NMR Shielding and Coupling Constants–Derivation

This appendix is designed for those who want to double-check whether the final formulas for the shielding and coupling constants in the nuclear magnetic resonance (NMR) are indeed valid (Chapter 12).

Shielding Constants

Let us begin from Eq. (12.88).

Applying Vector Identities

We are going to apply some vector identities[1] in the operators $\hat{B}_3$, $\hat{B}_4$, $\hat{B}_5$. The first identity is $\boldsymbol{u}\cdot(\boldsymbol{v}\times\boldsymbol{w})=\boldsymbol{v}\cdot(\boldsymbol{w}\times\boldsymbol{u})=\boldsymbol{w}\cdot(\boldsymbol{u}\times\boldsymbol{v})$, which simply means three equivalent ways of calculating the volume of a parallelepiped (cf., p. 515). This identity, applied to $\hat{B}_3$ and $\hat{B}_4$, gives

$$\hat{B}_3=\frac{e}{mc}\sum_A\sum_j\gamma_A\frac{\boldsymbol{I}_A\cdot\hat{\boldsymbol{L}}_{Aj}}{r_{Aj}^3}, \tag{W.1}$$

$$\hat{B}_4=\frac{e}{2mc}\sum_j\boldsymbol{H}\cdot\hat{\boldsymbol{L}}_{0j}. \tag{W.2}$$

Let us transform the term $\hat{B}_5$ by using the following identity $(\boldsymbol{u}\times\boldsymbol{v})\cdot(\boldsymbol{w}\times\boldsymbol{s})=(\boldsymbol{u}\cdot\boldsymbol{w})(\boldsymbol{v}\cdot\boldsymbol{s})-(\boldsymbol{v}\cdot\boldsymbol{w})(\boldsymbol{u}\cdot\boldsymbol{s})$:

$$\begin{aligned}\hat{B}_5&=\frac{e^2}{2mc^2}\sum_A\sum_j\gamma_A\left(\boldsymbol{H}\times\boldsymbol{r}_{0j}\right)\cdot\frac{\boldsymbol{I}_A\times\boldsymbol{r}_{Aj}}{r_{Aj}^3}\\&=\frac{e^2}{2mc^2}\sum_A\sum_j\gamma_A\left[(\boldsymbol{H}\cdot\boldsymbol{I_A})(\boldsymbol{r}_{0j}\cdot\boldsymbol{r}_{Aj})-(\boldsymbol{r}_{0j}\cdot\boldsymbol{I_A})(\boldsymbol{H}\cdot\boldsymbol{r}_{Aj})\right]\cdot\frac{1}{r_{Aj}^3}.\end{aligned}$$

[1] The reader may easily check each of these identities.

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Putting Things Together

We are now ready to put all this baroque furniture into its destination; i.e., into Eq. (12.88) for ΔE:

$$\Delta E = \sum_A \Delta E_A, \tag{W.3}$$

where ΔE_A stands for the contribution of nucleus A:

$$\begin{aligned}
\Delta E_A = & -\gamma_A \left\langle \psi_0^{(0)} | \left(\boldsymbol{I}_A \cdot \boldsymbol{H}\right) \psi_0^{(0)} \right\rangle \\
& + \frac{e^2}{2mc^2}\gamma_A \left\langle \psi_0^{(0)} | \sum_j \left[(\boldsymbol{H} \cdot \boldsymbol{I_A})(\boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj}) - \left(\boldsymbol{r}_{0j} \cdot \boldsymbol{I_A}\right)(\boldsymbol{H} \cdot \boldsymbol{r}_{Aj}) \right] \cdot \frac{1}{r_{Aj}^3} \psi_0^{(0)} \right\rangle \\
& + \frac{e^2}{2m^2c^2}\gamma_A \left[\left\langle \psi_0^{(0)} | \left(\sum_j \frac{\boldsymbol{I}_A \cdot \hat{\boldsymbol{L}}_{Aj}}{r_{Aj}^3} \right) \hat{R}_0 \left(\sum_j \boldsymbol{H} \cdot \hat{\boldsymbol{L}}_{0j} \right) \psi_0^{(0)} \right\rangle \right. \\
& \left. + \left\langle \psi_0^{(0)} | \left(\sum_j \boldsymbol{H} \cdot \hat{\boldsymbol{L}}_{0j} \right) \hat{R}_0 \left(\sum_j \frac{\boldsymbol{I}_A \cdot \hat{\boldsymbol{L}}_{Aj}}{r_{Aj}^3} \right) \psi_0^{(0)} \right\rangle \right],
\end{aligned}$$

