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# INTEGRALS OVER GTOs USEFUL IN THE CALCULATION OF nmr SHIELDING CONSTANTS*

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Analytical expressions for all the integrals occurring in the calculation of the nmr shielding constants in second-order perturbation theory are given for GTOs of the *s*-type and the *p*-type.

The nmr shielding constant can be calculated by second-order perturbation theory. For the most frequently used MO wave function the shielding constant $\sigma$ is estimated by the formula [1]:

$$\begin{aligned}
\sigma &= \sigma_{\text{dia}} + \sigma_{\text{para}}\,, \\
\sigma_{\text{dia}} &= \varkappa \sum_{i=1}^{n} \left\{ \left\langle \psi_i \left| \frac{1}{r_A} \right| \psi_i \right\rangle + \mathbf{R}_{A_0} \left\langle \psi_i \left| \frac{\mathbf{r}_A}{r_A^3} \right| \psi_i \right\rangle \right\}, \\
\sigma_{\text{para}} &= \varkappa \sum_{i=1}^{n} \sum_{p=n+1}^{m} (\psi_i \,|\, \mathbf{l}_0 \,|\, \psi_p) \left\langle \psi_p \left| \frac{\mathbf{l}_A}{r_A^3} \right| \psi_i \right\rangle \Big/ \Delta E_{ip}\,,
\end{aligned} \tag{1}$$

with

$$\mathbf{R}_{A_0} = \mathbf{R}_A - \mathbf{R}_0\,,$$

$$\mathbf{l}_0 = (\mathbf{r} - \mathbf{R}_0) \wedge \nabla\,,$$

$$\mathbf{l}_A = (\mathbf{r} - \mathbf{R}_A) \wedge \nabla\,,$$

where

$\mathbf{R}_A$: position vector of nucleus $A$ the shielding of which is to be estimated,

$\mathbf{R}_0$: origin of the gauge,

$r_A$: distance between electron and nucleus $A$,

$\mathbf{r}$: position vector of the electron,

$\psi_i$: occupied MO,

$\psi_p$: virtual MO,

$\Delta E_{ip}$: energy difference between ground and excited state,

$\varkappa = 35.50$ dimensionless constant.

* The formulae were derived by F. B. and the paper was compiled in absence of him by D. K.

If the MOs are approximated by a LCAO expansion we have to calculate the following integrals:

$$\left\langle \Phi_A \left| \frac{1}{r_B} \right| \Phi_C \right\rangle, \tag{2}$$

$$\left\langle \Phi_A \left| \frac{\mathbf{l}_B}{r_B^3} \right| \Phi_C \right\rangle, \tag{3}$$

$$\left\langle \Phi_A \left| \frac{\mathbf{r}_B}{r_B^3} \right| \Phi_C \right\rangle, \tag{4}$$

$$\left\langle \Phi_A \left| \mathbf{l}_B \right| \Phi_C \right\rangle. \tag{5}$$

$\Phi_A$, $\Phi_C$ are AOs centred at nuclei $A$ or $C$, respectively, $\mathbf{r}_B$ is the distance vector from the centre $B$ to the electron and $\mathbf{l}_B = \mathbf{r}_B \wedge \nabla$. The two centre integrals may be calculated either by integration in prolate spherical coordinates (type (2) [2], and type (5) [3]) or by the Fourier folding method (types (3), (4) [4]). For the three centre integrals closed analytical formulae exist only for integrals of type (5) [3]. However, the STO can be approximately expanded by finite sets of GTOs [5], and the integrals over GTOs can be expressed analytically.

We report here formulae for the integrals over GTOs in such a form that they can be used in computation at once. Here we give formulae for the integrals of type (2) and (4) too, although formulae for these in another form have already been published ([5], [6]).

