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Some Integrals for Molecular Properties and Relativistic Effects over Hermite-Gaussian Functions

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Formulas for some integrals over Hermite-Gaussian functions occurring in the calculations of the molecular first and second order properties as well as relativistic corrections arising in the Breit hamiltonian are discussed. It is shown that all these molecular properties integrals can be reduced to the integrals already encountered in the minimum energy calculations. More specifically, the one-electron and two-electron integrals involving $(1/r_{1j})^n$ operator, where j denotes either the coordinates of a nucleus or the coordinates of the electron 2 and n is an integer, are expressed in terms of nuclear attraction and Coulomb repulsion integrals, respectively. Therefore the electric and magnetic properties of molecules can be computed with little additional effort if the Hermite-Gaussian basis set is employed. The same conclusion holds for the matrix elements arising in the pseudo-potential calculations involving the Bonifačić-Huzinaga model potential which in turn give a fair description of the heavy atoms inner-shell electrons. Since the Hermite-Gaussian functions are particularly advantageous for atomic orbitals with higher angular momentum quantum numbers (*f, g, h* etc.) their use is expected to be preferable in molecules involving heavy atoms. The relativistic effects are of great importance for the latter and it is gratifying that the corresponding integrals over Hermite-Gaussians can be expressed in a closed form.

INTRODUCTION

The ease with which calculations of molecular many-center integrals over spherically symmetric Gaussian functions can be performed was first pointed out by Boys[1]. These functions, however, have poor physical behaviour in the vicinity of the nucleus and at large distances from it. Therefore, they are employed in quantum chemical calculations only as a mathematical device to facilitate the evaluation of many-center integrals. Linear combinations of Gaussian functions are widely used to describe Slater-type orbitals. This method, originally proposed by Foster and Boys[2], was extensively utilized in ab initio calculations and applied to organic chemistry by Pople and co-workers[3]. Although the calculation of many-center integrals over certain types

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of functions is not a bottleneck in molecular quantum mechanics any more, it is desirable to explore new approaches which may lead to even more efficient computational procedures. The use of a Hermite-Gaussian basis set seems to be quite promising in this respect. Namely, it was shown that all integrals over Hermite-Gaussian functions, required by the variation principle, are also analytically tractable[4]. It appears that, matrix elements based on Hermite-Gaussian (HG in the text) functions can be reduced to integrals over spherically symmetric Gaussians and consequently expressed in closed form. Since molecular wave functions, which contain all the information about the molecule in question, are necessarily of an approximate nature, it is desirable to examine their quality by calculating various molecular properties. Particularly sensitive tests of molecular wave functions are provided by electric and magnetic properties* such as molecular dipole and quadrupole moments, electric field gradients near magnetic nuclei, spin-spin coupling constants etc. Calculations of these properties are usually very troublesome because the corresponding integrals over Slater atomic orbitals are difficult to handle. It is the aim of this paper to show that the integrals related to the first and second order molecular properties and integrals arising from relativistic corrections can be expressed analytically if HG basis sets are used. We consider here in some detail the matrix elements of the following operators:

$$\mathbf{r}^2,\ -i\hbar\, \mathbf{r} \times \vec{\nabla},\ \mathbf{r}_N/r_N^3,\ (r_N^2 - 3x_N^2)/r_N^5,\ (x_N^2 + y_N^2)/r_N^3,\ -x_N z_N/r_N^3,\ \vec{\nabla}_1^4,\ \delta(\mathbf{r}_{12}),$$

$$(1/r_N^3)\, \mathbf{r}_N \times \vec{\nabla},\ (r_{12}^2 - 3x_{12}^2)/r_{12}^5,\ \mathbf{r}_{12} \times \vec{\nabla}_2/r_{12}^3,\ (1/r_{12})\, \vec{\nabla}_1 \cdot \vec{\nabla}_2$$

and

$$\mathbf{r}_{12} \cdot [(\mathbf{r}_{12}/r_{12}^3) \cdot \vec{\nabla}_1]\, \vec{\nabla}_2$$

In some cases only the representative component is given for the sake of brevity. Finally, the integrals arising in the Bonifačić-Huzinaga model potential[6] calculations are briefly discussed. In each case only the integrals with maximum numbers of different centers are discussed. The special cases obtained by the coalescence of two or more centers can be treated along the same lines.

1. METHOD OF CALCULATION

We follow here rather closely the notation introduced in the previous paper[4]. The HG fuction, placed on the nucleus A, is defined as

$$f(\mathbf{n}, a, \mathbf{r}_A) = \partial_{A_x}^{n_1}\ \partial_{A_y}^{n_2}\ \partial_{A_z}^{n_3}\ \exp(-a\,\mathbf{r}_A^2) \tag{1.1}$$

where $\mathbf{r}_A^2 = (x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2$ and $\mathbf{n}$, $\mathbf{r}$ and $\mathbf{A}$ are triads

$$\begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} \qquad \begin{pmatrix} x - A_x \\ y - A_y \\ z - A_z \end{pmatrix} \text{ and } \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}$$

Taking into account the definition of Hermite polynomials

$$H_n(x) = (-1)^n \exp(x^2)\, [d^n/dx^n] \exp(-x^2) \tag{1.2}$$

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* For a definition and thorough discussion of molecular properties the reader may consult for example ref. 5.

one finds out that

$$f(\mathbf{n},\ a,\ \mathbf{r}_A) = a^{n/2} H_{n_1}[a^{1/2} x_A] H_{n_2}[a^{1/2} y_A] H_{n_3}[a^{1/2} z_A] \exp(-a\,\mathbf{r}_A^2) \qquad (1.3)$$

The calculation of an integral over HG functions (1.1) is performed in three steps: (a) expressing the relevant operator in term of derivatives with respect to the coordinates of the nuclei*, (b) putting the differentiation operators in front of the integral sign, (c) calculating the remaining integral over the nuclear position coordinates. In stage (c) of this procedure we use the fundamental property of the Gaussian 1s functions

$$\exp(-a\mathbf{r}_A^2)\exp(-b\mathbf{r}_B^2) = \exp\{[-ab/(a+b)]\,\mathbf{AB}^2\}\exp[-(a+b)\,\mathbf{P}^2] \qquad (1.2)$$

where $\mathbf{AB} = \mathbf{A} - \mathbf{B}$ and $P_x = x - (aA_x + bB_x)/(a+b)$ etc. In other words the product of the Gaussian functions is a third Gaussian function located between the points A and B.