Averaging over Rotations

The expression for ΔE_A represents a bilinear form with respect to the components of vectors $\boldsymbol{I_A}$ and $\boldsymbol{H}$:

$$\Delta E_A = \boldsymbol{I}_A^T \boldsymbol{C}_A \boldsymbol{H},$$

where $\boldsymbol{C}_A$ stands for a square matrix[2] of dimension 3, and $\boldsymbol{I}_A$ and $\boldsymbol{H}$ are vertical three-component vectors.

A contribution to the energy such as ΔE_A cannot depend on our choice of coordinate system axes x, y, z; i.e., on the components of $\boldsymbol{I}_A$ and $\boldsymbol{H}$. We will obtain the same energy if we rotate the axes (orthogonal transformation) in such a way as to diagonalize $\boldsymbol{C}_A$. The resulting diagonalized matrix $\boldsymbol{C}_{A,diag}$ has three eigenvalues (composing the diagonal) corresponding to the new axes x', y', z'. *The very essence of averaging is that none of these axes are to be privileged in any sense.* This is achieved by constructing the averaged matrix

$$\begin{aligned}
& \frac{1}{3}\left[\left(\boldsymbol{C}_{A,diag}\right)_{x'x'} + \left(\boldsymbol{C}_{A,diag}\right)_{y'y'} + \left(\boldsymbol{C}_{A,diag}\right)_{z'z'} \right] \\
& = \left(\bar{\boldsymbol{C}}_{A,diag}\right)_{x'x'} = \left(\bar{\boldsymbol{C}}_{A,diag}\right)_{y'y'} = \left(\bar{\boldsymbol{C}}_{A,diag}\right)_{z'z'} \equiv C_A,
\end{aligned}$$

[2] We could write its elements from the equation for ΔE_A, but their general form will turn out to be unnecessary.

where $\left(\bar{\boldsymbol{C}}_{A,diag}\right)_{qq'} = \delta_{qq'} C_A$ for $q, q' = x', y', z'$. Note that since the transformation was orthogonal (i.e., the trace of the matrix is preserved), the number C_A may also be obtained from the original matrix $\boldsymbol{C}_A$:

$$C_A = \frac{1}{3}\left[\left(\boldsymbol{C}_{A,diag}\right)_{x'x'} + \left(\boldsymbol{C}_{A,diag}\right)_{y'y'} + \left(\boldsymbol{C}_{A,diag}\right)_{z'z'}\right] = \frac{1}{3}\left[\boldsymbol{C}_{A,xx} + \boldsymbol{C}_{A,yy} + \boldsymbol{C}_{A,zz}\right]. \quad \text{(W.4)}$$

Then the averaged energy ΔE becomes

$$\Delta \bar{E} = \sum_A \boldsymbol{I}_A^T \bar{\boldsymbol{C}}_{A,diag} \boldsymbol{H} = \sum_A C_A \left(\boldsymbol{I}_A \cdot \boldsymbol{H}\right).$$

Thus, we obtain the sum of energy contributions over the nuclei, each one with its own coefficient averaged over rotations[3]:

$$\Delta \bar{E} = -\sum_A \gamma_A \boldsymbol{I}_A \cdot \boldsymbol{H} \Bigg\{ 1 - \frac{e^2}{2mc^2} \left\langle \psi_0^{(0)} \right| \sum_j \frac{2}{3} (\boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj}) \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle - \frac{e^2}{2m^2c^2} \frac{1}{3} \left\langle \psi_0^{(0)} \right| \left[\left(\sum_j \frac{\hat{\boldsymbol{L}}_{Aj}}{r_{Aj}^3} \right) \hat{R}_0 \left(\sum_j \hat{\boldsymbol{L}}_{0j} \right) + \left(\sum_j \hat{\boldsymbol{L}}_{0j} \right) \hat{R}_0 \left(\sum_j \frac{\hat{\boldsymbol{L}}_{Aj}}{r_{Aj}^3} \right) \right] \left. \psi_0^{(0)} \right\rangle \Bigg\}, \quad \text{(W.5)}$$