We use normalized GTOs of the form

$$g_s(\mathbf{r}, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2} \qquad \text{for } s\text{-type orbitals and}$$

$$g_i(\mathbf{r}, \alpha) = 2\sqrt{\alpha}\left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} x_i e^{-\alpha r^2} \qquad \text{for } p\text{-type orbitals,}$$

and the normalization factors for the integrals become

$$\langle g_s(\mathbf{r}_A, \alpha) \,|\, \mathrm{Op} \,|\, g_s(\mathbf{r}_C, \gamma)\rangle = \left(\frac{2}{\pi}\right)^{\frac{3}{2}} (\alpha\gamma)^{3/4} \langle e^{-\alpha r_A^2} \,|\, \mathrm{Op} \,|\, e^{-\gamma r_C^2}\rangle,$$

$$\langle g_s(\mathbf{r}_A, \alpha) \,|\, \mathrm{Op} \,|\, g_i(\mathbf{r}_C, \gamma)\rangle = 2\left(\frac{2}{\pi}\right)^{\frac{3}{2}} (\alpha^3\gamma^5)^{1/4} \langle e^{-\alpha r_A^2} \,|\, \mathrm{Op} \,|\, x_i^C e^{-\gamma r_C^2}\rangle,$$

$$\langle g_i(\mathbf{r}_A, \alpha) \,|\, \mathrm{Op} \,|\, g_j(\mathbf{r}_C, \gamma) = 4\left(\frac{2}{\pi}\right) (\alpha\gamma)^{5/4} \langle x_i^A e^{-\alpha r_A^2} \,|\, \mathrm{Op} \,|\, x_j^C e^{-2r_C^2}\rangle.$$

where $\mathbf{r}$: location vector from the origin (components $x_i$),

$R_i^A$: $i$-th component of the location vector to $A$,
$x_i^A$: $x_i - R_i^A$.

In the following we use still the short hand writing

$R_i^{AB}$, for $R_i^A - R_i^B$ and
$R^{AB}$, for the distance between $A$ and $B$.

In the calculation with GTOs their unique property is used that the product of two Gaussians centred e.g. on $A$ and $C$ is again a Gaussian centred between $A$ and $C$:

$$e^{-\alpha r_a^2} e^{-\gamma r_c^2} = e^{-\frac{\alpha\gamma}{\alpha+\gamma} R_{AC}^2} e^{-(\alpha+\gamma) r_D^2}, \tag{6}$$

where the new centre $D$ has the coordinates

$$R_i^D = \frac{\alpha R_i^A + \gamma R_i^C}{\alpha + \gamma}.$$

In the actual calculation of the integrals we reduce the three centre integrals by using Eq. (6) to two centre integrals, which are transformed into a local coordinate system. This local system (LS) is chosen in such a way that the $Z$ axes lie along the internuclear axis and point toward each other. The $X$ axes are taken parallel and so are the $Y$ axes. We have a right-handed system on the centre $D$ and a left-handed one on the other centre. The components of a vector located at centre $D$ transforms by means of a matrix $R$ from the LS into the molecular coordinate system

$$\mathbf{r}_D = R \cdot \mathbf{r}'_D,$$

where $\mathbf{r}_D$ is the vector in the molecular and $\mathbf{r}'_D$ in the local coordinate system. The transformation matrix $R$ has the form

$$R = \begin{bmatrix} |\sin\alpha| & 0 & \cos\alpha \\ \dfrac{-\cos\alpha\cos\beta}{|\sin\alpha|} & \dfrac{\cos\gamma}{|\sin\alpha|} & \cos\beta \\ \dfrac{-\cos\alpha\cos\gamma}{|\sin\alpha|} & \dfrac{-\cos\beta}{|\sin\alpha|} & \cos\gamma \end{bmatrix},$$

where $\cos\alpha$, $\cos\beta$, $\cos\gamma$ are the directional cosine between the $X, Y, Z$ axes in the molecular and local system.

For a vector at the other centre we must use a transformation matrix $L$ which is connected with $R$ by the relation

$$L = R \cdot \begin{bmatrix} 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

because there is a left-handed system.

