Some Molecular Integrals over Ellipsoidal Hermite-Gaussian Functions

Z. B. Maksić

Theoretical Chemistry Group, The "Rudjer Bošković" Institute, 41001 Zagreb and
Faculty of Natural Sciences and Mathematics, The University of Zagreb, Marulićev trg 19,
41001 Zagreb, Yugoslavia

Z. Naturforsch. **41 a,** 921 – 927 (1986); received July 26, 1984

Some molecular integrals over ellipsoidal Hermite-Gaussian functions relevant for SCF calculations are considered. It is shown that all integrals can be expressed in a closed form if the $H_{n_{xA}}(a_{xA} x_A) H_{n_{yA}}(a_{yA} y_A) H_{n_{zA}}(a_{zA} z_A) \exp(-b r_A^2)$ basis set is employed. It appears also that this type of functions is convenient for the calculation of electric properties of molecules. Finally, a relation between the HG and harmonic oscillator functions is established.

1. Introduction

The elementary building blocks in rigorous quantum chemical calculations are integrals over the selected basis set functions. Their evaluation is in general very tedious and time-consuming. A breakthrough in computational quantum chemistry was made by the use of Gaussian functions as suggested first by Boys [1] and McWeeny [2]. It was shown that all molecular integrals are easily tractable if spherical Gaussians (SG) were employed. General formulas for Cartesian Gaussians (CG) were developed by Wright [3] and Huzinaga et al. [4, 5]. Browne and Poshusta [6] introduced the ellipsoidal Gaussian functions where additional gain in flexibility is obtained by different "screening" nonlinear parameters in different Cartesian coordinate directions. They provided the necessary formulas for Cartesian ellipsoidal Gaussians (CEG), but the nuclear attraction and electron repulsion integrals required a rather inconvenient computational procedure involving numerical integrations. An interesting refinement of the Browne and Poshusta CEG functions was offered by van Duijnen and Cook [7, 8]. Each CEG function is defined in its own local coordinate system, which is favourable for construction of bond orbitals and useful for the discussion and exploitation of transferability properties of local hybrid orbitals.

A serious shortcoming of Gaussian functions is their poor physical behaviour in the vicinity of the nucleus and in peripheral regions of an atom or a molecule. Here a large number of Gaussian functions is necessary in order to give a satisfactory description of inner and outer portions of electron density. Consequently it might be advantageous to employ more involved basis functions which could lead to smaller basis sets. The latter could prove more economical even at costs of some increase of the actual integral computation time, particularly if the basis functions are compatible with the physical picture of the chemical bond (vide infra). With this idea in mind we designed Hermite-Gaussian (HG) functions [9] which are of the form

$$f(\boldsymbol{n}_A, a_A, \boldsymbol{r}_A) = a_A^{n/2} H_{n_{xA}}[a_A^{1/2} x_A] \cdot H_{n_{yA}}[a_A^{1/2} y_A] H_{n_{zA}}[a_A^{1/2} z_A] \exp(-a_A r_A^2), \tag{1}$$

where $x_A = x - A_x$ etc., $n_A = n_{xA} + n_{yA} + n_{zA}$ and A_x is the coordinate of the nucleus A. It is easily seen that the Hermite polynomials H_{ni} are produced by the differentiation of the SG function over the corresponding nuclear coordinates (A_x, A_y, A_z). Since there are two different definitions of Hermite polynomials we give here their interrelation:

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} = \sqrt{2^n}\, He_n(\sqrt{2x}).$$

It was also hoped that Hermite polynomials would be advantageous because they are the simplest orthogonal polynomials with the $(-\infty, +\infty)$ range In particular, owing to the convenience mentioned

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Reprint requests to Prof. Dr. Z. B. Maksić, Theoretical Chemistry Group, The "Rudjer Bošković" Institute, 41001 Zagreb, Yugoslavia.

