

**Magnetic Dipole–Dipole Hyperfine Integrals for Slater-Type Orbitals**

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In molecular orbital calculations a linear combination of Slater-type atomic orbitals is frequently used as a trial wavefunction. To determine hyperfine energies, certain matrix elements, involving the electron orbitals and the hyperfine interaction operator, are required. In the paper explicit expressions are reported, which are valid for Slater-type orbitals with principal quantum number  $n = 3$ , and s- or p-type angular dependence. The expressions allow for a fast computation of the integrals.

In Rechnungen mit molekularen Orbitalen werden häufig lineare Kombinationen atomarer Orbitale vom Slater-Typ als Wellenfunktion angewandt. Zur Berechnung der Hyperfeinenergie braucht man bestimmte Matrixelemente, die sich aus den Elektronenorbitalen und aus dem Hyperfeinwechselwirkungsoperator zusammensetzen. In diesem Bericht werden explizite Formeln gegeben, die ihre Gültigkeit haben für Orbitale vom Slater-Typ mit Hauptquantenzahl  $n = 3$ , und s- oder p-Typ-Winkelabhängigkeit. Die Formeln ermöglichen eine schnelle Berechnung dieser Integrale.

**1. Introduction**

The dipole–dipole interaction between an electron, with magnetic moment  $\boldsymbol{\mu}_e = -g_e \mu_B \mathbf{S}$ , and a nucleus, with magnetic moment  $\boldsymbol{\mu}_N = g_N \mu_N \mathbf{I}$ , is given by the Hamiltonian  $H = \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_N / r^3 - 3(\boldsymbol{\mu}_e \cdot \mathbf{r})(\boldsymbol{\mu}_N \cdot \mathbf{r}) / r^5$ . For an electron with spatial wave function  $\varphi$  the matrix elements, which are bilinear in the spin operators  $S_x, S_y, S_z, I_x, I_y$ , and  $I_z$ , are of the general form  $g_e g_N \mu_B \mu_N \mathbf{S} \cdot \mathbf{B} \cdot \mathbf{I}$ . The components of the symmetric tensor  $\mathbf{B}$  are obtained by integrating the interaction over the spatial part  $\varphi$  of the electron wave function:  $B_{\alpha\beta} = \langle \varphi | (3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}) / r^5 | \varphi \rangle$ , with  $r$  the distance to the magnetic nucleus, and  $\alpha, \beta = x, y, z$ . Singularities in the integrals, due to the s-part of the wave function: are eliminated by subtracting from the probability density a non-divergent radial function with equal value at the origin  $r = 0$ . The contact interaction has to be dealt with separately.

To describe the electron, a wave function which is a linear combination of Slater-type atomic orbitals with principal quantum number  $n = 3$  and s- or p-type angular part, is adopted. Expressions for the 3s- and 3p-type atomic orbitals are

$$\chi_{3s,j} = \frac{N_s}{\sqrt{4\pi}} r_j^2 \exp\left(-\alpha_s \frac{r_j}{a_0}\right),$$

$$\chi_{3pz,j} = N_p \frac{\sqrt{3}}{\sqrt{4\pi}} x_j r_j \exp\left(-\alpha_p \frac{r_j}{a_0}\right)$$

with similar expression for  $\chi_{3py,j}$  and  $\chi_{3pz,j}$ . The coefficients  $N_s$  and  $N_p$  are fixed by the requirement of normalization:  $N_s^2 = (2\alpha_s/a_0)^7/6!$ ,  $N_p^2 = (2\alpha_p/a_0)^7/6!$ , where  $a_0 = 0.529 \times 10^{-10}$  m is the Bohr radius, while the Slater orbital exponents  $\alpha_s$  and  $\alpha_p$  are, suitably chosen, dimensionless parameters. The orbitals have their centers,  $r_j = 0$ , at the various sites in the crystal or molecule around the site of the magnetic nucleus. The electron wave function is given by  $\varphi = \sum_i c_i \chi_i$ , with  $\chi_i$  a 3s- or 3p-type

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orbital on some site, and  $c_i$  the appropriate coefficient in the expansion. After substitution of  $\varphi$  into the expression for  $B_{\alpha\beta}$  four different types of terms, as listed below, are obtained.