The formulae of this transformation are:

Integrals of the type $\langle \Phi_A \mid \frac{1}{r_B} \mid \Phi_B \rangle$:

$$\left\langle e^{-\alpha r_A^2} \left| \frac{1}{r_B} \right| e^{-\gamma r_C^2} \right\rangle = K \left\langle e^{-\delta r_D^2} \left| \frac{1}{r_B} \right\rangle_{LS},$$

$$\left\langle e^{-\alpha r_A^2} \left| \frac{1}{r_B} \right| x_i^C e^{\gamma r_C^2} \right\rangle = K \left[ L_{i,3} \left\langle e^{-\delta r_D^2} \left| \frac{z_B}{r_B} \right\rangle_{LS} + R_i^{BC} \left\langle e^{-\delta r_D^2} \left| \frac{1}{r_B} \right\rangle_{LS} \right] \right],$$

$$\left\langle x_i^A e^{-\alpha r_A^2} \left| \frac{1}{r_B} \right| x_j^C e^{-\gamma r_C^2} \right\rangle = \left[ K \left\langle e^{-\delta r_D^2} \left| \frac{x^2}{r_B} \right\rangle_{LS} \cdot (L_{i,1} L_{j,1} + L_{i,2} L_{j,2}) + \right. \right.$$

$$+ \left\langle e^{-\delta r_D^2} \left| \frac{z_B^2}{r_B} \right\rangle_{LS} \cdot L_{i,3} \cdot L_{j,3} + \left\langle e^{-\delta r_D^2} \left| \frac{z_B}{r_B} \right\rangle_{LS} \cdot (R_j^{BC} L_{i,3} + R_i^{BA} L_{j,3}) + \right.$$

$$\left. \left. + \left\langle e^{-\delta r_D^2} \left| \frac{1}{r_B} \right\rangle_{LS} \cdot R_i^{BA} \cdot R_j^{BC} \right] \right].$$

Integrals of the type $\left\langle \Phi_A \left| \frac{\mathbf{r}_B}{r_B^3} \right| \Phi_C \right\rangle$:

$$\left\langle e^{-\alpha r_A^2} \left| \frac{x_k^B}{r_B^3} \right| e^{-\gamma r_C^2} \right\rangle = K L_{k,3} \cdot \left\langle e^{-\delta r_D^2} \left| \frac{z_B}{r_B^3} \right\rangle_{LS},$$

$$\left\langle e^{-\alpha r_A^2} \left| \frac{x_k^B}{r_B^3} \right| x_j^C e^{\gamma r_C^2} \right\rangle = K \left\{ \left\langle e^{-\delta r_D^2} \left| \frac{x^2}{r_B^3} \right\rangle_{LS} \cdot (L_{K,1} L_{j,1} + L_{k,2} L_{j,2}) + \right. \right.$$

$$\left. \left. + \left\langle e^{-\delta r_D^2} \left| \frac{z_B^2}{r_B^3} \right\rangle_{LS} L_{k,3} L_{j,3} + \left\langle e^{-\delta r_D^2} \left| \frac{z_B}{r_B^3} \right\rangle_{LS} R_j^{BC} L_{k,3} \right\} \right\},$$

$$\left\langle x_i^A e^{-\alpha r_A^2} \left| \frac{x_k^B}{r_B^3} \right| x_j^C e^{-\gamma r_C^2} \right\rangle = K \left\{ \left\langle e^{-\delta r_D^2} \left| \frac{y^2 z_B}{r_B^3} \right\rangle_{LS} [L_{i,} L_{k,1} L_{j,3} + L_{i,1} L_{k,3} L_{j,1} + \right. \right.$$

$$\left. \left. + L_{i,2} L_{k,2} L_{j,3} + L_{i,2} L_{k,3} L_{j,2} + L_{i,3} L_{k,1} L_{j,1} + L_{i,3} L_{k,2} L_{j,2}] + \right. \right.$$

$$+\left\langle e^{-\delta r_D^2}\left|\frac{z_B^3}{r_B^3}\right\rangle_{LS} L_{i,3}L_{k,3}L_{j,3}+\left\langle e^{-\delta r_D^2}\left|\frac{x^2}{r_B^3}\right\rangle_{LS}[R_j^{BC}(L_{k,1}L_{i,1}+L_{k,2}L_{i,2})+\right.\right.$$

$$+R_i^{BA}(L_{k,1}L_{j,1}+L_{k,2}L_{j,2})]+\left\langle e^{-\delta r_D^2}\left|\frac{z_B^2}{r_B^3}\right\rangle_{LS}[R_j^{BC}L_{k,3}L_{i,3}+R_i^{BA}L_{k,3}L_{j,3}]+\right.$$

$$\left.+\left\langle e^{-\delta r_D^2}\left|\frac{z_B}{r_B^3}\right\rangle R_i^{BA}R_j^{BC}L_{k,3}\right\}.\right.$$