0340-4811 / 86 / 0700-0921 $ 01.30/0. – Please order a reprint rather than making your own copy.

above, all molecular integrals were expressed in closed forms [9]. These formulas were simpler that earlier expressions for Cartesian Gaussians [4–6]. The gain in efficiency upon using HG functions raises quickly by the increase of the angular quantum number l, or in other words, with the increase of the order of H_{ni} polynomials. This is of some importance because higher AOs play an important role in accurate molecular calculations. For example, the effect of f-functions has to be taken into account in all calculations involving d-bonding [10]. Their influence is considerably magnified in correlated wave functions [11, 12]. Hence in these type of calculations HG functions should be preferred over CG ones. Their merits were rediscovered by Golebiewski and Mrozek [13]. Similar idea was used by McMurchie and Davidson [14] who expanded the products of Cartesian coordinates belonging to CGs in series of Hermite polynomials. The performance of HG functions was further improved by Van der Welde algorithm [15]. In addition, it should be mentioned that integrals required for treatment of molecular properties and relativistic effects in molecules can be also expressed in analytical form if the HG basis is employed [16, 17]. The formulas were superior in efficiency to the previous ones based on CG functions [18, 19].

The HG functions seem to be the subject matter of continuous interest. They were employed in ab initio SCF calculations [20] and in the implementation of the LCAO-X_α method [21, 22]. The HG basis functions proved useful in the theoretical treatment of dynamic electron densities in molecular crystals [23a] and the calculation of photoelectron cross sections [23b]. Finally, one should mention important work of Salvetti et al. [24] on potential energy curves in diatomics and correlation energy.

Although substantially improved algorithms were devised in the meantime for the calculation of CG integrals for energy quantities [25, 26], molecular properties [27] and matrix elements of the Breit-Pauli Hamiltonian [28], it seems worthwile to explore in more detail the potential capabilities of the HG functions. The useful modification of the HG set was introduced by Katriel and Adam [29, 30] which allows distinction of parameters entering the Hermite polynomials and Gaussian parts of the HG functions (vide infra). Furthermore, ellipticity is taken into account by using different parameters for different directions of coordinate axes. This increased flexibility makes ellipsoidal HG functions more suitable for the description of the anisotropy of the atomic charge distributions in molecular environments. The algorithm provided by Katriel and Adam is however, rather complicated. It is the aim of the present paper to offer an alternative and possibly a better computational procedure. In addition, some properties of ellipsoidal HG functions are briefly discussed.

2. Molecular Energy Integrals

a) Methodology

The ellipsoidal Hermite-Gaussian function (EHG)* placed on the nucleus A can be written in a concise form:

$$\varphi(\boldsymbol{n}_A, \boldsymbol{a}_A, \boldsymbol{b}_A, \boldsymbol{r}_A) = \prod_\alpha \varphi(n_{\alpha A}, a_{\alpha A}, b_{\alpha A}, \alpha_A) \quad (2)$$
$$(\alpha = x, y, z),$$

where

$$\varphi(n_{xA}, a_{xA}, b_{xA}, x_A) = H_{n_{xA}}(a_{xA}^{1/2} x_A) \exp(-b_{xA} x_A^2)$$

is the X-component of the EHG function and $\boldsymbol{n}$, $\boldsymbol{a}$, $\boldsymbol{b}$ are triads of numbers $n_{\alpha A}$, $a_{\alpha A}$ and $b_{\alpha A}$ ($\alpha = x, y, z$), respectively. A salient feature of HG and EHG functions is that they are factorized into Cartesian components which makes easy the calculation of many one-electron integrals. Secondly, Hermite polynomials have some remarkable and useful properties which can be exploited in the numerical work. They describe the shape of the orbital if properly combined, whilst the exponential function has a dominant effect on the radial dependence determining thus its size.

It is well known that orbital energies of the AOs are mostly affected by their size. Therefore the minimum energy criterion will optimize the nonlinear parameters, scaling at the same time the corresponding Hermite polynomials entering into the HG functions in question. Consequently, it is

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* The functions (2) were denoted by Katriel and Adam as generalized HG functions [29]. We find it somewhat inappropriate because this name implies the use of generalized Hermite polynomials (see e.g. [31]) which is certainly not the case. In full analogy with EG functions the set (2) should be termed as ellipsoidal HG set of functions.