**Integrals type I.** Both orbitals have their center,  $r_j = 0$ , on the hyperfine site at  $r = 0$ . As  $r = r_j$  one obtains familiar one-center integrals. For completeness sake and for reference the results are reported in the next section.

**Integrals type II.** For this case one orbital has its center on the hyperfine site, while the other orbital has its center at a distance  $R \neq 0$  from the origin. The resulting two-center integrals were evaluated using spheroidal coordinates with azimuth measured around the connecting axis of the two centers. Results, however, only valid for the special case  $\alpha_s = \alpha_p$ , are given in Section 3.

**Integrals type III.** For this case both orbitals have a common center at a distance  $R \neq 0$  from the magnetic nucleus. This again gives rise to two-center integrals, for which explicit expressions are given in Section 4.

**Integrals type IV.** In this most general case the two orbitals involved are centered on different sites, none of which coincides with the hyperfine site.

## 2. Integrals Type I

In this simplest situation the  $\mathbf{B}$ -tensor is axially symmetric, with the axis of symmetry coinciding with that of the wave function. If we take the  $z$ -direction along this axis then the  $\mathbf{B}$ -tensor components for arbitrary form of the radial part  $R_p(r)$  of the orbital are

$$\begin{aligned} B_{xx}^I &= B_{yy}^I = -\frac{2}{5} \left\langle \frac{1}{r^3} \right\rangle_p, \\ B_{zz}^I &= \frac{4}{5} \left\langle \frac{1}{r^3} \right\rangle_p, \\ B_{xy}^I &= B_{xz}^I = B_{yz}^I = 0 \end{aligned}$$

with  $\langle 1/r^3 \rangle_p \equiv \int_0^\infty (1/r^3) R_p^2(r) 4\pi r^2 dr / \int_0^\infty R_p^2(r) 4\pi r^2 dr$ . Returning to the specific case of

Slater-type orbitals, and inserting their radial dependence  $R_p(r) = r^2 \exp(-\alpha_p r/a_0)$ , one obtains  $\langle 1/r^3 \rangle_p = (\alpha_p/a_0)^3/15$ , with the final result

$$\begin{aligned} B_{xx}^I &= B_{yy}^I = -\frac{2}{75} \left( \frac{\alpha_p}{a_0} \right)^3, \\ B_{zz}^I &= \frac{4}{75} \left( \frac{\alpha_p}{a_0} \right)^3, \\ B_{xy}^I &= B_{xz}^I = B_{yz}^I = 0. \end{aligned}$$

## 3. Integrals Type II

Let us specify the part of the electron wave function  $\varphi$  consisting of orbitals which have their center on the hyperfine site,  $r = 0$ , as  $\sigma_0 \chi_{3s,0} + \xi_0 \chi_{3px,0} + \eta_0 \chi_{3py,0} + \zeta_0 \chi_{3pz,0}$ . Orbitals centered on the position  $(0, 0, R)$ , at a distance  $R$  from the magnetic nucleus, similarly form the linear combination  $\sigma_j \chi_{3s,j} + \xi_j \chi_{3px,j} + \eta_j \chi_{3py,j} + \zeta_j \chi_{3pz,j}$ . The hyperfine tensor components of type II, due to overlap of charges, are then given by

$$B_{xx}^{II} = \frac{1}{R^3} (\sigma_0 \sigma_j I_{ss}^{II} + \xi_0 \xi_j I_{xx}^{II} + \eta_0 \eta_j I_{yy}^{II} + \zeta_0 \zeta_j I_{zz}^{II} + \sigma_0 \zeta_j I_{sz}^{II} + \zeta_0 \sigma_j I_{zs}^{II}),$$

