

## ***Ab initio* Calculation of Magnetic Shielding and Susceptibility. I. Molecular Integrals over Gauge Invariant Gaussian Orbitals.**

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Received August 21, 1974

The analytical solutions for the integrals needed in the SCF computation of magnetic shielding and susceptibility with gauge invariant Gaussian atomic functions are described. All the integrals can be expressed in terms of known functions.

### INTRODUCTION

The advantages of the application of gauge invariant atomic orbitals (GIAO) in the calculations of magnetic susceptibility or magnetic shielding have been shown<sup>1,2</sup>. The integrals that appear in such calculations are in general complex. Ditchfield<sup>1</sup> expanded the gauge factors and retained only the first and the second terms. Though this method seems to be accurate enough it is easier and more explicit if the integrals with GIAO are solved analytically.

We would like to show that these integrals are not much more cumbersome than the ones without GI factors<sup>3</sup>, if the Gaussian type orbitals are used as a basis set.

### MATRIX ELEMENTS IN THE PRESENCE OF PERTURBATION

The electronic Hamiltonian in the presence of the uniform magnetic field  $\mathbf{H}$  is given by

$$\mathbf{H} = \frac{1}{2m} \sum_i \left( \frac{\hbar}{i} \nabla_i + \frac{e}{c} \mathbf{A}_i \right)^2 + V$$

where  $\mathbf{A}_i$  is the magnetic vector potential at the site of the  $i$ -th electron. Magnetic properties of molecules can be calculated with the gauge invariant atomic orbitals simply and accurately. GIAO is defined as

$$\chi_A(\mathbf{A}) = \exp\left(-\frac{ie}{\hbar c} \mathbf{A}_A \cdot \mathbf{r}\right) \chi_A(0) \quad (1)$$

where  $\mathbf{A}_A$  is the vector potential at the point on which the atomic orbital  $\chi_A$  is located.

The perturbed wavefunction can be calculated with the Hamiltonian including only those parts which describe the unperturbed problem and the

effect of the external magnetic field. For this case the magnetic vector potential is of the form

$$\mathbf{A} = \frac{1}{2} \mathbf{H} \times \mathbf{r}$$

Using the property of GIAO

$$\begin{aligned} & \left( \frac{\hbar}{i} \nabla + \frac{e}{c} \mathbf{A} \right)^2 \exp \left( -\frac{ie}{\hbar c} \mathbf{A}_A \cdot \mathbf{r} \right) \chi_A(0) = \\ & = \exp \left( -\frac{ie}{\hbar c} \mathbf{A}_A \cdot \mathbf{r} \right) \left[ \frac{\hbar}{i} \nabla + \frac{e}{c} (\mathbf{A} - \mathbf{A}_A) \right]^2 \chi_A(0) \end{aligned}$$

we can write the matrix elements including the linear and the quadratic perturbations in the form

$$\langle \chi_A(\mathbf{A}) | -\frac{ie\hbar}{mc} \mathbf{A} \cdot \nabla | \chi_B(\mathbf{A}) \rangle = -\frac{ie\hbar}{mc} \langle \exp \left[ \frac{ie}{\hbar c} (\mathbf{A}_A - \mathbf{A}_B) \cdot \mathbf{r} \right] \chi_A(0) | (\mathbf{A} - \mathbf{A}_B) \cdot \nabla | \chi_B(0) \rangle \quad (2)$$

$$\langle \chi_A(\mathbf{A}) | \frac{e^2}{2mc^2} \mathbf{A}^2 | \chi_B(\mathbf{A}) \rangle = \frac{e^2}{2mc^2} \langle \exp \left[ \frac{ie}{\hbar c} (\mathbf{A}_A - \mathbf{A}_B) \cdot \mathbf{r} \right] \chi_A(0) | (\mathbf{A} - \mathbf{A}_B)^2 | \chi_B(0) \rangle \quad (3)$$

#### GENERAL INTEGRALS FOR THE MATRIX ELEMENTS

Here we give the analytical expressions for the matrix elements needed in the SCF computation. The derivations of the integrals are similar to those of Huzinaga<sup>3,4</sup>.