desirable to relax the $a = b$ condition increasing thus the flexibility of the basis set. Matrix elements between the more general functions (2) can be reduced to the already encountered integrals over HG functions [9, 13] as follows. Any polynomial of the n-th order can be expressed in terms of the H-polynomials up to the n-th order. Specifically

$$H_{n_{xA}}(a_{xA}^{1/2}\, x_A) = \sum_{m_{xA}=(0,1)}^{n_{xA}} c(n_{xA}, a_{xA}, b_{xA}, m_{xA})\, H_{m_{xA}}(b_{xA}^{1/2}\, x_A). \tag{3}$$

It is useful to observe that H-polynomials are either odd or even. Hence, the summation in (3) is restricted to odd or even m_{xA} values. The coefficients c are easily determined by using the orthogonality relations of the H-polynomials

$$\int_{-\infty}^{+\infty} \exp(-b_{xA}\, x_A^2)\, H_{m_{xA}}(b_{xA}^{1/2}\, x_A)\, H_{n_{xA}}(b_{xA}^{1/2}\, x_A)\, \mathrm{d}(b_{xA}^{1/2}\, x_A) = \sqrt{\pi}\, 2^{m_{xA}}(m_{xA}!)\, \delta_{m_{xA} n_{xA}} \tag{4}$$

and the related integrals involving $H_{n_{xA}}(a_{xA}^{1/2}\, x_A) \cdot H_{m_{xA}}(b_{xA}^{1/2}\, x_A)$ products [32]. It appears that the expansion coefficients depend on the ratio $\sqrt{a_{xA}/b_{xA}} = \omega_{xA}$:

$$c(n_{xA}, a_{xA}, b_{xA}, m_{xA}) = \delta'_{n_{xA}-m_{xA}} \{n_{xA}!/m_{xA}!\,[(n_{xA}-m_{xA})/2]!\}\, \omega_{xA}^{m_{xA}} \cdot (\omega_{xA}^2 - 1)^{(n_{xA}-m_{xA})/2}, \tag{5}$$

where δ' is a sort of the Kronecker delta symbol. It is a parity switch factor

$$\delta'_{n_{xA}-m_{xA}} = \begin{cases} 1 & \text{if } n_{xA} - m_{xA} \text{ is even} \\ 0 & \text{if } n_{xA} - m_{xA} \text{ is odd} \end{cases}$$

which diminishes the number of terms by 1/2. Generalization of the formula (3) to three-dimensional EHG function yields

$$\varphi(\boldsymbol{n}_A, \boldsymbol{a}_A, \boldsymbol{b}_A, \boldsymbol{r}_A) = \prod_{\alpha} \sum_{m_{xA}}^{n_{\alpha A}} c(n_{\alpha A}, a_{\alpha A}, b_{\alpha A}, m_{\alpha A}) \cdot H_{m_{xA}}(b_{\alpha A}^{1/2}\, \alpha_A) \exp(-b_{\alpha A}\, \alpha_A^2). \tag{6}$$

This expression enables reduction of most of the one-electron integrals to the known formulas for the HG functions given earlier [9, 13]. However, if the operator does not allow separation into three Cartesian components like, e.g., the Coulomb potential $1/r_N$ of the nucleus N, another approach is necessary. The same applies to the two-electron operators. In this case the exponential function will be written as a product of the spherical part and the ellipticity correction:

$$\prod_{\alpha=x,y,z} \exp(-b_{\alpha A}\, \alpha_A^2) = \exp(-d_A\, r_A^2) \prod_{\alpha=x,y,z} \exp(-b'_{\alpha A}\, \alpha_A^2), \tag{7}$$

where $b'_{\alpha A} = b_{\alpha A} - d_A$. The spherical portion multiplied with the H polynomials $\prod_{\alpha=x,y,z} H_{n_{xA}}(d_A^{1/2}\, \alpha_A)$ leads to the integrals which can be tackled in analytical fashion. Therefore we shall try to eliminate the ellipsoidal Gaussian part by a truncated series:

$$H_{n_{zA}}(a_{xA}^{1/2}\, x_A) \exp[-(b_{xA} - d_A)\, x_A^2] = \sum_{m_{xA}}^{m_{xA}(\max)} e(a_{xA}, b_{xA}, d_A, m_{xA})\, H_{m_{xA}}(d_A^{1/2}\, x_A), \tag{8}$$