$$B_{yy}^{\text{II}} = \frac{1}{R^3} (\sigma_0 \sigma_j I_{ss}^{\text{II}} + \xi_0 \xi_j I_{yy}^{\text{II}} + \eta_0 \eta_j I_{xx}^{\text{II}} + \zeta_0 \zeta_j I_{zz}^{\text{II}} + \sigma_0 \zeta_j I_{sz}^{\text{II}} + \zeta_0 \sigma_j I_{zs}^{\text{II}}),$$

$$B_{zz}^{\text{II}} = -B_{xx}^{\text{II}} - B_{yy}^{\text{II}},$$

$$B_{xy}^{\text{II}} = \frac{1}{R^3} (\xi_0 \eta_j + \eta_0 \xi_j) I_{xy}^{\text{II}},$$

$$B_{xz}^{\text{II}} = \frac{1}{R^3} (\sigma_0 \xi_j I_{sx}^{\text{II}} + \xi_0 \sigma_j I_{xs}^{\text{II}} + \xi_0 \zeta_j I_{xz}^{\text{II}} + \zeta_0 \xi_j I_{zx}^{\text{II}}),$$

$$B_{yz}^{\text{II}} = \frac{1}{R^3} (\sigma_0 \eta_j I_{sx}^{\text{II}} + \eta_0 \sigma_j I_{xs}^{\text{II}} + \eta_0 \zeta_j I_{xz}^{\text{II}} + \zeta_0 \eta_j I_{zx}^{\text{II}}).$$

Although in principle 96 integrals have to be evaluated, many of these vanish, while others may be transformed into each other because of existing symmetry, leaving only eleven independent integrals, denoted  $I_{ss}^{\text{II}}$ ,  $I_{xx}^{\text{II}}$ , etc. in the above expressions. Introducing the abbreviations  $s \equiv \alpha_s R/a_0$ ,  $p \equiv \alpha_p R/a_0$ ,  $q \equiv (sp)^{1/2}$ ,  $t$  an arithmetical average of  $s$  and  $p$ , the results for the integrals then read

$$\begin{aligned} I_{ss}^{\text{II}} = & [(-s^6 - 51s^5 - 480s^4 - 2640s^3 - 7560s^2 - 15120s) + \\ & + \{\ln(2s) + \gamma\} (12s^5 + 144s^4 + 900s^3 + 3420s^2 + 7560s + 7560) + \\ & + \exp(2s) E_1(2s) (-12s^5 + 144s^4 - 900s^3 + 3420s^2 - 7560s + \\ & + 7560)]/45 \exp(s), \end{aligned}$$

$$\begin{aligned} I_{xx}^{\text{II}} = & [(-p^7 - 200p^6 - 3542p^5 - 30150p^4 - 163620p^3 - 464940p^2 - 929880p) + \\ & + \{\ln(2p) + \gamma\} (40p^6 + 900p^5 + 9228p^4 + 55980p^3 + 210960p^2 + \\ & + 464940p + 464940) + \\ & + \exp(2p) E_1(2p) (40p^6 - 900p^5 + 9228p^4 - 55980p^3 + 210960p^2 - \\ & - 464940p + 464940)]/15p^2 \exp(p), \end{aligned}$$

$$\begin{aligned} I_{yy}^{\text{II}} = & [(-p^7 - 78p^6 - 1256p^5 - 10290p^4 - 55020p^3 - 154980p^2 - 309960p) + \\ & + \{\ln(2p) + \gamma\} (16p^6 + 324p^5 + 3180p^4 + 18900p^3 + 70560p^2 + \\ & + 154980p + 154980) + \\ & + \exp(2p) E_1(2p) (16p^6 - 324p^5 + 3180p^4 - 18900p^3 + 70560p^2 - \\ & - 154980p + 154980)]/15p^2 \exp(p), \end{aligned}$$