In the Cartesian coordinates a GI GTO centered at A is written as

$$\chi_A(\mathbf{A}) = \chi(\mathbf{A}, a, l, m, n, \mathbf{M}_A) = \exp(-i \mathbf{M}_A \cdot \mathbf{r}) \chi(\mathbf{A}, a, l, m, n) \quad (4)$$

where

$$\chi(\mathbf{A}, a, l, m, n) = x_A^l y_A^m z_A^n \exp(-a r_A^2) \quad (5)$$

Here  $x_A$ ,  $y_A$  and  $z_A$  are the components of a position vector  $\mathbf{r}_A$  relative to  $\mathbf{A}$ ,  $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$ , and  $l, m, n$  are zeros or positive integers.  $\mathbf{M}_A$  is a constant vector proportional to the vector potential at the central point  $\mathbf{A}$  of the Gaussian function (5):

$$\mathbf{M}_A = \frac{e}{\hbar c} \cdot \frac{1}{2} \mathbf{H} \times \mathbf{A}$$

The normalization factor for the GI GTO (4) is the same as for the Gaussian function (5):

$$N(a, l, m, n) = \left[ \left( \frac{\pi}{2a} \right)^{\frac{3}{2}} \frac{(2l-1)!! (2m-1)!! (2n-1)!!}{2^{2(l+m+n)} a^{l+m+n}} \right]^{-\frac{1}{2}} \quad (6)$$

The characteristic property of GTO's that the product of two GTO's yields another GTO, enables us to calculate molecular integrals with the aid of the following integral formula:

$$\int_{-\infty}^{\infty} e^{izx} x^n \exp(-ax^2) dx = i^n \left( \frac{\pi}{a} \right)^{\frac{1}{2}} \left( \frac{1}{2\sqrt{a}} \right)^n H_n \left( \frac{z}{2\sqrt{a}} \right) \exp \left( -\frac{z^2}{4a} \right) \quad (7)$$

For the integrals with GI GTO this formula was used with a complex value of the parameter  $y$ .  $H_n(z)$  is the Hermitian function and is defined as

$$H_n(z) = n! \sum_{i=0}^{[n/2]} \frac{(-1)^i (2z)^{n-2i}}{i! (n-2i)!} \quad (8)$$

where  $[x]$  means »largest integer less or equal to  $x$ «.

In defining the integrals, the following auxiliary functions are used:

$$(x + \overline{PA_x})^{l_1} (x + \overline{PB_x})^{l_2} = \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \overline{PA_x}, \overline{PB_x}) x^i$$

$$(M_{ABx} + k_x)^\nu = \sum_{d=0}^{\nu} g_d(\nu, M_{ABx}) (k_x)^d$$

$$F_\nu(z) = \int_0^1 u^{2\nu} \exp(-zu^2) du; \quad \nu = 0, 1, 2, \dots$$

with the complex value of the argument,  $z = x + iy$ . When the imaginary component of the argument is much smaller than the real one, we can expand the expression  $\exp(-zu^2)$  into power series of  $y$  and retain only the first term. Using the recurrence relation for  $F_\nu(x)$  it is possible to write

$$F_\nu(x + iy) \approx F_\nu(x) + \frac{i}{2} \frac{y}{x} [e^{-x} - (2\nu + 1) F_\nu(x)]$$

### 1. The Overlap Integral

$$\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A \mid \mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B \rangle = N_1 N_2 \left( \frac{\pi}{a_1 + a_2} \right)^{\frac{3}{2}}$$

$$\exp\left(-\frac{a_1 a_2}{a_1 + a_2}\right) \overline{AB}^2 \exp(i\mathbf{M}_{AB} \cdot \mathbf{P})$$

$$\exp\left(-\frac{\mathbf{M}_{AB}^2}{4(a_1 + a_2)}\right) \Sigma_x \Sigma_y \Sigma_z \quad (9)$$

where

$$\Sigma_x = \sum_{i=0}^{l_1+l_2} \sum_{r=0}^{[i/2]} f_i(l_1, l_2, \overline{PA_x}, \overline{PB_x}) \left( \frac{i}{2(a_1 + a_2)} \right)^i i! \frac{(-1)^r (a_1 + a_2)^r}{r! (i-2r)!} M_{ABx}^{i-2r} \quad (10)$$

and  $\Sigma_y, \Sigma_z$  are similarly defined in terms of the corresponding exponents and components in the  $y$ - and  $z$ - directions, respectively.