where the upper limit $m_{xA}(\max)$ depends on the predetermined accuracy. Since the Gaussian is symmetric with respect to the reflection in the origin, the summation is restricted only to either even or odd m_{xA} depending on the parity of the $H_{n_{xA}}$ polynomial. The expression (8) can be viewed as a development of the differently gauged modified HG functions $H(a^{1/2}\, x) \exp(-b\, x^2)$ in a series of the customary HG functions of the $H(d^{1/2}\, x) \cdot \exp(-d x^2)$ type. It should be pointed out at this moment that statistical distribution functions are frequently expanded in terms of the HG basis, and the first few terms usually suffice [33]. By using (3) one straightforwardly obtains the coefficients of the expansion (8):

$$e(a_{xA}, b_{xA}, d_A, m_{xA}) = \frac{\sqrt{d_A/b_{xA}}}{2^{m_{xA}}\, m_{xA}!} \sum_{k_{xA}}^{\min(n_{xA}, m_{xA})} 2^{k_{xA}}(k_{xA})! \cdot c(n_{xA}, a_{xA}, b_{xA}, k_{xA})\, c(m_{xA}, d_A, b_{xA}, k_{xA}). \tag{9}$$

Hence, the EHG function (2) takes the form

$$\varphi(\boldsymbol{n}_A, \boldsymbol{a}_A, \boldsymbol{b}_A, \boldsymbol{r}_A) = \sum_{m_{xA}} \sum_{m_{yA}} \sum_{m_{zA}} k(m_{xA}, m_{yA}, m_{zA}) f(\boldsymbol{m}_A, d_A, \boldsymbol{r}_A), \tag{10}$$

where

$$k(m_{xA}, m_{yA}, m_{zA}) = \prod_{\alpha=x,y,z} e(a_{\alpha A}, b_{\alpha A}, d_A, m_{\alpha A})\, d_A^{-m_{\alpha A}/2} \tag{11}$$

and $\boldsymbol{m}_{\mathrm{A}}$ is a triad of summation indices $m_{x\mathrm{A}}, m_{y\mathrm{A}}$ and $m_{z\mathrm{A}}$. In other words, the EHG function is a linear combination of HG basis functions. Following the strategy outlined above one can readily obtain the formulas required in the variational calculation.

b) Overlap integrals

We shall illustrate the procedure first by treating the simplest matrix elements – overlap integrals. By using (6) one gets

$$\begin{aligned}&\langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\mathrm{B}}, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &= \prod_{\alpha} \prod_{\beta} \sum_{m_{\alpha\mathrm{A}}}^{n_{\alpha\mathrm{A}}} \sum_{m_{\beta\mathrm{B}}}^{n_{\beta\mathrm{B}}} c(n_{\alpha\mathrm{A}}, a_{\alpha\mathrm{A}}, b_{\alpha\mathrm{A}}, m_{\alpha\mathrm{A}})\\ &\quad \cdot c(n_{\beta\mathrm{B}}, a_{\beta\mathrm{B}}, b_{\beta\mathrm{B}}, m_{\beta\mathrm{B}}) \langle H_{m_{\alpha\mathrm{A}}}(b_{\alpha\mathrm{A}}^{1/2}\,\alpha_{\mathrm{A}})\\ &\quad \cdot \exp(-b_{\alpha\mathrm{A}}\,\alpha_{\mathrm{A}}^2) | H_{m_{\beta\mathrm{B}}}(b_{\beta\mathrm{B}}^{1/2}\,\beta_{\mathrm{B}}) \exp(-b_{\beta\mathrm{B}}\,\beta_{\mathrm{B}}^2)\rangle .\end{aligned}$$