[3] Indeed, making $C_A = \frac{1}{3}\left[\boldsymbol{C}_{A,xx} + \boldsymbol{C}_{A,yy} + \boldsymbol{C}_{A,zz}\right]$ for the terms of Eq. (W.3), we have the following contributions (term by term):

- $-\gamma_A \frac{1}{3}\left[1+1+1\right] = -\gamma_A$
- $\frac{e^2}{2mc^2}\gamma_A \frac{1}{3}\left[\left\langle \psi_0^{(0)} \right| \sum_j \boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj} \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle + \left\langle \psi_0^{(0)} \right| \sum_j \boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj} \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle + \left\langle \psi_0^{(0)} \right| \sum_j \boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj} \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle\right]$ $= \frac{e^2}{2mc^2}\gamma_A \left\langle \psi_0^{(0)} \right| \sum_j \boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj} \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle$
- $-\frac{e^2}{2mc^2}\gamma_A \left\langle \psi_0^{(0)} \right| \sum_j \frac{1}{3}\left[x_{0j}x_{Aj} + y_{0j}y_{Aj} + z_{0j}z_{Aj}\right] \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle = -\frac{e^2}{2mc^2}\gamma_A \left\langle \psi_0^{(0)} \right| \sum_j \frac{1}{3} \boldsymbol{r}_{0j} \cdot \boldsymbol{r}_{Aj} \frac{1}{r_{Aj}^3} \left. \psi_0^{(0)} \right\rangle$
- $+\frac{1}{3}\frac{e^2}{2m^2c^2}\gamma_A {\sum_k}' \frac{1}{E_0^{(0)} - E_k^{(0)}} \times \left[\left\langle \psi_0^{(0)} \middle| \left(\sum_j \frac{\hat{L}_{Ajx}}{r_{Aj}^3}\right) \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \sum_j \hat{L}_{0jx} \psi_0^{(0)} \right\rangle + similarly\ y, z + cc\right]$ $= \frac{1}{3}\frac{e^2}{2m^2c^2}\gamma_A {\sum_k}' \frac{1}{E_0^{(0)} - E_k^{(0)}} \times \frac{1}{3}\left[\left\langle \psi_0^{(0)} \middle| \left(\sum_j \frac{\hat{\boldsymbol{L}}_{Aj}}{r_{Aj}^3}\right) \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \middle| \sum_j \hat{\boldsymbol{L}}_{0j} \psi_0^{(0)} \right\rangle + cc\right],$

where *cc* means the "*complex conjugate*" counterpart. This reproduces Eq. (W.5).

with the matrix elements $\left(\hat{\boldsymbol{U}}\right)_{kl} = \left\langle \psi_k^{(0)} | \hat{\boldsymbol{U}} \psi_l^{(0)} \right\rangle$ of the corresponding operators $\hat{\boldsymbol{U}} = (\hat{U}_x, \hat{U}_y, \hat{U}_z)$.

Finally, after comparing the formula with Eq. (12.81), we obtain the shielding constant for nucleus A (the change of sign in the second part of the formula comes from the change in the denominator) given in Eq. (12.89).