The conventions  $\overline{PA} = \mathbf{P} - \mathbf{A}$ ,  $\overline{AB} = \mathbf{A} - \mathbf{B}$  and  $\mathbf{M}_{AB} = \mathbf{M}_A - \mathbf{M}_B$  apply throughout, and the point  $\mathbf{P}$  appearing in (9) and the following formulas is the center of the new Gaussian function, the product of the Gaussians on  $\mathbf{A}$  and  $\mathbf{B}$ :

$$\mathbf{P} = \frac{a_1 \mathbf{A} + a_2 \mathbf{B}}{a_1 + a_2}$$

## 2. The Kinetic Integral

$$\begin{aligned}
\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | -\frac{1}{2} \nabla^2 | \mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B \rangle &= N_1 N_2 [\alpha_2 \{2(l_2 + m_2 + n_2) + 3\} \\
&\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B \rangle - \\
&2\alpha_2^2 \{ \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 2, m_2, n_2, \mathbf{M}_B \rangle + \\
&\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 + 2, n_2, \mathbf{M}_B \rangle + \\
&\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2, n_2 + 2, \mathbf{M}_B \rangle \} - \\
&-\frac{1}{2} \{ l_2(l_2 - 1) \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 - 2, m_2, n_2, \mathbf{M}_B \rangle + \\
&m_2(m_2 - 1) \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 - 2, n_2, \mathbf{M}_B \rangle + \\
&n_2(n_2 - 1) \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2, n_2 - 2, \mathbf{M}_B \rangle \}]. \tag{11}
\end{aligned}$$

## 3. The Linear Perturbation Integral

$$\begin{aligned}
\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | -i \frac{e\hbar}{mc} \mathbf{A} \nabla | \mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B \rangle &= N_1 N_2 (-i) \frac{e\hbar}{2mc} \\
&[ H_x \{ n_2 \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 + 1, n_2 - 1, \mathbf{M}_B \rangle - \\
&m_2 \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 - 1, n_2 + 1, \mathbf{M}_B \rangle \} + \\
&H_y \{ l_2 \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 - 1, m_2, n_2 + 1, \mathbf{M}_B \rangle - \\
&n_2 \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 1, m_2, n_2 - 1, \mathbf{M}_B \rangle \} + \\
&H_z \{ m_2 \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 1, m_2 - 1, n_2, \mathbf{M}_B \rangle - \\
&l_2 \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 - 1, m_2 + 1, n_2, \mathbf{M}_B \rangle \}]. \tag{12}
\end{aligned}$$

## 4. The Quadratic Perturbation Integral

$$\begin{aligned}
\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \frac{e^2}{2mc^2} \mathbf{A}^2 | \mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B \rangle &= N_1 N_2 \frac{e^2}{8mc^2} \\
&[ H_x^2 \{ \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 + 2, n_2, \mathbf{M}_B \rangle + \\
&\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2, n_2 + 2, \mathbf{M}_B \rangle \} + \\
&H_y^2 \{ \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 2, m_2, n_2, \mathbf{M}_B \rangle + \\
&\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2, n_2 + 2, \mathbf{M}_B \rangle \} + \\
&H_z^2 \{ \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 2, m_2, n_2, \mathbf{M}_B \rangle + \\
&\langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 + 2, n_2, \mathbf{M}_B \rangle \} - \\
&2 H_x H_y \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 1, m_2 + 1, n_2, \mathbf{M}_B \rangle - \\
&2 H_x H_z \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2 + 1, m_2, n_2 + 1, \mathbf{M}_B \rangle - \\
&2 H_y H_z \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A | \mathbf{B}, a_2, l_2, m_2 + 1, n_2 + 1, \mathbf{M}_B \rangle ]. \tag{13}
\end{aligned}$$