2. MOLECULAR QUADRUPOLE MOMENTS AND MAGNETIC SUSCEPTIBILITIES INTEGRALS

The molecular quadrupole moments measure the deviation of molecular charge distribution from spherical symmetry. In order to calculate molecular quadrupole moments and the related diamagnetic part of the magnetic susceptibilities we need the matrix elements of the operators x^2, y^2, z^2, $\mathbf{r}^2$. The paramagnetic part of the molecular magnetic susceptibility requires the matrix elements of the angular momentum operator $\mathbf{l}$. Integrals involving x^2, y^2, z^2 are called second moments of the electronic charge distribution. Let us consider the integral of $\mathbf{r}^2$

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{r}^2 \,|\, \mathbf{n}', b, \mathbf{B} \rangle = \int f(\mathbf{n}, a, \mathbf{r}_A)\ f(\mathbf{n}', b, \mathbf{r}_B)\,\mathbf{r}^2\,d^3\mathbf{r} \qquad (2.1)$$

By using the relationship

$$\mathbf{r}\exp(-b\,\mathbf{r}_B^2) = \mathbf{B}\exp(-b\,\mathbf{r}_B^2) + (1/2b)\,\vec{\nabla}_B \exp(-b\,\mathbf{r}_B^2) \qquad (2.2)$$

where $\vec{\nabla}_B$ is the gradient with respect to B and employing a similar formula involving $\mathbf{r}\exp(-a\,\mathbf{r}_A^2)$ one can easily express the integral (2.1) as a linear combination of overlap integrals

$$\begin{aligned} \langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{r}^2 \,|\, \mathbf{n}', b, \mathbf{B} \rangle &= \mathbf{A}\cdot\mathbf{B}\,\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{n}', b, \mathbf{B} \rangle + \\ &+ (1/4ab)\sum_{i=1}^{3}[\langle \mathbf{n}+\mathbf{u}_i, a, \mathbf{A} \,|\, \mathbf{n}'+\mathbf{u}_i, b, \mathbf{B} \rangle + \\ &+ 2\,\mathbf{e}_i\,(b\mathbf{B} - a\mathbf{A})\,\langle \mathbf{n}+\mathbf{u}_i, a, \mathbf{A} \,|\, \mathbf{n}', b, \mathbf{B} \rangle] \end{aligned} \qquad (2.3)$$

where $\mathbf{e}_i$ and $\mathbf{u}_i$ are Cartesian unit vectors and unit triads respectively. In the course of the calculation of formula (2.3) we took advantage of the property of the overlap integral

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{n}'+\mathbf{u}_1, b, \mathbf{B} \rangle = (-)\,\langle \mathbf{n}+\mathbf{u}_1, a, \mathbf{A} \,|\, \mathbf{n}', \mathbf{b}, \mathbf{B} \rangle \qquad (2.4)$$

The integrals of x^2, y^2 and z^2 are easily obtained in a similar manner. The

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* It should be mentioned that this technique of evaluating multi-center spin-spin and spin-orbit integrals over Gaussian functions was developed to some extent by Matcha and Kern, ref 7.

paramagnetic part of the magnetic susceptibility requires matrix elements of the angular momentum operator $\mathbf{l} = -i\hbar\,\mathbf{r} \times \vec{\nabla}$

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, -i\hbar\,\mathbf{r} \times \vec{\nabla} \,|\, \mathbf{n}', b, \mathbf{B} \rangle = -i\hbar \int f(\mathbf{n}, a, \mathbf{r}_A)\,(\mathbf{r} \times \vec{\nabla})\, f(\mathbf{n}', b, \mathbf{r}_B)\, d^3\mathbf{r} \tag{2.5}$$

The integrals (2.5) are calculated by replacing formally the $\vec{\nabla}$ operator with $\vec{\nabla}_B$ which includes derivatives with respect to the coordinates of atom B

$$\vec{\nabla} = -\vec{\nabla}_B \tag{2.6}$$

Next the $\vec{\nabla}_B$ operator is put in front of the integral symbol and the matrix element (2.5) takes the form

$$-i\hbar\,\vec{\nabla}_B \times \int f(\mathbf{n}, a, \mathbf{r}_A)\,\mathbf{r}\, f(\mathbf{n}', b, \mathbf{r}_B)\, d^3\mathbf{r} \tag{2.7}$$

Thus, the angular momentum integrals are reduced to the dipole moment integrals which are easily calculated

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{r} \,|\, \mathbf{n}', b, \mathbf{B} \rangle = (1/2)\,(\mathbf{A} + \mathbf{B})\,\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{n}', b, \mathbf{B} \rangle +$$
$$+ [(b - a)/4ab] \sum_{i=1}^{3} e_i \,\langle \mathbf{n} + \mathbf{u}_i, a, \mathbf{A} \,|\, \mathbf{n}', b, \mathbf{B} \rangle \tag{2.8}$$

By using eq 2.8 one finds that the $\mathbf{e}_1$ component of the vector (2.7) is

$$(i\hbar/2)\,\{(A_y + B_y)\,\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{n}' + \mathbf{u}_3, b, \mathbf{B} \rangle - (A_z + B_z)\,\langle \mathbf{n}, a, \mathbf{A} \,|\, \mathbf{n} + \mathbf{u}_2, b, \mathbf{B} \rangle\} \tag{2.9}$$

The remaining components are generated by cyclic permutations of the subscripts x, y, z and unit triads $\mathbf{u}_i$ $(i = 1, 2, 3)$.

3. ELECTRIC FIELD AND ELECTRIC FIELD GRADIENT INTEGRALS

The electric field operator, which is related to Hellmann-Feynman force[8] exerted by the nucleus N, is of the form

$$\mathbf{r}_N / r_N^3 = \vec{\nabla}_N (1/r_N) \tag{3.1}$$

Its matrix elements are

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \vec{\nabla}_N (1/r_N) \,|\, \mathbf{n}', b, \mathbf{B} \rangle = \vec{\nabla}_N \int f(\mathbf{n}, a, \mathbf{r}_A)\,(1/r_N)\, f(\mathbf{n}', b, \mathbf{r}_B)\, d^3\mathbf{r} \tag{3.2}$$

The integral on the right hand side of the identity (3.2) is the Coulomb attraction integral. Since this integral as well as its derivatives are heavily used in this paper we give here the most important formulas[4,9]. Briefly, the three-center nuclear attraction integrals assumes the form

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, 1/|\mathbf{r} - \mathbf{N}| \,|\, \mathbf{n}', b, \mathbf{B} \rangle = (-)^{n'} \frac{2\pi}{a+b} \sum_{k_1} \sum_{k_2} \sum_{k_3} \left[\frac{b}{(a+b)^{1/2}} \right]^k$$
$$h\left(n_1, n'_1, k_1, -\frac{a}{b}\right) h\left(n_2, n_2', k_2, -\frac{a}{b}\right) h\left(n_3, n_3', k_3, -\frac{a}{b}\right) g(\mathbf{k}, \mathbf{K})\, f\left(\mathbf{n} + \mathbf{n}' - \mathbf{k}\frac{ab}{a+b}, \mathbf{R}\right) \tag{3.3}$$

where

$$\mathbf{K} = (a + b)^{1/2}\,\{\mathbf{N} - [(a\mathbf{A} + b\mathbf{B})/(a + b)]\}$$

and

$$\mathbf{R}=\mathbf{B}-\mathbf{A}, \qquad k=k_1+k_2+k_3, \qquad i=i_1+i_2+i_3, \qquad n'=n_1'+n_2'+n_3'$$

