K|\tau_1; \tau_1).$$

(50)

The first order transition density matrix between states $K$ and $K'$ has the form

$$\rho(K'|\tau_1; \tau'_1) = N \int \Psi_K(\tau_1, \tau_2, ..., \tau_N)\Psi^*_K(\tau'_1, \tau_2, ..., \tau_N), d\tau_2..., d\tau_N.$$

(51)
For the one-density transition function we have a similar expression, which follows by analogy with Eq.(50).

After separation of the space and spin variables, the one-density matrix takes the form

$$\rho(\tau_1; \tau'_1) = \sum_{\gamma, \gamma' = \alpha, \beta} \rho_{\gamma, \gamma'}(r_1; r'_1) \gamma(\sigma_1) \gamma'(\sigma'_1),$$  \hspace{1cm} (52)

where the $\rho_{\gamma, \gamma'}(r_1; r'_1)$ are the space components of one-density matrix and the $\gamma(\sigma)$ ($\gamma = \alpha, \beta$) are the electron spin wave-functions.

The space density matrix of charge distribution has the form

$$\rho(r_1; r'_1) = \int_{\tau'_1 = \tau_i} \rho(\tau_1; \tau'_1) d\tau_1 = \rho^{\alpha, \alpha}(r_1; r'_1) + \rho^{\beta, \beta}(r_1; r'_1)$$  \hspace{1cm} (53)

and the space density function of charge distribution

$$\rho(r_1) = \rho(r_1; r'_1)_{r'_1 = r_1} = \rho^{\alpha}(r_1) + \rho^{\beta}(r_1).$$  \hspace{1cm} (54)

Here $\rho(r_1)$ is local and $\rho(r_1; r'_1)$ non-local electron density functional.

The matrix elements of a sum of identical one-particle operators, can be written down as

$$\langle K | \sum_i \hat{F}(i) | K' \rangle \equiv \langle \Psi_{K'}(\tau_1, ..., \tau_N) | \sum_i \hat{F}(i) | \Psi_{K}(\tau_1, ..., \tau_N) \rangle = \int_{\tau'_1 = \tau_i} \hat{F}(1) \rho(KK' | \tau_1; \tau'_1) d\tau_1.$$  \hspace{1cm} (55)

The one particle operators $\hat{F}(i)$ do not depend of spin variable we have

$$\langle K | \sum_i \hat{F}(i) | K' \rangle \equiv \int_{r'_1 = r_1} \hat{F}(1) \rho(KK' | r_1; r'_1) dr_1,$$  \hspace{1cm} (56)

and if in addition the $\hat{F}(i)$ is the operator of multiplication then

$$\langle K | \sum_i \hat{F}(i) | K' \rangle \equiv \int \hat{F}(1) \rho(KK' | r_1) dr_1.$$  \hspace{1cm} (57)

### 5.2 Spin Distribution Density Functionals

In a spin eigenstate (with eigenvalues $S(S + 1)$ and $M$ ) the spin distribution non-local density functional, can be written in the following form: [11, 12, 21]

$$q(r_1; r'_1) = 1/2[\rho^{\alpha, \alpha}(r_1; r_1') - \rho^{\beta, \beta}(r_1; r'_1)].$$  \hspace{1cm} (58)
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 $M$

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

(59)

with:

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

(60)

Here $K$ is the index of the spin state corresponding to $\langle S_z \rangle = M$, $\overline{K}$ is the index of the state corresponding to the maximal value of $M = S$.

Using the general definition for the transition spin distribution density functional we can write [10]-[12]

$$q(KK'|\mathbf{r}_1; \mathbf{r}_1')_{m} = \int_{\sigma_1'} S_m^1(1) \rho(KK'|\tau_1; \tau_1') d\sigma_1.$$  

(61)

Here the $S_m^1(i) (m = 0, \pm 1)$ are symmetrized components of the $i$-electron spin operator $S(i)$. Similar formulae can be written for the transition local spin-distribution density functional setting $\mathbf{r}_1 = \mathbf{r}_1'$.

The spin-distribution functionals for transitions between states $K(SM_S)$ and $K'(S'M_{S'}$) satisfy the relations

$$q(KK'|\mathbf{r}_1; \mathbf{r}_1')_{m} = \{C_{S, S'}^{1 S_m M_{S_m}} / C_{S, S'}^{1 S_m M_{S_m}} \} q(K\overline{K}|\mathbf{r}_1; \mathbf{r}_1')_{m}$$

(62)

where $C_{S, S'}^{1 S_m M_{S_m}}$ are Clebsch-Gordon coefficients. By analogy with Eq.(61) one obtains

$$q(K\overline{K}|\mathbf{r}_1; \mathbf{r}_1')_{m} = \int_{\sigma_1'} S_m^1(1) \rho(K\overline{K}|\tau_1; \tau_1') d\sigma_1.$$  

(63)

Using the Wigner-Eckart theorem we have

$$q(KK'|\mathbf{r}_1; \mathbf{r}_1')_{m} = \{C_{S, S'}^{1 S_m M_{S_m}} / C_{S, S'}^{1 S_m M_{S_m}} \} q(K\overline{K}|\mathbf{r}_1; \mathbf{r}_1')$$

$$= <SM_s|S_m'|SM_{s'} > D_S(\mathbf{r}_1; \mathbf{r}_1'),$$

(64)

where the $S_m^1 (m = 0, \pm 1)$ are symmetrized components of the total spin $S$. Equation(64) is a generalization of the equation(59) for a transition between different spin states.
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