## 5. The Nuclear Attraction Integral

$$\begin{aligned}
& \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A \mid \frac{1}{|\mathbf{r} - \mathbf{C}|} \mid \mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B \rangle = \\
& N_1 N_2 \frac{2\pi}{\gamma} \exp\left(-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2\right) \\
& \exp(i \mathbf{M}_{AB} \cdot \mathbf{P}) \exp\left(-\frac{\mathbf{M}_{AB}^2}{4\gamma}\right) \\
& \sum_{i,r,d,u} A_{i,r,d,u}(l_1, l_2, A_x, B_x, C_x, \gamma, M_{Ax}, M_{Bx}) \\
& \sum_{j,s,e,v} A_{j,s,e,v}(m_1, m_2, A_y, B_y, C_y, \gamma, M_{Ay}, M_{By}) \\
& \sum_{k,t,f,w} A_{k,t,f,w}(n_1, n_2, A_z, B_z, C_z, \gamma, M_{Az}, M_{Bz}) \\
& F_\nu \left[ \gamma \left( \overline{PC} + i \frac{\mathbf{M}_{AB}}{2\gamma} \right)^2 \right] \tag{14}
\end{aligned}$$

where  $\gamma = \alpha_1 + \alpha_2$ ,  $\overline{PC} = \mathbf{P} - \mathbf{C}$ ,  $\nu = d + e + f - (u + v + w)$

$$\begin{aligned}
& A_{i,r,d,u}(l_1, l_2, A_x, B_x, C_x, \gamma, M_{Ax}, M_{Bx}) = \\
& \frac{i^t}{2^i} i! f_i(l_1, l_2, \overline{PA}_x, \overline{PB}_x) \frac{(-1)^r \gamma^{r-1}}{r! (i-2r)!} \\
& g_d(i-2r, M_{ABx}) \frac{i^d}{2^d} d! \frac{(-1)^u (4\gamma)^{d-u}}{u! (d-2u)!} \left( \overline{PC}_x + i \frac{M_{ABx}}{2\gamma} \right)^{d-2u}
\end{aligned}$$

$A_{j,s,e,v}$  and  $A_{k,t,f,w}$  are defined similarly in terms of the  $y$ - and  $z$ - components. In eq. (14) the summations with respect to the indices  $i, r, d$  and  $u$  extend from 0 to  $l_1 + l_2$ ,  $[i/2]$ ,  $i - 2r$  and  $[d/2]$ , respectively. The ranges of  $(j, s, e, v)$  or  $(k, t, f, w)$  can be found easily in the same way.

## 6. The Electron Repulsion Integral

$$\begin{aligned}
& \langle \mathbf{A}, a_1, l_1, m_1, n_1, \mathbf{M}_A \mid (\mathbf{C}, a_3, l_3, m_3, n_3, \mathbf{M}_C) \mid \frac{1}{r_{12}} \mid \\
& (\mathbf{B}, a_2, l_2, m_2, n_2, \mathbf{M}_B) (\mathbf{D}, a_4, l_4, m_4, n_4, \mathbf{M}_D) \rangle = \\
& N_1 N_2 N_3 N_4 \frac{2\pi^2}{\gamma_1 \gamma_2} \left( \frac{\pi}{\gamma_1 + \gamma_2} \right)^{\frac{1}{2}} \\
& \exp\left(-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2 - \frac{\alpha_3 \alpha_4}{\alpha_3 + \alpha_4} \overline{CD}^2\right) \\
& \exp[-i(\mathbf{M}_{AB} \cdot \mathbf{P} + \mathbf{M}_{CD} \cdot \mathbf{Q})] \exp\left[-\frac{M_{AB}^2}{4\gamma_1} - \frac{M_{CD}^2}{4\gamma_2}\right] \\
& \sum_{i_1, i_2, r_1, r_2, d_1, d_2, u} B_{i_1, i_2, r_1, r_2, d_1, d_2, u}
\end{aligned}$$