The auxilliary functions g and h are defined as follows

$$g(\mathbf{k}, \mathbf{r}) = \partial_x^{k_1} \quad \partial_y^{k_2} \quad \partial_z^{k_3} \int_0^1 \exp(-\mathbf{r}^2 t^2)\, dt \tag{3.4}$$

and

$$h(m, n, t, x) = \sum_s \binom{m}{s}\binom{n}{t-s} x^s \tag{3.5}$$

The summations over k_1, k_2 and k_3 are extended from 0 to $n_1 + n_1'$, $n_2 + n_2'$ and $n_3 + n_3'$, respectively. Derivatives of the matrix elements (3.3) with respect to Cartesian coordinates of the nucleus N are given by

$$\partial_{N_x}^{i_1} \quad \partial_{N_y}^{i_2} \quad \partial_{N_z}^{i_3} \langle \mathbf{n}, a, \mathbf{A} \,|\, 1/\,|\mathbf{r}-\mathbf{N}|\,\,|\, \mathbf{n}', b, \mathbf{B}\rangle = (-)\,\mathbf{n}' \frac{2\pi}{a+b} \sum_{k_1}\sum_{k_2}\sum_{k_3} b^k (a+b)^{(i-k)/2}$$

$$h\left(n_1, n_1', k_1, -\frac{a}{b}\right) h\left(n_2, n_2', k_2, -\frac{a}{b}\right) h\left(n_3, n_3', k_3, -\frac{a}{b}\right)$$

$$g(\mathbf{k}+\mathbf{i}, \mathbf{K})\, f\left[\mathbf{n}+\mathbf{n}'-\mathbf{k}, \frac{ab}{a+b}, \mathbf{R}\right] \tag{3.6}$$

where **i** is a triad of numbers i_1, i_2 and i_3. Here we employed an obvious identity

$$\partial_{N_x}^{i_1} \quad \partial_{N_y}^{i_2} \quad \partial_{N_z}^{i_3}\, g(\mathbf{k}, \mathbf{K}) = (a+b)^{1/2}\, g(\mathbf{k}+\mathbf{i}, \mathbf{K})$$

There is, however, an equivalent and more convenient expression which is based on the observation that the translation of the nucleus N in an arbitrary direction is identical to the simultaneous translation of the nuclei A and B in the opposite direction. Thus we can formally write

$$\partial_{N_x} = -(\partial_{A_x} + \partial_{B_x}) \quad \text{etc.} \tag{3.7}$$

Straightforward application of (3.7) yields

$$\partial_{N_x}^{i_1} \quad \partial_{N_y}^{i_2} \quad \partial_{N_z}^{i_3} \langle \mathbf{n}, a, \mathbf{A} \,|\, 1/\,|\mathbf{r}-\mathbf{N}|\,\,|\, \mathbf{n}', b, \mathbf{B}\rangle = (-)^i \sum_{s_1=0}^{i_1} \sum_{s_2=0}^{i_2} \sum_{s_3=0}^{i_3} \binom{i_1}{s_1}\binom{i_2}{s_2}\binom{i_3}{s_3}$$

$$\langle \mathbf{n}+\mathbf{i}-\mathbf{s}, a, \mathbf{A} \,|\, 1/\,|\mathbf{r}-\mathbf{N}\,|\, \mathbf{n}'+\mathbf{s}, b, \mathbf{B}\rangle \tag{3.8}$$

Thus a derivative of the nuclear attraction integral with respect to the Cartesian coordinates of the operator's origin is given by a sum of the attraction integrals over the higher HG functions. The use of the two formulas (3.6) and (3.8) provides a useful check of the computer program. However, the formula (3.8) will be used throughout this paper because it is more compact. We can turn back now to the integral (3.2). By using the eq. 3.8 one immediately obtaines

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \vec{\nabla}_N (1/r_N) \,|\, \mathbf{n}', b, \mathbf{B}\rangle = -\sum_{i=1}^{3} \sum_{m=0}^{1} \mathbf{e}_i \langle \mathbf{n} + m\,\mathbf{u}_i, a, \mathbf{A} \,|\, 1/r_N \,|\, \mathbf{n}' +$$

$$+ (1-m)\,\mathbf{u}_i, b, \mathbf{B}\rangle \tag{3.9}$$

Next, we shall focus our attention to the matrix elements of the electric field gradient operator which is a sensitive probe of the charge density in the immediate vicinity of the nucleus in question. Let us consider the diagonal element of the electric field gradient tensor, e. g. $(r_N^2 - 3x_N^2)/r_N^5$ first. It can be conveniently expressed in the following equivalent form

$$\lim_{\varepsilon \to 0} [(3\, x_N^2 - r_N^2)/r_N^5]_\varepsilon = \partial^2_{N_x} (1/r_N) + (4\,\pi/3)\, \delta\,(\mathbf{r}_N) \tag{3.10}$$

where $\delta\,(\mathbf{r}_N)$ is the three dimensional Dirac delta function. One has to mention here that the operator $(r_N^2 - 3x_N^2)/r_N^5$ has a strong singularity at the nucleus N. The conditionally convergent integrals of this kind were discussed at some length in references (10—12). Thus only final formula for the matrix elements of the operator (3.10) will be given here

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \partial^2_{N_x} (1/r_N) + (4\,\pi/3)\, \delta\,(\mathbf{r}_N) \,|\, \mathbf{n}, b, \mathbf{B} \rangle = \sum_{m=0}^{2} \binom{2}{m} \langle \mathbf{n} + m\, \mathbf{u}_1, a, \mathbf{A} \,|\, 1/r_N \,|\, \mathbf{n}' + (2 - m)\, \mathbf{u}_1, b, \mathbf{B} \rangle + (4\,\pi/3)\, f\,(\mathbf{n}, a, \mathbf{r}_{NA})\, \mathbf{f}\,(\mathbf{n}', b, \mathbf{r}_{NB}) \tag{3.11}$$

where $\mathbf{r}_{NA}$ and $\mathbf{r}_{NB}$ are the vectors **N—A** and **N—B**, respectively. It appears that the electric field gradient integrals are also linear combinations of Coulomb integrals followed by a simple product of the two HG functions taken at the position vectors of the nuclei A and B relative to the origin of the operator.

We shall turn our attention to the off-diagonal matrix element $x_N\, z_N/r_N^5$. It is reduced to the nuclear attraction type of integrals in the same way. Namely, the operator in question can be written in the following equivalent form

$$x_N\, z_N/r_N^5 = \frac{\partial^2}{\partial N_x\, \partial N_z} (1/r_N) \tag{3.12}$$

By using the formula (3.8) one readily obtains

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, x_N\, z_N/r_N^5 \,|\, \mathbf{n}', b, \mathbf{B} \rangle = \sum_{s_1=0}^{1} \sum_{s_3=0}^{1} \binom{1}{s_1} \binom{1}{s_3} \langle \mathbf{n} + \mathbf{i} - \mathbf{s}, a, \mathbf{A} \,|\, 1/\,|\,\mathbf{r} - \mathbf{N}\,|\,|\, \mathbf{n}' + \mathbf{s}, b, \mathbf{B} \rangle \tag{3.13}$$

where **i** and **s** are the triads (1, 0, 1,) and (s_1, 0, s_3), respectively.