**Integrals of the type** $\left\langle \Phi_A\left|\frac{\mathbf{l}_B}{r_B^3}\right|\Phi_C\right\rangle$**:**

$$\left\langle e^{-\alpha r_A^2}\left|\frac{l_{Bk}}{r_B^3}\right|e^{-\gamma r_C^2}\right\rangle = 2\gamma K\left\langle e^{-\delta r_D^2}\left|\frac{z_B}{r_B^3}\right\rangle_{LS}(R_{k+1}^{BC}L_{k-1,3}-R_{k-1}^{BC}L_{k+1,3}),\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{l_{Bk}}{r_B^3}\right|x_j^C e^{-\gamma r_C^2}\right\rangle =$$

$$=2\alpha K\left\{\left\langle e^{-\delta r_D^2}\left|\frac{x^2}{r_B^3}\right\rangle_{LS}[R_{k-1}^{BA}(L_{j,1}L_{k+1,1}+L_{j,2}L_{k+1,2})+\right.\right.$$

$$-R_{k+1}^{BA}(L_{j,1}L_{k-1,1}+L_{j,2}L_{k-1,2})]+$$

$$+\left\langle e^{-\delta r_D^2}\left|\frac{z_B^2}{r_B^3}\right\rangle_{LS}\cdot L_{j,3}[L_{k+1,3}R_{k-1}^{BA}-L_{k-1,3}R_{k+1}^{BA}]+\right.$$

$$\left.+\left\langle e^{-\delta r_D^2}\left|\frac{z_B}{r_B^3}\right\rangle_{LS}\cdot R_j^{BC}[L_{k+1,3}R_{k-1}^{BA}-L_{k-1,3}R_{k+1}^{BA}]\right\},\right.$$

$$\left\langle x_i^A e^{-\alpha r_A^2}\left|\frac{l_{Bk}}{r_B^3}\right|x_j^C e^{-\gamma r_C^2}\right\rangle =$$

$$=K\left\{\left\langle e^{-\delta r_D^2}\left|\frac{z_B}{r_B^3}\right\rangle_{LS}[R_i^{BA}(L_{k+1,3}\delta_{j,k-1}-L_{k-1,3}\delta_{j,k+1})+\right.\right.$$

$$+2\gamma R_j^{BC}R_i^{BA}(R_{k+1}^{BC}L_{k-1,3}-R_{k-1}^{BC}L_{k+1,3})]+$$

$$+\left\langle e^{-\delta r_D^2}\left|\frac{x^2}{r_B^3}\right\rangle_{LS}[L_{i,1}(L_{k+1,1}\delta_{j,k-1}-L_{k-1,1}\delta_{j,k+1})+\right.$$

$$+2\gamma(R_j^{BC}L_{i,1}+L_{j,1}R_i^{BA})(R_{k+1}^{BC}L_{k-1,1}-R_{k-1}^{BC}L_{k+1,1})+$$

$$+L_{i,2}(L_{k+1,2}\delta_{j,k-1}-L_{k-1,2}\delta_{j,k+1})+$$

$$+2\gamma(R_j^{BC}L_{i,2}+R_i^{BA}L_{j,2})(R_{k+1}^{BC}L_{k-1,2}-R_{k-1}^{BC}L_{k+1,2})]+$$

$$+\left\langle e^{-\delta r_D^2}\left|\frac{z_B^2}{r_B^3}\right\rangle_{LS}[L_{i,3}(L_{k+1,3}\delta_{j,k-1}-L_{k-1,3}\delta_{j,k+1})+\right.$$

$$+2\gamma(R_j^{BC}L_{i,3}+R_i^{BA}L_{j,3})(R_{k+1}^{BC}L_{k-1,3}-R_{k-1}^{BC}L_{k+1,3})]+$$