$$\begin{aligned} I_{zz}^{\text{II}} = & [(p^8 + 75p^7 + 1100p^6 + 9628p^5 + 55020p^4 + 247800p^3 + \\ & + 619920p^2 + 1239840p) + \\ & + \{\ln(2p) + \gamma\} (-16p^7 - 292p^6 - 2856p^5 - 18900p^4 - 89460p^3 - \\ & - 296100p^2 - 619920p - 619920) + \\ & + \exp(2p) E_1(2p) (16p^7 - 292p^6 + 2856p^5 - 18900p^4 + 89460p^3 - \\ & - 296100p^2 + 619920p - 619920)]/15p^2 \exp(p), \end{aligned}$$

$$I_{sz}^{\text{II}} = \left(\frac{q}{t}\right)^7 \sqrt{3} [(3t^7 + 152t^6 + 1490t^5 + 8460t^4 + 37080t^3 + 90720t^2 + 181440t) + \\ + \{\ln(2t) + \gamma\} (-36t^6 - 432t^5 - 2916t^4 - 13500t^3 - 43740t^2 - \\ - 90720t - 90720) + \\ + \exp(2t) E_1(2t) (-36t^6 + 432t^5 - 2916t^4 + 13500t^3 - 43740t^2 + \\ + 90720t - 90720)]/135t \exp(t),$$

$$I_{zs}^{\text{II}} = \left(\frac{q}{t}\right)^7 \sqrt{3} [(-3t^7 - 226t^6 - 3328t^5 - 25830t^4 - 134820t^3 - \\ - 374220t^2 - 748440t) + \\ + \{\ln(2t) + \gamma\} (48t^6 + 876t^5 + 8100t^4 + 46620t^3 + 171360t^2 + \\ + 374220t + 374220) + \\ + \exp(2t) E_1(2t) (48t^6 - 876t^5 + 8100t^4 - 46620t^3 + 171360t^2 - \\ - 374220t + 374220)]/135t \exp(t),$$

$$I_{xy}^{\text{II}} = [(-61p^6 - 1143p^5 - 9930p^4 - 54300p^3 - 154980p^2 - 309960p) + \\ + \{\ln(2p) + \gamma\} (12p^6 + 288p^5 + 3024p^4 + 18540p^3 + 70200p^2 + \\ + 154980p + 154980) + \\ + \exp(2p) E_1(2p) (12p^6 - 288p^5 + 3024p^4 - 18540p^3 + 70200p^2 - \\ - 154980p + 154980)]/15p^2 \exp(p),$$

$$I_{sx}^{\text{II}} = \left(\frac{q}{t}\right)^7 \sqrt{3} [(3t^6 + 161t^5 + 1740t^4 + 10200t^3 + 30240t^2 + 60480t) + \\ + \{\ln(2t) + \gamma\} (-36t^5 - 504t^4 - 3420t^3 - 13500t^2 - \\ - 30240t - 30240) + \\ + \exp(2t) E_1(2t) (36t^5 - 504t^4 + 3420t^3 - 13500t^2 + 30240t - \\ - 30240)]/45t \exp(t),$$

$$I_{xs}^{\text{II}} = \left(\frac{q}{t}\right)^7 \sqrt{3} [(-61t^6 - 1027t^5 - 8370t^4 - 44460t^3 - 124740t^2 - 249480t) + \\ + \{\ln(2t) + \gamma\} (12t^6 + 264t^5 + 2592t^4 + 15300t^3 + 56880t^2 + \\ + 124740t + 124740) + \\ + \exp(2t) E_1(2t) (12t^6 - 264t^5 + 2592t^4 - 15300t^3 + 56880t^2 - \\ - 124740t + 124740)]/45t \exp(t),$$

$$I_{zx}^{\text{II}} = [(61p^7 + 1021p^6 + 9363p^5 + 54300p^4 + 246360p^3 + 619920p^2 + 1239840p) + \\ + \{\ln(2p) + \gamma\} (-12p^7 - 264p^6 - 2736p^5 - 18540p^4 - 88740p^3 - \\ - 295380p^2 - 619920p - 619920) + \\ + \exp(2p) E_1(2p) (12p^7 - 264p^6 + 2736p^5 - 18540p^4 + 88740p^3 - \\ - 295380p^2 + 619920p - 619920)]/15p^2 \exp(p),$$