4. MAGNETIC SCHIELDING OF THE NUCLEI BY THE ELECTRON CLOUD

Magnetic shielding has two terms — the diamagnetic and the paramagnetic or high frequency part. The diamagnetic shielding is described by a symmetric tensor of the second rank. We shall consider the characteristic diagonal and off-diagonal matrix elements $\sigma_{zz}^{(d)}$ and $\sigma_{xz}^{(d)}$ which are of the form $(x_N^2 + y^2_N)/r_N^3$ and $x_N\, z_N/r_N^3$, respectively. In order to calculate the diagonal matrix element $\sigma_{zz}^{(d)}$ we use the identity

$$(x_N^2 + y_N^2)/r_N^3 = (1/r_N) - z \frac{\partial}{\partial\, N_z} (1/r_N) + N_z \frac{\partial}{\partial\, N_z} (1/r_N) \tag{4.1}$$

which indicates that the diamagnetic shielding tensor can be expressed as a sum of nuclear attraction integrals too. By using eq 3.8 and 4.1 and the identity

$$z\, f(\mathbf{n}', b, \mathbf{B}) = \mathbf{B}_z\, f(\mathbf{n}', b, \mathbf{B}) + (1/2b)\, f(\mathbf{n}' + \mathbf{u}_3, b, \mathbf{B}) + \mathbf{n}'_3\, f(\mathbf{n}' - \mathbf{u}_3, b, \mathbf{B})$$

one obtains

$$\begin{aligned}\langle \mathbf{n}, a, \mathbf{A} \mid (x_N^2 + y_N^2)/r_N^3 \mid \mathbf{n}', b, \mathbf{B}\rangle &= \langle \mathbf{n}, a, \mathbf{A} \mid 1/r_N \mid \mathbf{n}', b, \mathbf{B}\rangle + \\ &+ (B_z - N_z) \sum_{m=0}^{1} \langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' + m\,\mathbf{u}_3, b, \mathbf{B}\rangle + \\ &+ \sum_{m=0}^{1} (1/2\,b)\, \langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n} + (1+m)\,\mathbf{u}_3, b, \mathbf{B}\rangle - \\ &- n_3' \sum_{m=0}^{1} \langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' - (1-m)\,\mathbf{u}_3, b, \mathbf{B}\rangle \qquad (4.2)\end{aligned}$$

The off-diagonal element $\sigma_{xz}^{(d)}$ is analogously calculated

$$\langle n, a, \mathbf{A} \mid x_N z_N/r_N^2 \mid \mathbf{n}', b, \mathbf{B}\rangle = \frac{\partial}{\partial N_z} \langle \mathbf{n}, a, \mathbf{A} \mid (x/r_N) \mid \mathbf{n}', b, \mathbf{B}\rangle - \mathbf{N}_x \frac{\partial}{\partial N_z} \langle \mathbf{n}, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}', b, \mathbf{B}\rangle$$

Substituting the derivative of the nuclear attraction integrals one finds out

$$\begin{aligned}\langle \mathbf{n}, a, \mathbf{A} \mid x_N z_N/r_N^3 \mid \mathbf{n}', b, \mathbf{B}\rangle &= (N_x - B_x) \sum_{m=0}^{1} \langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' + \\ &+ m\,\mathbf{u}_3, b, \mathbf{B}\rangle - \sum_{m=0}^{1} [(1/2\,b)\, \langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' + \mathbf{u}_1 + m\,\mathbf{u}_3, b, \mathbf{B}\rangle + \\ &+ n_1' \langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' - \mathbf{u}_1 + m\,\mathbf{u}_3, b, \mathbf{B}\rangle \qquad (4.3)\end{aligned}$$

The remaining components are easily obtained by the cyclic permutation of coordinates and indices of unit triads.

The paramagnetic part of the magnetic shielding involves the operators l_{zN} and $(1/r_N^3)\, l_{zN}$ where l_{zN} is the z-component of the angular momentum operator. Since the **l** operator was already encountered in section 2 of this paper we shall turn our attention to the operator $(1/r_N^3)\, l_{zN}$. It is conviently written in a form

$$-i\hbar\,(1/r_N^3) \left(x_N \frac{\partial}{\partial y} - y_N \frac{\partial}{\partial x} \right) = i\hbar \left[\frac{\partial}{\partial N_x} (1/r_N) \frac{\partial}{\partial B_y} - \frac{\partial}{\partial N_y} (1/r_N) \frac{\partial}{\partial B_x} \right]$$

Employing the familiar procedure one obtains

$$\begin{aligned}\langle \mathbf{n}, a, \mathbf{A} \mid (1/r_N^3)\, l_{zN} \mid \mathbf{n}'\, b, \mathbf{B}\rangle &= -i\hbar \sum_{m=0}^{1} \{\langle \mathbf{n} + (1-m)\,\mathbf{u}_1, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' + \\ &+ m\,\mathbf{u}_1 + \mathbf{u}_2, b, \mathbf{B}\rangle + \langle \mathbf{n} + (1-m)\,\mathbf{u}_2, a, \mathbf{A} \mid (1/r_N) \mid \mathbf{n}' + \mathbf{u}_1 + m\,\mathbf{u}_2, b, \mathbf{B}\rangle\} \qquad (4.4)\end{aligned}$$

5. INTEGRALS ARISING IN RELATIVISTIC CALCULATIONS OF MOLECULAR STRUCTURE

The relativistic effects in first row atoms are negligible. However, they increase very rapidly ($\sim Z^4$) with atomic number. The hydrogen like systems consisting of a core and one valence electron provide an interesting illustrative example. It was shown by Boys and Price[13] that the relativistic correction for $Z = 30$ exceeds 1% of the total energy. Thus, the relativistic effect should be explicitly considered in molecules involving heavy atoms if chemical accuracy ($\sim$ 1 kcal/mol) is desired. The relativistic treatment of the inter-particle interactions in atoms and molecules is particularly difficult. There are several approximate approaches the most popular among them being Breit's[10] method which handles the relativistic effects by perturbation theory. The relevant operators can be found in ref 10 and 14.

5.1. *Variation of Electron Mass with Velocity*

The correction due to the increase of the electron mass with velocity is proportional to $\vec{\nabla}_1^4$. The corresponding one- electron integral is consequently of the form

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \vec{\nabla}_1^4 \,|\, \mathbf{n}', b, \mathbf{B} \rangle \tag{5.1.1}$$

Integrating twice by parts and taking into account a boundary condition which states that the physically acceptable wavefunction must vanish at infinity, one readily obtains

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \vec{\nabla}_1^4 \,|\, \mathbf{n}', b, \mathbf{B} \rangle = \int \vec{\nabla}_1^2 f(\mathbf{n}, a, \mathbf{r}_{1A})\, \vec{\nabla}_1^2 f(\mathbf{n}', b, \mathbf{r}_{1B})\, d^3 \mathbf{r}_1 \tag{5.1.2}$$

Since $\vec{\nabla}_1^2 f(\mathbf{n}', b, \mathbf{r}_{1B}) = \sum_{j=1}^{3} |\, \mathbf{n}' + 2\, \mathbf{u}_j, b, \mathbf{r}_{1B} \rangle$ the mass variation integral (5.1.1) is reduced to a sum of overlap integrals

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, \vec{\nabla}_1^4 \,|\, \mathbf{n}', b, \mathbf{B} \rangle = \sum_{i=1}^{3} \sum_{j=1}^{3} \langle \mathbf{n} + 2\, \mathbf{u}_i, a, \mathbf{A} \,|\, \mathbf{n}' + 2\, \mathbf{u}_j, b, \mathbf{r}_{1B} \rangle \tag{5.1.3}$$