$$\begin{aligned}
& \sum_{j_1, j_2, s_1, s_2, e_1, e_2, v} B_{j_1, j_2, s_1, s_2, e_1, e_2, v} \\
& \sum_{k_1, k_2, t_1, t_2, f_1, f_2, w} B_{k_1, k_2, t_1, t_2, f_1, f_2, w} \\
F_v & \left\{ \frac{1}{4 \delta} \left[ \overline{QP} + i \left( \frac{\mathbf{M}_{CD}}{2 \gamma_2} - \frac{\mathbf{M}_{AB}}{2 \gamma_1} \right) \right]^2 \right\} \quad (15)
\end{aligned}$$

where  $\gamma_1 = \alpha_1 + \alpha_2$   $\gamma_2 = \alpha_3 + \alpha_4$

$$\overline{QP} = \mathbf{Q} - \mathbf{P}$$

$$\delta = \frac{1}{4} \left( \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) \quad \mathbf{Q} = \frac{\alpha_3 \mathbf{C} + \alpha_4 \mathbf{D}}{\alpha_3 + \alpha_4}$$

$$v = d_1 + d_2 + e_1 + e_2 + f_1 + f_2 - u - v - w$$

$$B_{i_1, i_2, r_1, r_2, d_1, d_2, u}(l_1, l_2, A_x, B_x, P_x, \gamma_1, M_{ABx})$$

$$|l_3, l_4, C_x, D_x, Q_x, \gamma_2, M_{CDx}) = (-1)^{d_1} f_{i_1}(l_1, l_2, \overline{PA}_x, \overline{PB}_x)$$

$$f_{i_2}(l_3, l_4, \overline{QC}_x, \overline{QD}_x) g_{d_1}(i_1 - 2r_1, M_{ABx})$$

$$g_{d_2}(i_2 - 2r_2, M_{CDx}) \left( \frac{i}{2 \gamma_1} \right)^{i_1} \left( \frac{i}{2 \gamma_2} \right)^{i_2} i_1! i_2!$$

$$\frac{(-1)^{r_1+r_2} \gamma_1^{r_1} \gamma_2^{r_2}}{r_1! (i_1 - 2r_1)! r_2! (i_2 - 2r_2)!} \left( \frac{i}{2 \delta} \right)^{d_1+d_2} (d_1 + d_2)!$$

$$\frac{(-1)^u \delta^u}{u! (d_1 + d_2 - 2u)!} \left[ \overline{QP}_x + i \left( \frac{M_{CDx}}{2 \gamma_2} - \frac{M_{ABx}}{2 \gamma_1} \right) \right]^{d_1+d_2-2u}$$

$B_{k_1, k_2, t_1, t_2, f_1, f_2, w}$  and  $B_{j_1, j_2, s_1, s_2, e_1, e_2, v}$  are defined similarly in terms of the  $y$ - and  $z$ - components, respectively.

The summations in (15) with respect to the indices  $i_1, i_2, r_1, r_2, d_1, d_2$  and  $u$  extend from 0 to  $l_1 + l_2, l_3 + l_4, [i_1/2], [i_2/2], i_1 - 2r_1, i_2 - 2r_2$  and  $\frac{d_1 + d_2}{2}$ , and similarly for the indices of the summations over the  $y$ - and  $z$ - components.

#### CONCLUSION

It has been shown that all the integrals involved in the SCF computation of magnetic shielding and susceptibility with GIAO can be written in a form which is compact enough.

The computation of these integrals requires the values of  $F_v(z)$  with a complex argument, but a good approximation can be found owing to its imaginary part being much smaller than the real one. Due to the additional summations in expressions for integrals the computation of their values is only a little more difficult than in the case of real atomic orbitals for the unperturbed system.

*Acknowledgement.* This work was partially supported by the Boris Kidrič Fund.

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## IZVLEČEK

**Ab initio računi kemijskega premika in susceptibilnosti. I. Molekularni integrali z gradientno invariantnimi Gaussovimi orbitalami**

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Podani so analitični izrazi za integrale, ki jih potrebujemo pri SCF računanju kemijskega premika in susceptibilnosti s gradientno invariantnimi Gaussovimi atomskimi orbitalami. Vse integrale lahko izrazimo z znanimi funkcijami.

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Sprejeto 21. avgusta 1975.