Coupling Constants

Averaging over Rotations

In each contribution on pp. 781 and 782, there is a double summation over the nuclear spins, which, after averaging over rotations (similarly as for the shielding constant), gives rise to an energy dependence of the kind $\sum_{A<B} \gamma_A \gamma_B K_{AB} (\hat{\boldsymbol{I}}_A \cdot \hat{\boldsymbol{I}}_B)$, which is required in the NMR Hamiltonian. Now, let us take the terms E_{DSO}, E_{PSO}, E_{SD}, E_{FC} and average them over rotations producing $\bar{E}_{\text{DSO}}$, $\bar{E}_{\text{PSO}}$, $\bar{E}_{\text{SD}}$, $\bar{E}_{\text{FC}}$:

- $$\bar{E}_{\text{DSO}} = \frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \boldsymbol{I}_A \cdot \boldsymbol{I}_B \left\langle \psi_0^{(0)} | \frac{\boldsymbol{r}_{Aj} \cdot \boldsymbol{r}_{Bj}}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right\rangle - \frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \frac{1}{3} \boldsymbol{I}_A \cdot \boldsymbol{I}_B \left\{ \left\langle \psi_0^{(0)} | \frac{x_{Aj} x_{Bj}}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right\rangle + \left\langle \psi_0^{(0)} | \frac{y_{Aj} y_{Bj}}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right\rangle + \left\langle \psi_0^{(0)} | \frac{z_{Aj} z_{Bj}}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right\rangle \right\},$$

because the first part of the formula does not need any averaging (it is already in the appropriate form), the second part is averaged according to Eq. (W.4). Therefore,

$$\bar{E}_{\text{DSO}} = \frac{e^2}{3mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \boldsymbol{I}_A \cdot \boldsymbol{I}_B \left\langle \psi_0^{(0)} | \frac{\boldsymbol{r}_{Aj} \cdot \boldsymbol{r}_{Bj}}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right\rangle .$$

- $$\bar{E}_{\text{PSO}} = \left\langle \psi_0^{(0)} | \hat{B}_3 \hat{R}_0 \hat{B}_3 \psi_0^{(0)} \right\rangle_{\text{aver}}$$
$$= \left(\frac{i\hbar e}{mc}\right)^2 \sum_{A,B} \sum_{j,l} \gamma_A \gamma_B \left\langle \psi_0^{(0)} | \nabla_j \cdot \frac{\boldsymbol{I}_A \times \boldsymbol{r}_{Aj}}{r_{Aj}^3} \hat{R}_0 \nabla_l \cdot \frac{\boldsymbol{I}_B \times \boldsymbol{r}_{Bl}}{r_{Bl}^3} \psi_0^{(0)} \right\rangle_{\text{aver}}$$
$$= \left(\frac{i\hbar e}{mc}\right)^2 \sum_{A,B} \sum_{j,l} \gamma_A \gamma_B \left\langle \psi_0^{(0)} | \nabla_j \cdot \frac{\boldsymbol{r}_{Aj} \times \boldsymbol{I}_A}{r_{Aj}^3} \hat{R}_0 \nabla_l \cdot \frac{\boldsymbol{r}_{Bl} \times \boldsymbol{I}_B}{r_{Bl}} \psi_0^{(0)} \right\rangle_{\text{aver}}$$
$$= -\left(\frac{\hbar e}{mc}\right)^2 \sum_{A,B} \sum_{j,l} \gamma_A \gamma_B \left\langle \psi_0^{(0)} | \boldsymbol{I}_A \cdot \left(\nabla_j \times \frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}\right) \hat{R}_0 \boldsymbol{I}_B \cdot \left(\nabla_l \times \frac{\boldsymbol{r}_{Bl}}{r_{Bl}}\right) \psi_0^{(0)} \right\rangle_{\text{aver}},$$

where the subscript *aver* means the averaging of Eq. (W.4) and the identity $\boldsymbol{A}\cdot\left(\boldsymbol{B}\times\boldsymbol{C}\right)=\left(\boldsymbol{A}\times\boldsymbol{B}\right)\cdot\boldsymbol{C}$ has been used. We have the following chain of equalities (involving[4] the electronic momenta $\hat{\boldsymbol{p}}_j$ and angular momenta $\boldsymbol{L}_{Aj}$ with respect to the nucleus A, where j means electron number j):