5.2. *Spin-Spin Interaction Integrals*

In order to calculate the magnetic dipolar interaction between the two electrons one needs to consider the matrix elements of the operators $(r_{12}^2 - 3\, z_{12}^2)/r_{12}^5$ and $x_{12}\, z_{12}/r_{12}^5$ as well as the operators obtained by the cyclic permutation of the Cartesian coordinates. They form the dipolar coupling tensor of the second rank which is traceless and symmetric. The former operator is easily transformed to the following equivalent form

$$(3\, x_{12}^2 - r_{12}^2)/r_{12}^5 = - \frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} (1/r_{12}) + (4\,\pi/3)\, \delta(\mathbf{r}_{12}) \tag{5.2.1}$$

by a straighforward generalization of the eq 3.10. The corresponding four center matrix element

$$\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}', b, \mathbf{B} \,|\, (3\, x_{12}^2 - r_{12}^2)/r_{12}^5 \,|\, \mathbf{n}'', c, \mathbf{C}; \mathbf{n}''', d, \mathbf{D} \rangle$$

is a sum of the two contributions I_1 and I_2 where

$$I_1 = - \int\int f(\mathbf{n}, a, \mathbf{r}_{1A})\, f(\mathbf{n}', b, \mathbf{r}_{1B}) \frac{\partial}{\partial x_1} \frac{\partial}{\partial x_2} (1/r_{12})$$

$$f(\mathbf{n}'', c, \mathbf{r}_{2C})\, f(\mathbf{n}''', d, \mathbf{r}_{2D})\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2$$

and

$$I_2 = (+ 4\pi/3) \int\int f(\mathbf{n}, a, \mathbf{r}_{1A})\, f(\mathbf{n}', b, \mathbf{r}_{1B})\, \delta(\mathbf{r}_{12})\, f(\mathbf{n}'', c, \mathbf{r}_{2C})$$

$$f(\mathbf{n}''', d, r_{2D})\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \tag{5.2.3}$$

Employing partial integrations the integral I_1 is brought to the form

$$I_1 = \int\int (1/r_{12}) \frac{\partial}{\partial x_1} f(\mathbf{n}, a, \mathbf{r}_{1A})\, f(\mathbf{n}', b, \mathbf{r}_{1B}) \frac{\partial}{\partial x_2} f(\mathbf{n}'', c, \mathbf{r}_{2C})\, f(\mathbf{n}''', d, \mathbf{r}_{2D})\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \tag{5.2.4}$$

By substituting[*] $\frac{\partial}{\partial x_1} = - \left(\frac{\partial}{\partial A_x} + \frac{\partial}{\partial B_x}\right)$ and $\frac{\partial}{\partial x_2} = - \left(\frac{\partial}{\partial C_x} + \frac{\partial}{\partial D_x}\right)$ into the expression (5.2.4) one finds that the integral I_1 is a sum of four two-electron Coulomb integrals

$$I_1 = \sum_{m_1=0}^{1} \sum_{m_2=0}^{1} \langle \mathbf{n} + m_1 \mathbf{u}_1, a, \mathbf{A}; \mathbf{n}' + (1 - m_1)\, \mathbf{u}_1, b, \mathbf{B} \,|\, 1/r_{12}$$

$$|\, \mathbf{n}'' + m_2 \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + (1 - m_2)\, \mathbf{u}_1, d, \mathbf{D} \rangle \tag{5.2.5}$$

These integrals can be calculated analytically with the aid of simple auxiliary functions (3.4) and (3.5)[4]. The integral I_2 (5.2.3) is the general overlap integral which involves four HG fuctions placed on four different centers. It can be calculated straightforwardly by using the expression (5.2.6) which gives the integral of the delta function $\delta(\mathbf{r}_{12})$ over the spherically symmetric Gaussians

$$\int\int \exp(- a\, \mathbf{r}_{1A}^2 - b\, \mathbf{r}_{1B}^2)\, \delta(\mathbf{r}_{12})\, \exp(- c\, \mathbf{r}_{2C}^2 - d\, \mathbf{r}_{2D}^2)\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 =$$

$$= [\pi/(p + q)]^{3/2} \exp\{(- a\, b/p)\, \mathbf{AB}^2\} \exp\{(- c\, d/q)\, \mathbf{CD}^2\}$$

$$\exp\{- p\, q/(p + q)\, \mathbf{PQ}^2\} \tag{5.2.6}$$

where $p = a + b$, $q = c + d$ and coordinates of the vectors $\mathbf{P}$ and $\mathbf{Q}$ are $P_x = x - (aA_x + bB_x)/p$ etc. $Q_x = x - (cC_x + dD_x)/q$ etc., respectively. The formula for the I_2 integral is obtained by the appropriate differentiation of the expression (5.2.6) over the coordinates of the nuclei. It reads

$$I_2 = (4\pi/3)\, [\pi/(p + q)]^{3/2} \{ (-)^{n+n''} f(\mathbf{n} + \mathbf{n}', ab/p, \mathbf{AB})$$

$$f(\mathbf{n}'' + \mathbf{n}''', cd/q, \mathbf{CD})\, f(\mathbf{O}, pq/(p + q), \mathbf{PQ}) + (-)^{n''+n'''}$$

$$[a^{n}\, b^{n'}\, c^{''n}\, d^{n'''} / (p^{n+n'}\, q^{n''+n'''})]\, f(\mathbf{O}, ab/p, \mathbf{AB})\, f(\mathbf{O}, ab/q, \mathbf{CD})$$

$$f(\mathbf{n} + \mathbf{n}' + \mathbf{n}'' + \mathbf{n}''', pq/(p + q), \mathbf{PQ}) \} \tag{5.2.7}$$

---

[*] It should be pointed out that derivative with respect to x_1 is not equal to $- \frac{\partial}{\partial A_x} - \frac{\partial}{\partial B_x}$ but it can be exchanged within various expressions and integrals. The similar relationships should be interpreted in this way too.

Here $n = n_1 + n_2 + n_3$ and the corresponding primed entities have similar meaning.

The off-diagonal element $x_{12}\, z_{12}/r_{12}^5$ can be calculated in a similar way. One makes use of the identity

$$\frac{3\, x_{12}\, y_{12}}{r_{12}^5} = - \frac{\partial}{\partial x_1} \frac{\partial}{\partial y_2} [1/r_{12}]$$

Integration by parts yields

$$\int\!\!\int f(\mathbf{n}, a, \mathbf{A})\, f(\mathbf{n}', b, \mathbf{B})\, [3\, x_{12}\, y_{12}/r_{12}^5]\, f(\mathbf{n}'', c, \mathbf{C})\, f(\mathbf{n}''', d, \mathbf{D})$$

$$d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 = - \int\!\!\int \left(\frac{1}{r_{21}}\right) \frac{\partial}{\partial x_1} [f(\mathbf{n}, a, \mathbf{A})\, f(\mathbf{n}', b, \mathbf{B})] \frac{\partial}{\partial y_2}$$

$$[f(\mathbf{n}'', c, \mathbf{C})\, f(\mathbf{n}''', d, \mathbf{D})]\, d^3 \mathbf{r}_1\, d^3 \mathbf{r}_2 \qquad (5.2.8)$$