$$+\left\langle e^{-\delta r_D^2}\left|\frac{x^2 z_B}{r_B^3}\right\rangle_{LS}\cdot 2\gamma\,[(L_{i,1}L_{j,1}+L_{i,2}L_{j,2})\cdot\right.$$

$$(R_{k+1}^{BC'}L_{k-1,3}-R_{k-1}^{BC}L_{k+1,3})+(L_{i,1}L_{j,3}+L_{i,3}L_{j,1})\cdot(R_{k+1}^{BC}L_{k-1,1}-R_{k-1}^{BC}L_{k+1,1})+$$

$$+(L_{i,2}L_{j,3}+L_{i,3}L_{j,2})\cdot(R_{k+1}^{BC}L_{k-1,2}-R_{k-1}^{BC}L_{k+1,2})]+$$

$$\left.+\left\langle e^{-\delta r_D^2}\left|\frac{z_B^3}{r_B^3}\right\rangle_{LS}\cdot 2\gamma\cdot[L_{i,3}L_{j,3}(R_{k+1}^{BC}L_{k-1,3}-R_{k-1}^{BC}L_{k+1,3})]\right\}.\right.$$

In the formulae we have used the abbreviations

$$e^{-\frac{\alpha\gamma}{\alpha+\gamma}R_{AC}^2}=K$$

and $L_{k+1,1}$ etc. is to be understood in a cyclic way (e.g. $L_{k+1,1}=L_{1,1}$ for $k=3$).

The integrals in the local coordinate system can by solved by integration in prolate spherical coordinates. The result of the integration can be expressed in terms of the incomplete error function

$$F_m(x)=\int_0^1 t^{2m}e^{-xt^2}\,dt\,,$$

which can be computed by standard methods [7].

$$\left\langle e^{-\alpha r_A^2}\left|\frac{1}{r_B}\right\rangle_{LS}=\frac{2\pi}{\alpha}F_0(\alpha R_{AB}^2)\,,\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{z_B}{r_B}\right\rangle_{LS}=\frac{2\pi}{\alpha}R_{AB}[F_0(\alpha R_{AB}^2)-F_1(\alpha R_{AB}^2)]\,,\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{z_B^2}{r_B}\right\rangle_{LS}=\frac{2\pi}{\alpha}R_{AB}\left[\{F_0(\alpha R_{AB}^2)-F_1(\alpha R_{AB}^2)\}+\frac{1}{\alpha R_{AB}^2}F_1(\alpha R_{AB}^2)\right],\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{z_B}{r_B^3}\right\rangle_{LS}=4\pi R_{AB}F_1(\alpha R_{AB}^2)\,,\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{z_B^2}{r_B^3}\right\rangle_{LS}=\frac{2\pi}{\alpha}[F_0(\alpha R_{AB}^2)-2F_1(\alpha R_{AB}^2)]\,,\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{z_B^3}{r_B^3}\right\rangle_{LS}=\frac{2\pi R_{AB}}{\alpha}[F_0(\alpha R_{AB}^2)-3F_1(\alpha R_{AB}^2)+2F_2(\alpha R_{AB}^2)]\,,\right.$$

$$\left\langle e^{-\alpha r_A^2}\left|\frac{x^2}{r_B}\right\rangle_{LS}=\frac{\pi}{\alpha}[F_0(\alpha R_{AB}^2)-\frac{1}{2}F_1(\alpha R_{AB}^2)]\,,\right.$$

$$\left\langle e^{-\alpha r_A^2} \left| \frac{x^2}{r_B^3} \right\rangle = \frac{2\pi}{\alpha} F_1(\alpha R_{AB}^2) \right.,$$

$$\left\langle e^{-\alpha r_A^2} \left| \frac{y^2 z_B}{r_B^3} \right\rangle_{LS} = \frac{2\pi R_{AB}}{\alpha} [F_1(\alpha R_{AB}^2) - F_2(\alpha R_{AB}^2)] \right..$$

The formulae were checked by calculating the two centre integrals with these expressions in a 6-GTO expansion of the STO and by direct calculation with STO using the formulae of [2] and [4]. No discrepancy was detected.

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