$$\begin{aligned}
&\left(\frac{i\hbar e}{mc}\right)^2\sum_{A,B}\sum_{j,l}\gamma_A\gamma_B\left\langle\psi_0^{(0)}|\boldsymbol{I}_A\cdot\frac{1}{i\hbar}\left(\boldsymbol{r}_{Aj}\times\hat{\boldsymbol{p}}_j\right)\hat{R}_0\boldsymbol{I}_B\cdot\frac{1}{i\hbar}\left(\boldsymbol{r}_{Bl}\times\hat{\boldsymbol{p}}_l\right)\psi_0^{(0)}\right\rangle_{\text{aver}}\\
&=\left(\frac{e}{mc}\right)^2\sum_{A,B}\sum_{j,l}\gamma_A\gamma_B\left\langle\psi_0^{(0)}|\boldsymbol{I}_A\cdot\left(\boldsymbol{r}_{Aj}\times\hat{\boldsymbol{p}}_j\right)\hat{R}_0\boldsymbol{I}_B\cdot\left(\boldsymbol{r}_{Bl}\times\hat{\boldsymbol{p}}_l\right)\psi_0^{(0)}\right\rangle_{\text{aver}}\\
&=\left(\frac{e}{mc}\right)^2\sum_{A,B}\sum_{j,l}\gamma_A\gamma_B\left\langle\psi_0^{(0)}|\boldsymbol{I}_A\cdot\hat{\boldsymbol{L}}_{Aj}\hat{R}_0\boldsymbol{I}_B\cdot\hat{\boldsymbol{L}}_{Bl}\psi_0^{(0)}\right\rangle_{\text{aver}}\\
&=\left(\frac{e}{mc}\right)^2\sum_{A,B}\sum_{j,l}\gamma_A\gamma_B\boldsymbol{I}_A\cdot\boldsymbol{I}_B\frac{1}{3}\left\{\left\langle\psi_0^{(0)}|\hat{\boldsymbol{L}}_{Aj,x}\hat{R}_0\hat{\boldsymbol{L}}_{Bl,x}\psi_0^{(0)}\right\rangle+\left\langle\psi_0^{(0)}|\hat{\boldsymbol{L}}_{Aj,y}\hat{R}_0\hat{\boldsymbol{L}}_{Bl,y}\psi_0^{(0)}\right\rangle\right.\\
&\quad\left.+\left\langle\psi_0^{(0)}|\hat{\boldsymbol{L}}_{Aj,z}\hat{R}_0\hat{\boldsymbol{L}}_{Bl,z}\psi_0^{(0)}\right\rangle\right\}.
\end{aligned}$$

Thus, finally,

$$\bar{E}_{\text{PSO}}=\frac{1}{3}\left(\frac{e}{mc}\right)^2\sum_{A,B}\sum_{j,l}\gamma_A\gamma_B\boldsymbol{I}_A\cdot\boldsymbol{I}_B\left\langle\psi_0^{(0)}|\hat{\boldsymbol{L}}_{Aj}\hat{R}_0\hat{\boldsymbol{L}}_{Bl}\psi_0^{(0)}\right\rangle.$$

[4] Let us take a closer look at the operator $\left(\nabla_j\times\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}\right)$ acting on a function f (it is necessary to remember that ∇_j in $\nabla_j\times\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}$ is not acting on the components of $\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}$ alone, but in fact on $\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}$ times a wave function). Let us see:

$$\begin{aligned}
&\left(\nabla_j\times\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}\right)f=\boldsymbol{i}\left(\nabla_j\times\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}\right)_x f+\boldsymbol{j}\left(\nabla_j\times\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}\right)_y f+\boldsymbol{k}\left(\nabla_j\times\frac{\boldsymbol{r}_{Aj}}{r_{Aj}^3}\right)_z f\\
&=\boldsymbol{i}\left(\frac{\partial}{\partial y_j}\frac{z_{Aj}}{r_{Aj}^3}-\frac{\partial}{\partial z_j}\frac{y_{Aj}}{r_{Aj}^3}\right)_x f+\text{similarly with } y \text{ and } z\\
&=\boldsymbol{i}\left(-3\frac{y_{Aj}z_{Aj}}{r_{Aj}^4}+\frac{z_{Aj}}{r_{Aj}^3}\frac{\partial}{\partial y_j}+3\frac{y_{Aj}z_{Aj}}{r_{Aj}^4}-\frac{y_{Aj}}{r_{Aj}^3}\frac{\partial}{\partial z_j}\right)_x f+\text{similarly with } y \text{ and } z\\
&=\boldsymbol{i}\left(\frac{z_{Aj}}{r_{Aj}^3}\frac{\partial}{\partial y_j}-\frac{y_{Aj}}{r_{Aj}^3}\frac{\partial}{\partial z_j}\right)_x f+\text{similarly with } y \text{ and } z=\boldsymbol{i}\left(\frac{z_{Aj}}{r_{Aj}^3}\frac{\partial}{\partial y_j}-\frac{y_{Aj}}{r_{Aj}^3}\frac{\partial}{\partial z_j}\right)_x f\\
&\quad+\text{similarly with } y \text{ and } z=-\frac{1}{i\hbar}\left(-\boldsymbol{r}_{Aj}\times\hat{\boldsymbol{p}}_j\right)f=\frac{1}{i\hbar}\left(\boldsymbol{r}_{Aj}\times\hat{\boldsymbol{p}}_j\right)f.
\end{aligned}$$

- $$\begin{aligned}\bar{E}_{\mathrm{SD}} &= \left\langle \psi_0^{(0)} | \hat{B}_6 \hat{R}_0 \hat{B}_6 \psi_0^{(0)} \right\rangle_{\mathrm{aver}} \\ &= \gamma_{el}^2 \sum_{j,l=1}^{N} \sum_{A,B} \gamma_A \gamma_B \left\langle \psi_0^{(0)} | \left[\frac{\hat{\boldsymbol{s}}_j \cdot \boldsymbol{I}_A}{r_{Aj}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_j \cdot \boldsymbol{r}_{Aj}\right)\left(\boldsymbol{I}_A \cdot \boldsymbol{r}_{Aj}\right)}{r_{Aj}^5} \right] \right. \\ &\quad \left. \times \hat{R}_0 \left[\frac{\hat{\boldsymbol{s}}_l \cdot \boldsymbol{I}_B}{r_{Bl}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_l \cdot \boldsymbol{r}_{Bl}\right)\left(\boldsymbol{I}_B \cdot \boldsymbol{r}_{Bl}\right)}{r_{Bl}^5} \right] \psi_0^{(0)} \right\rangle_{\mathrm{aver}} \\ &= \gamma_{el}^2 \sum_{j,l=1}^{N} \sum_{A,B} \gamma_A \gamma_B \boldsymbol{I}_A \cdot \boldsymbol{I}_B \frac{1}{3} \left\{ \left\langle \psi_0^{(0)} | \left[\frac{\hat{\boldsymbol{s}}_{j,x}}{r_{Aj}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_j \cdot \boldsymbol{r}_{Aj}\right) x_{Aj}}{r_{Aj}^5} \right] \right. \right. \\ &\quad \left. \times \hat{R}_0 \left[\frac{\hat{\boldsymbol{s}}_{l,x}}{r_{Bl}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_l \cdot \boldsymbol{r}_{Bl}\right)\left(x_{Bl}\right)}{r_{Bl}^5} \right] \psi_0^{(0)} \right\rangle \\ &\quad + \left\langle \psi_0^{(0)} | \left[\frac{\hat{\boldsymbol{s}}_{j,y}}{r_{Aj}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_j \cdot \boldsymbol{r}_{Aj}\right) y_{Aj}}{r_{Aj}^5} \right] \hat{R}_0 \left[\frac{\hat{\boldsymbol{s}}_{l,y}}{r_{Bl}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_l \cdot \boldsymbol{r}_{Bl}\right)\left(y_{Bl}\right)}{r_{Bl}^5} \right] \psi_0^{(0)} \right\rangle \\ &\quad \left. + \left\langle \psi_0^{(0)} | \left[\frac{\hat{\boldsymbol{s}}_{j,z}}{r_{Aj}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_j \cdot \boldsymbol{r}_{Aj}\right) z_{Aj}}{r_{Aj}^5} \right] \hat{R}_0 \left[\frac{\hat{\boldsymbol{s}}_{l,z}}{r_{Bl}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_l \cdot \boldsymbol{r}_{Bl}\right)\left(z_{Bl}\right)}{r_{Bl}^5} \right] \psi_0^{(0)} \right\rangle \right\}.\end{aligned}$$