Replacing the differential operators $\partial/\partial x_1$ and $\partial/\partial y_2$ by $-\left(\frac{\partial}{\partial A_x} + \frac{\partial}{\partial B_x}\right)$ and $-\left(\frac{\partial}{\partial C_y} + \frac{\partial}{\partial D_y}\right)$, respectively, one obtains:

$$\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}', b, \mathbf{B} \,|\, 3\, x_{12}\, y_{12}/r_{12}^5 \,|\, \mathbf{n}'', c, \mathbf{C}; \mathbf{n}''', d, \mathbf{D} \rangle =$$

$$= - \sum_{k=0}^{1} \sum_{m=0}^{1} \langle \mathbf{n} + (1-k)\, \mathbf{u}_1, a, \mathbf{A}; \mathbf{n}' + k\, \mathbf{u}_1, b, \mathbf{B} \,|\, 1/r_{12}$$

$$|\, \mathbf{n}'' + (1-m)\, \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + m\, \mathbf{u}_1, d, \mathbf{D} \rangle \qquad (5.2.9)$$

Thus, we can draw the conclusion that the two-electron spin-spin dipolar interaction matrix elements are easily reduced to sums of two-electron repulsion integrals.

5.3. *Electron Spin-Same Orbit Integrals*

The relevant operator describing the spin-same orbit coupling takes the form

$$- i\hbar\, (1/r_N^3)\, \mathbf{r}_N \times \vec{\nabla}_1 \qquad (5.3.1)$$

Let us consider its **x**-component only for the sake of simplicity. Putting this operator in equivalent form

$$i\hbar \left[\frac{\partial}{\partial N_y} (1/r_N) \frac{\partial}{\partial B_z} - \frac{\partial}{\partial N_z} (1/r_N) \frac{\partial}{\partial B_y} \right]$$

the following formula is obtained after some algebra

$$\langle \mathbf{n}, a, \mathbf{A} \,|\, - i\hbar\, (1/r_N^3)\, \mathbf{r}_N \times \vec{\nabla} \,|\, \mathbf{n}', b, \mathbf{B} \rangle =$$

$$= - i\hbar \sum_{m=0}^{1} (\langle \mathbf{n} + (1-m)\, \mathbf{u}_2, a, \mathbf{A} \,|\, (1/r_N) \,|\, \mathbf{n}' + m\, \mathbf{u}_2 + \mathbf{u}_3, b, \mathbf{B} \rangle -$$

$$\langle \mathbf{n} + (1-m)\, \mathbf{u}_3, a, \mathbf{A} \,|\, (1/r_N) \,|\, \mathbf{n}' + \mathbf{u}_2 + m\, \mathbf{u}_3, b, \mathbf{B} \rangle] \qquad (5.3.2)$$

Therefore, the one-electron spin-orbit coupling operator (5.1) is expressed as a sum of nuclear-attraction integrals.

5.4. *Electron Spin-Other Orbit Integrals*

The interaction between the spin angular momentum of the electron and the magnetic field produced by the orbital motion of other electrons is described by the operator $-i\hbar\,(1/r_{12}^{3})\,\mathbf{r}_{12} \times \vec{\nabla}_2$. By using the identity

$$-i\hbar\,(1/r_{12}^{3})\,\mathbf{r}_{12} \times \vec{\nabla}_2 = i\hbar\,\vec{\nabla}_{1}(1/r_{12}) \times \vec{\nabla}_2$$

and performing partial integration over the coordinates of the electron 1 we get

$$\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}'', c, \mathbf{C} \,|\, -i\hbar\,(1/r_{12}^{3}) \times \vec{\nabla}_2 \,|\, \mathbf{n}', b, \mathbf{B}; \mathbf{n}''', d, \mathbf{D}\rangle =$$

$$= -i\hbar \int\!\!\int (1/r_{12})\,\vec{\nabla}_{1}\,[f(\mathbf{n}, a, \mathbf{r}_{1A})\, f(\mathbf{n}', b, \mathbf{r}_{1B})] \times$$

$$\times f(\mathbf{n}'', c, \mathbf{r}_{2C})\,\vec{\nabla}_2\, f(\mathbf{n}''', d, \mathbf{r}_{2D})\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \qquad (5.4.1)$$

One has to point out here that the orbitals describing electron 1 are placed on the nuclei A and B and those related to the electron 2 are centered on the nuclei C and D. Therefore in breaking down the matrix elements over the two Slater determinats to elementary integrals one obtains the sequence of orbitals as indicated on the left side of the eq 5.4.1. Replacing the operators $\vec{\nabla}_1$ and $\vec{\nabla}_2$ by $-(\vec{\nabla}_A + \vec{\nabla}_B)$ and $-\vec{\nabla}_D$, respectively, the spin-other orbit matrix elements are given in terms of four-center two-electron Coulomb repulsion integrals. We shall treat only the x-component of the expression (5.4.1) again for the sake of brevity. By using

$$\partial/\partial y_{1} = -(\partial/\partial A_y + \partial/\partial B_y),\ \partial/\partial_{z1} = -(\partial/\partial A_z + \partial/\partial B_z),\ \partial/\partial_{z2} = -\,\partial/\partial D_z$$

$$\partial/\partial_{y2} = -\,\partial/\partial D_y$$

we obtain

$$\int\!\!\int \{ (1/r_{12})\, f(\mathbf{n}'', c, \mathbf{r}_{2C})\, [\, \frac{\partial}{\partial y_1} (f(\mathbf{n}, a, \mathbf{r}_{1A})\, f(\mathbf{n}'\, b, \mathbf{r}_{1B}))\, \frac{\partial}{\partial z_2} f(\mathbf{n}''', d, \mathbf{r}_{2D}) - \frac{\partial}{\partial z_1}$$

$$(f(\mathbf{n}, a, \mathbf{r}_{1A})\, f(\mathbf{n}', b, \mathbf{r}_{1B}))\, \frac{\partial}{\partial y_2} f(\mathbf{n}''', d, \mathbf{r}_{2D})]\, \}\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 =$$

$$= -\sum_{m=0}^{1} [\langle \mathbf{n} + (1-m)\,\mathbf{u}_2, a, \mathbf{A}; \mathbf{n}' + m\,\mathbf{u}_2, b, \mathbf{B} \,|\, (1/r_{12}) \,|\, \mathbf{n}'', c, \mathbf{C}; \mathbf{n}''' + \mathbf{u}_3, d, \mathbf{D}\rangle -$$

$$-\langle \mathbf{n} + (1-m)\,\mathbf{u}_3, a, \mathbf{A}; \mathbf{n}' + m\,\mathbf{u}_3, b, \mathbf{B} \,|\, (1/r_{12}) \,|\, \mathbf{n}'', c, \mathbf{C}''; \mathbf{n}''' +$$

$$+ \mathbf{u}_2, d, \mathbf{D}\rangle] \qquad (5.4.2)$$

5.5. *Electron Orbit-Orbit Integrals*

The orbit-orbit part of the Breit hamiltonian in the Pauli approximation comprises two operators

$$(1/r_{12})\,\vec{\nabla}_1 \cdot \vec{\nabla}_2 \quad \text{and} \quad \mathbf{r}_{12} \cdot [(\mathbf{r}_{12}/r_{12}^{3}) \cdot \vec{\nabla}_1]\,\vec{\nabla}_2 \qquad (5.5.1)$$