$$\begin{aligned}
I_{zx}^{\text{II}} = & [(3p^7 + 295p^6 + 4911p^5 + 40800p^4 + 219360p^3 + 619920p^2 + 1239840p) + \\
& + \{\ln(2p) + \gamma\} (-60p^6 - 1260p^5 - 12564p^4 - 75240p^3 - 281880p^2 - \\
& - 619920p - 619920) + \\
& + \exp(2p) E_1(2p) (-60p^6 + 1260p^5 - 12564p^4 + 75240p^3 - 281880p^2 + \\
& + 619920p - 619920)]/15p^2 \exp(p).
\end{aligned}$$

The results for the integrals with overlap between an s- and a p-type orbital, i.e.  $I_{sz}^{\text{II}}$ ,  $I_{zs}^{\text{II}}$ ,  $I_{sx}^{\text{II}}$ , and  $I_{xs}^{\text{II}}$ , are strictly valid only for  $s = p = t$ . If  $\alpha_s \neq \alpha_p$ , then a best compromise is obtained by taking  $t = (s + 3p)/4$  for  $I_{sz}^{\text{II}}$  and  $I_{zs}^{\text{II}}$ , and  $t = (3s + p)/4$  for  $I_{sx}^{\text{II}}$  and  $I_{xs}^{\text{II}}$ . Function  $E_1(y)$  is the exponential integral:  $\int_y^\infty dx/x \exp(x)$ , for which tables and approximations are found in mathematical handbooks [1]. The constant  $\gamma = 0.5772$  is Euler's constant. In the limit of  $R \rightarrow 0$  the present results for the type II components of the  $\mathbf{B}$ -tensor reduce to those of the previous section.

#### 4. Integrals Type III

As in the previous section we again take the center of the atomic orbitals at a distance  $R$  from the hyperfine site along the  $z$ -direction and use the same expansion for  $\varphi$ . The hyperfine tensor components due to the charge in the orbitals around position  $(0, 0, R)$  are given by

$$B_{xx}^{\text{III}} = \frac{1}{R^3} (\sigma_j^2 I_{ss}^{\text{III}} + \xi_j^2 I_{xx}^{\text{III}} + \eta_j^2 I_{yy}^{\text{III}} + \zeta_j^2 I_{zz}^{\text{III}} + \sigma_j \zeta_j I_{sz}^{\text{III}}),$$

$$B_{yy}^{\text{III}} = \frac{1}{R^3} (\sigma_j^2 I_{ss}^{\text{III}} + \xi_j^2 I_{yy}^{\text{III}} + \eta_j^2 I_{xx}^{\text{III}} + \zeta_j^2 I_{zz}^{\text{III}} + \sigma_j \zeta_j I_{sz}^{\text{III}}),$$

$$B_{zz}^{\text{III}} = -B_{xx}^{\text{III}} - B_{yy}^{\text{III}},$$

$$B_{xy}^{\text{III}} = \frac{1}{R^3} \xi_j \eta_j I_{xy}^{\text{III}},$$

$$B_{xz}^{\text{III}} = \frac{1}{R^3} (\sigma_j \xi_j I_{sx}^{\text{III}} + \xi_j \zeta_j I_{xz}^{\text{III}}),$$

$$B_{yz}^{\text{III}} = \frac{1}{R^3} (\sigma_j \eta_j I_{sy}^{\text{III}} + \eta_j \zeta_j I_{yz}^{\text{III}}).$$