Therefore,

$$\begin{aligned}\bar{E}_{\mathrm{SD}} &= \frac{1}{3} \gamma_{el}^2 \sum_{j,l=1}^{N} \sum_{A,B} \gamma_A \gamma_B \boldsymbol{I}_A \cdot \boldsymbol{I}_B \left\langle \psi_0^{(0)} | \left[\frac{\hat{\boldsymbol{s}}_j}{r_{Aj}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_j \cdot \boldsymbol{r}_{Aj}\right) \boldsymbol{r}_{Aj}}{r_{Aj}^5} \right] \right. \\ &\quad \left. \times \hat{R}_0 \left[\frac{\hat{\boldsymbol{s}}_l}{r_{Bl}^3} - 3 \frac{\left(\hat{\boldsymbol{s}}_l \cdot \boldsymbol{r}_{Bl}\right)\left(\boldsymbol{r}_{Bl}\right)}{r_{Bl}^5} \right] \psi_0^{(0)} \right\rangle.\end{aligned}$$

- $$\begin{aligned}\bar{E}_{\mathrm{FC}} &= \left\langle \psi_0^{(0)} | \hat{B}_7 \hat{R}_0 \hat{B}_7 \psi_0^{(0)} \right\rangle \\ &= \gamma_{el}^2 \sum_{j,l=1} \sum_{A,B} \gamma_A \gamma_B \left\langle \psi_0^{(0)} | \delta\left(\boldsymbol{r}_{Aj}\right) \hat{\boldsymbol{s}}_j \cdot \boldsymbol{I}_A \hat{R}_0 \delta\left(\boldsymbol{r}_{Bl}\right) \hat{\boldsymbol{s}}_l \cdot \boldsymbol{I}_B \psi_0^{(0)} \right\rangle_{\mathrm{aver}} \\ &= \gamma_{el}^2 \sum_{j,l=1} \sum_{A,B} \gamma_A \gamma_B \boldsymbol{I}_A \cdot \boldsymbol{I}_B \frac{1}{3} \left\{ \left\langle \psi_0^{(0)} | \delta\left(\boldsymbol{r}_{Aj}\right) \hat{\boldsymbol{s}}_{j,x} \hat{R}_0 \delta\left(\boldsymbol{r}_{Bl}\right) \hat{\boldsymbol{s}}_{l,x} \psi_0^{(0)} \right\rangle \right. \\ &\quad \left. + \left\langle \psi_0^{(0)} | \delta\left(\boldsymbol{r}_{Aj}\right) \hat{\boldsymbol{s}}_{j,y} \hat{R}_0 \delta\left(\boldsymbol{r}_{Bl}\right) \hat{\boldsymbol{s}}_{l,y} \psi_0^{(0)} \right\rangle + \left\langle \psi_0^{(0)} | \delta\left(\boldsymbol{r}_{Aj}\right) \hat{\boldsymbol{s}}_{j,z} \hat{R}_0 \delta\left(\boldsymbol{r}_{Bl}\right) \hat{\boldsymbol{s}}_{l,z} \psi_0^{(0)} \right\rangle \right\}.\end{aligned}$$

Hence,

$$\bar{E}_{\mathrm{FC}} = \frac{1}{3} \left(\frac{8\pi}{3} \right)^2 \gamma_{el}^2 \sum_{j,l=1} \sum_{A,B} \gamma_A \gamma_B \boldsymbol{I}_A \cdot \boldsymbol{I}_B \left\langle \psi_0^{(0)} | \delta\left(\boldsymbol{r}_{Aj}\right) \hat{\boldsymbol{s}}_j \hat{R}_0 \delta\left(\boldsymbol{r}_{Bl}\right) \hat{\boldsymbol{s}}_l \psi_0^{(0)} \right\rangle.$$

The results mean that the coupling constants J are as reported on p. 783.