Accordingly we have to consider two integrals the first being

$$\int\int f\,(\mathbf{n}, a, \mathbf{r}_{1A})\, f\,(\mathbf{n}'', c, \mathbf{r}_{2C})\, [(1/r_{12})\, \vec{\nabla}_1 \cdot \vec{\nabla}_2]\, f\,(\mathbf{n}', b, \mathbf{r}_{1B})\, f\,(\mathbf{n}''', d, \mathbf{r}_{2D})\, d^3\, \mathbf{r}_1\, d^3\, \mathbf{r}_2 \tag{5.5.2}$$

Substituting $\vec{\nabla}_1 \cdot \vec{\nabla}_2 = \vec{\nabla}_B\, \vec{\nabla}_D$ it is easily proven that the following formula holds

$$\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}'', c, \mathbf{C} \,|\, (1/\mathbf{r}_{12})\, \vec{\nabla}_1 \cdot \vec{\nabla}_2 \,|\, \mathbf{n}', b, \mathbf{B}; \mathbf{n}''', d, \mathbf{D} \rangle =$$

$$= \sum_{i=1}^{3} \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}'', c, \mathbf{C} \,|\, (1/\mathbf{r}_{12}) \,|\, \mathbf{n}' + \mathbf{u}_i, b, \mathbf{B}; \mathbf{n}''' + \mathbf{u}_i, d, \mathbf{D} \rangle \tag{5.5.3}$$

Concomitant with Lo's treatment we shall write the second operator in the form[15]

$$(1/r_{12}{}^3)\, \mathbf{r}_{12} \cdot (\mathbf{r}_{12} \cdot \vec{\nabla}_1)\, \vec{\nabla}_2 = \sum_{\mu\,\nu} (1/r_{12}{}^3)\, \mu_{12}\, \nu_{12}\, \frac{\partial}{\partial \mu_1}\, \frac{\partial}{\partial \nu_2} \tag{5.5.4}$$

where the Greek letters μ and ν assume the Cartesian coordinates x, y and z. Let us consider two representative members of the sum (5.5.4)

$$(x_{12}{}^2/r_{12}{}^3)\, \frac{\partial}{\partial x_1}\, \frac{\partial}{\partial x_2} \quad \text{and} \quad (x_{12}\, y_{12}/r_{12}{}^3)\, \frac{\partial}{\partial x_1}\, \frac{\partial}{\partial y_2}$$

The partial integration yields the following expression for the first operator

$$\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}'', c, \mathbf{C} \,|\, (x_{12}{}^2/r_{12}{}^3)\, \frac{\partial}{\partial x_1}\, \frac{\partial}{\partial x_2} \,|\, \mathbf{n}', b, \mathbf{B}; \mathbf{n}''', d, \mathbf{D} \rangle =$$

$$\begin{aligned}
&\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/r_{12}) \,|\, \mathbf{n}'', c, \mathbf{C}; \mathbf{n}''' + \mathbf{u}_1, d, \mathbf{D} \rangle + \\
&+ \sum_{m=0}^{1} [(A_x - C_x)\, \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/r_{12}) \,|\, \mathbf{n}'' + (1 - m)\, \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + \\
&+ (1 + m)\, \mathbf{u}_1, d, \mathbf{D} \rangle + (1/2\, b)\, \langle \mathbf{n} + \mathbf{u}_1, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/_{12}) \,|\, \mathbf{n}'' + \\
&+ (1 - m)\, \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + (1 + m)\, \mathbf{u}_1, d, \mathbf{D} \rangle + \mathbf{n}_1\, \langle \mathbf{n} - \mathbf{u}_1, a, \mathbf{A}; \mathbf{n}' + \\
&+ \mathbf{u}_1, b, \mathbf{B} \,|\, (1/\mathbf{r}_{12}) \,|\, \mathbf{n}'' + (1 - m)\, \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + (1 + m)\, \mathbf{u}_1, d, \mathbf{D} \rangle - \\
&- (1/2\, b)\, \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_i, b, \mathbf{B} \,|\, (1/\mathbf{r}_{12}) \,|\, \mathbf{n}'' + (2 - m)\, \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + \\
&+ (1 + m)\, \mathbf{u}_1, d, \mathbf{D} \rangle - \mathbf{n}_1{}'''\, \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/r_{12}) \,|\, \mathbf{n}'' - \\
&- m\, \mathbf{u}_1, c, \mathbf{C}; \mathbf{n}''' + (1 + m)\, \mathbf{u}_1, d, \mathbf{D} \rangle]
\end{aligned} \tag{5.5.5}$$

The formula for operator $(x_{12}\, y_{12}/r_{12}{}^3)\, \frac{\partial}{\partial x_1}\, \frac{\partial}{\partial y_2}$ can be analogously worked out

$$\langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}'', c, \mathbf{C} \,|\, (\mathbf{x}_{12}\, y_{12}/\mathbf{r}_{12}{}^3) \,|\, \frac{\partial}{\partial x_1}\, \frac{\partial}{\partial y_2} \,|\, \mathbf{n}', b, \mathbf{B}; \mathbf{n}''', d, \mathbf{D} \rangle =$$

$$\begin{aligned}
&= \sum_{m=0}^{1} [(A_x - C_x)\, \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/\mathbf{r}_{12}) \,|\, \mathbf{n}'' + (1 - m)\, \mathbf{u}_2, c, \mathbf{C}; \mathbf{n}''' + \\
&+ (1 + m)\, \mathbf{u}_2, d, \mathbf{D} \rangle + (1/2\, b)\, \langle \mathbf{n} + \mathbf{u}_1, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/r_{12}) \,|\, \mathbf{n}'' +
\end{aligned}$$

$$+ (1 - m)\,\mathbf{u}_2, c, \mathbf{C}; \mathbf{n}''' + (1 + m)\,\mathbf{u}_2, d, \mathbf{D}\rangle + \mathbf{n}_1 \langle \mathbf{n} - \mathbf{u}_1, a, \mathbf{A}; \mathbf{n}' +$$
$$+ \mathbf{u}_1, b, \mathbf{B} \,|\, (1/\mathbf{r}_{12}) \,|\, \mathbf{n}'' + (1 - m)\,\mathbf{u}_2, c, \mathbf{C}; \mathbf{n}''' + (1 + m)\,\mathbf{u}_2, d, \mathbf{D}\rangle -$$
$$- (1/2\,b) \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1/\mathbf{r}_{12}) \,|\, \mathbf{n}'' + (1 - m)\,\mathbf{u}_2, c, \mathbf{C}; \mathbf{n}''' +$$
$$+ (1 + m)\,\mathbf{u}_2, d, \mathbf{D}\rangle - \mathbf{n}_1 \langle \mathbf{n}, a, \mathbf{A}; \mathbf{n}' + \mathbf{u}_1, b, \mathbf{B} \,|\, (1r_{12}) \,|\, \mathbf{n}'' - \mathbf{u}_1 +$$
$$+ (1 - m)\,\mathbf{u}_2, c, \mathbf{C}; \mathbf{n}''' + \langle 1 + m)\,\mathbf{u}_2, d, \mathbf{D}\rangle] \tag{5.5.6}$$

It appears that the orbit-orbit integrals can be reduced to the Coulomb repulsion matrix elements.