Only eight independent integrals have to be determined. Defining similarly as before  $s \equiv \alpha_s R/a_0$ ,  $p \equiv \alpha_p R/a_0$ ,  $q \equiv (sp)^{1/2}$ , and  $t \equiv (s + p)/2$ , the required results are:

$$\begin{aligned}
I_{ss}^{\text{III}} = & -1 + (s^7 + 3s^6 + 18s^5 + 90s^4 + 360s^3 + 1080s^2 + 2160s + \\
& + 2160)/2160 \exp(s),
\end{aligned}$$

$$\begin{aligned}
I_{xx}^{\text{III}} = & -1 + \frac{100.8}{p^2} - (p^7 + 11p^6 + 80p^5 + 444p^4 + 1896p^3 + 5928p^2 + \\
& + 12096p + 12096)/120p^2 \exp(p),
\end{aligned}$$

$$\begin{aligned}
I_{yy}^{\text{III}} = & -1 + \frac{33.6}{p^2} - (p^6 + 14p^5 + 108p^4 + 552p^3 + 1896p^2 + 4032p + \\
& + 4032)/120p^2 \exp(p),
\end{aligned}$$

$$I_{zz}^{\text{III}} = -1 - \frac{134.4}{p^2} + (p^9 + 3p^8 + 24p^7 + 162p^6 + 924p^5 + 4392p^4 + 16848p^3 + 49104p^2 + 96768p + 96768)/720p^2 \exp(p),$$

$$I_{sz}^{\text{III}} = \left(\frac{q}{t}\right)^7 \sqrt{3} \left\{ \frac{14}{t} - (t^8 + 3t^7 + 21t^6 + 126t^5 + 630t^4 + 2520t^3 + 7560t^2 + 15120t + 15120)/1080t \exp(t) \right\},$$

$$I_{xy}^{\text{III}} = \frac{67.2}{p^2} - (p^7 + 10p^6 + 66p^5 + 336p^4 + 1344p^3 + 4032p^2 + 8064p + 8064)/120p^2 \exp(p),$$

$$I_{sz}^{\text{III}} = \left(\frac{q}{t}\right)^7 \sqrt{3} \left\{ \frac{14}{t} - (t^7 + 7t^6 + 42t^5 + 210t^4 + 840t^3 + 2520t^2 + 5040t + 5040)/360t \exp(t) \right\},$$

$$I_{xz}^{\text{III}} = -\frac{268.8}{p^2} + (p^8 + 7p^7 + 46p^6 + 270p^5 + 1344p^4 + 5376p^3 + 16128p^2 + 32256p + 32256)/120p^2 \exp(p).$$

For the special case  $R = 0$  the results for the type III integrals are identical to those given in Section 2.

### 5. Integrals Type IV

The two orbitals involved have their center on different sites which do not coincide with the hyperfine site at  $r = 0$ . For the resulting three-center integrals no analytical expressions were derived. A method to compute these integrals was outlined by Steinborn and Ruedenberg [2]. We carried out only some numerical calculations for the specific values of the Slater orbital exponents  $\alpha_s = 1.87$  and  $\alpha_p = 1.60$ , for the nearest-neighbor distance in the silicon lattice,  $R = 2.351 \times 10^{-10}$  m. As expected, from the reduced overlap between the three functions in the integrand, the resulting values have a tendency of being small. Often, the contributions from the type IV integrals are negligibly small when compared to the values of the type I, II, and III integrals.

### 6. Concluding Remarks

To check for possible errors in the reported formula's results by using them were compared with the results obtained from numerical integrations. This was done for the specific case of Slater orbital exponents  $\alpha_s = 1.87$  and  $\alpha_p = 1.60$ , for nearest neighbors and next-nearest neighbors in a silicon lattice, at  $R = 2.351 \times 10^{-10}$  and  $3.839 \times 10^{-10}$  m, respectively. Always the numerical results could be brought into agreement with the results obtained analytically to within 0.1%. The time required for the numerical computations, however, is then about  $10^6$  times larger.

### References

- [1] M. ABRAMOWITZ and I. A. STEGUN, Handbook of Mathematical Functions, Dover Publ., Inc., New York 1965.
- [2] E. O. STEINBORN and K. RUEDENBERG, Internat. J. Quantum Chem. **6**, 413 (1972).

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