5.6. *Model-Potential Integrals*

Description of the inner-core electrons by a suitable model pseudo-potential is an attractive and useful idea. It becomes a necessity when the molecules involving one or several heavy atoms are to be studied. Comprehensive account of the pseudo-potential methods is out of the scope of this paper and the reader is referred to a review article of Rice et al.[16] We shall consider the Bonifačić-Huzinaga model[6] potential because it is appropriate for our basis set and gives a fair account of the inner-valence shells interactions[17]. It is of the form

$$M_p = V^c(r) + \Omega^c \tag{5.6.1}$$

where M_p, $V^c(r)$ and Ω^c stand for the model potential, the total core potential and the total projection operator Ω^c, respectively. Explicitly

$$V^c(r) = -\sum_N [(Z_N - n_N^c)/r_N]\,[1 + \sum_{j=1}^{m_N} A_{jN} \exp(-\alpha_{jN}\, \mathbf{r}_N^2)] \tag{5.6.2}$$

and

$$\Omega^c = \sum_N \sum_{k=1}^{n_N^c} B_{kN}^c\, \Omega_{kN}^c \tag{5.6.3}$$

where n_N^c is a number of core electrons of the atom N, m_N is an arbitrary integer which determines the flexibility of the model potential and the sum over N is extended over heavy atoms in a molecule. The adjustable parameters are denoted by A_{jN}, α_{jN} and B_{kN}^c. One observes that the effect of screening of the nuclear charge Z_N is described by a sum of spherically symmetric Gaussians which soften the effect of total coalescence of the core electrons n_N^c with nucleus N included in the first term. The projection operator $\Omega_{kN}^c = |\,\Psi_{kN}^0 > < \Psi_{kN}^0\,|$ ensures that the valence orbitals are orthogonal to the particular core orbitals. Thus the operator (5.6.3) is not of our concern here and will be dropped from further discussion. The first term in the core pseudo-potential is the well known nuclear attraction operator. We shall consider the Coulomb attraction potential screened by a spherical Gaussian $\exp(-\alpha_{jN}\, r_N^2)$. Its matrix elements are readily obtained by using the general property of spherical Gauss functions (1.2) where b and $\mathbf{B}$ are replaced by α_{jN} and $\mathbf{N}$, respectively. Employing the Leibniz formula for higher derivatives of a product one gets

$$
\begin{aligned}
&-\sum_{N} (Z_N - n_N^c) \sum_{j=1}^{m_N} A_{jN} \langle \mathbf{n}, a, \mathbf{A} \,|\, \exp(-\alpha_{jN}\, \mathbf{r}_N^2)/r_N \,|\, \mathbf{n}', b, \mathbf{B} \rangle = \\
&= -\sum_{N} (Z_N - n_N^c) \sum_{j=1}^{m_N} A_{jN} \sum_{s_1=0}^{n_1} \sum_{s_2=0}^{n_2} \sum_{s_3=0}^{n_3} \binom{n_1}{s_1} \binom{n_2}{s_2} \binom{n_3}{s_3} \\
&\beta_{jN}^{n-s} \left(\frac{a}{a + \alpha_{jN}} \right)^{s} H_{n_1 - s_1} (\beta_{jN} (A_x - N_x))\, H_{n_2 - s_2} (\beta_{jN} (A_y - N_y))\, H_{n_3 - s_3} \\
&(\beta_{jN} (A_z - N_z)) \langle \mathbf{s}, a + \alpha_{jN}, \mathbf{P} \,|\, 1/r_N \,|\, \mathbf{n}', b, \mathbf{B} \rangle \qquad (5.6.4)
\end{aligned}
$$

where $\beta_j = a\,\alpha_{jN}/(a + \alpha_{jN})^{1/2}$, $n = n_1 + n_2 + n_3$, $s = s_1 + s_2 + s_3$, H is the Hermite polynomial and the coordinates of the vector $\mathbf{P}$ are $P_x = x - (a\,A_x + \alpha_{jN}\,N_x)/(a + \alpha_{jN})$ etc. It follows that the integrals arising in model pseudo-potential calculations are expressed as linear combinations of nuclear attraction integrals.

6. DISCUSSION

The molecular integrals necessary for the calculation of first and second order properties and the relativistic corrections appearing in the Breit-Pauli hamiltonian can be reduced to the integrals already encountered in the Hartree-Fock-Roothaan calculations if the Hermite-Gaussian basis set is employed. More specifically, the one- and two-electron integrals involving r^n operator, where n is a negative integer, are reduced to one- and two-electron nuclear attraction and Coulomb repulsion integrals, respectively. Thus the electric and magnetic properties of polyatomic molecules may be computed with a modest additional effort. This is of some importance because these properties provide very sensitive accuracy test of the computed wave-functions[18]. It should be pointed out that the required formulas are given in closed form which are simpler than those obtained by Brown and Poshusta[19] and Matsuoka[20] who used a spherical Gaussians basis set multiplied by products of Cartesian coordinates. The gain in efficiency is increasing with the increase in angular quantum number indicating that the HG basis sets would be advantageous in molecules involving heavy atoms. It is gratifying in this respect that the integrals appearing in suitable model pseudo-potential calculations are also easily computed. The derivatives of the relevant integrals over the nonlinear parameters and coordinates of the operators can also be analytically expressed in closed forms[9]. Therefore the optimization of the HG functions in the sense of the variation theorem[21] may be efficiently performed. Furthermore, the basis sets comprised by HG functions provide convenient means for the energy optimization over a range of molecular structural parameters (e. g. interatomic distances), force field calculations, the studies of the vibrational effects on the one-electron properties etc. We conclude that Hermite-Gaussian functions are to be preferred over the customary Gaussian basis sets now in widespread use when the molecules involving heavy atoms are considered. Finally, it should be mentioned that some of the integrals for molecular properties employing HG functions appeared recently in the literature[22].

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SAŽETAK

Razmatranje integrala potrebnih za računanje relativističkih efekata u molekulama kao i integrala vezanih za jedno- i dvoelektronska molekularna svojstva primjenom Hermite-Gaussovih funkcija

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Izvedene su formule za računanje relativističkih efekata u molekulama kao i formule za računanje integrala vezanih za studij jednoelektronskih i dvoelektronskih svojstava molekula. Pri tome se kao osnovni skup funkcija koriste Hermite-Gaussove funkcije. Pokazano je da se spomenuti integrali mogu svesti na standardne integrale koji se pojavljuju u računu osnovnog stanja molekula primjenom varijacijskog teorema. Kako se ovi posljednji mogu izraziti analitički, ako se računaju pomoću Hermite-Gaussovih funkcija, proizlazi da se električna i magnetska svojstva molekula mogu dobiti s malim dodatnim naporom. Isti zaključak vrijedi i za uključivanje u račun unutrašnjih elektrona primjenom metode pseudo potencijala oblika koji su predložili Bonifačić i Huzinaga. Kako su Gauss-Hermiteove funkcije pogodnije za atomske orbitale viših kvantnih brojeva kutne količine gibanja od standardnih postupaka slijedi da će njihova upotreba kod molekula koje sadrže teške atome biti izuzetno korisna.

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