It is easily seen that only terms with $\alpha = \beta$ survive. The expression for the overlap integrals reads

$$\begin{aligned}&\langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}\ \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\mathrm{B}}, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &= [\pi^{3/2}/\sqrt{(b_{x\mathrm{A}} + b_{x\mathrm{B}})(b_{y\mathrm{A}} + b_{y\mathrm{B}})(b_{z\mathrm{A}} + b_{z\mathrm{B}})}\,]\\ &\quad \cdot \prod_{\alpha = x, y, z} \sum_{m_{\alpha\mathrm{A}}}^{n_{\alpha\mathrm{A}}} \sum_{m_{\alpha\mathrm{B}}}^{n_{\alpha\mathrm{B}}} (-1)^{m_{\alpha\mathrm{A}}} c(n_{\alpha\mathrm{A}}, a_{\alpha\mathrm{A}}, b_{\alpha\mathrm{A}}, m_{\alpha\mathrm{A}})\\ &\quad \cdot c(n_{\alpha\mathrm{B}}, a_{\alpha\mathrm{B}}, b_{\alpha\mathrm{B}}, m_{\alpha\mathrm{B}}) \qquad (12)\\ &\quad \cdot H_{m_{\alpha\mathrm{A}} + m_{\alpha\mathrm{B}}}[\sqrt{p_\alpha}(\mathrm{A}_\alpha - \mathrm{B}_\alpha)] \exp[-p_\alpha(\mathrm{A}_\alpha - \mathrm{B}_\alpha)^2],\end{aligned}$$

where $p_\alpha = b_{\alpha\mathrm{A}}\, b_{\alpha\mathrm{B}}/(b_{\alpha\mathrm{A}} + b_{\alpha\mathrm{B}})$.

c) Dipole Moment Integrals

The dipole moment integrals are not involved in the ground state energy minimization of a free molecule. However, the dipole moment is frequently used in the quantitative appraisal of the quality of the computed wave functions, because the total molecular energy is rather insensitive to the finer details of the electron density distribution. Therefore it is appropriate to report the relevant dipole moment integrals. Utilizing the identity

$$\alpha \exp(-b_{\alpha\mathrm{B}}\,\alpha_{\mathrm{B}}^2) = \left[\mathrm{B}_\alpha + (1/2 b_{\alpha\mathrm{B}}) \frac{\partial}{\partial \mathrm{B}_\alpha}\right] \cdot \exp(-b_{\alpha\mathrm{B}}\,\alpha_{\mathrm{B}}^2) \qquad (13)$$

and the relation [34]

$$H_m(x)\, H_n(x) = \sum_{k=0}^{\min(m,n)} 2^k k! \binom{m}{k} \binom{n}{k} H_{m+n-2k}(x) \qquad (14)$$

one straightforwardly obtains the matrix element for the arbitrary component α of the dipole moment:

$$\begin{aligned}&\langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \alpha | \varphi(\boldsymbol{n}_{\mathrm{b}}, \boldsymbol{a}_{\mathrm{b}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &= \mathrm{B}_\alpha \langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\mathrm{b}}, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &+ (1/2\sqrt{a_{\alpha\mathrm{B}}})[\langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\mathrm{B}} + \boldsymbol{u}_\alpha, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &\quad + 2 n_{x\mathrm{B}} \langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\mathrm{B}} - \boldsymbol{u}_\alpha, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle]\\ &\qquad\qquad (\alpha = x, y, z), \qquad (15)\end{aligned}$$

where $\boldsymbol{u}_\alpha$ is a unit triad [9]. Hence, the dipole moment integrals are linear combinations of the overlaps given by (12).

d) Kinetic Energy Integrals

These integrals are also related to overlapping of the basis functions:

$$\begin{aligned}&\langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | -\Delta/2 | \varphi(\boldsymbol{n}_{\mathrm{B}}, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &= -\sum_{\alpha = x, y, z} \{(2 n_{\alpha\mathrm{B}} - 1)(b_{\alpha\mathrm{B}}/a_{\alpha\mathrm{B}})(b_{\alpha\mathrm{B}} - a_{\alpha\mathrm{B}})\\ &\quad \cdot \langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\mathrm{B}}, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &\quad - 4 n_{\alpha\mathrm{B}}(n_{\alpha\mathrm{B}} - 1)\, b_{\alpha\mathrm{B}}[1 - (a_{\alpha\mathrm{B}}^2 + b_{\alpha\mathrm{B}}^2)/2 a_{\alpha\mathrm{B}}\, b_{\alpha\mathrm{B}}]\\ &\quad \cdot \langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\alpha\mathrm{B}} - 2\boldsymbol{u}_\alpha, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\\ &\quad + (b_{\alpha\mathrm{B}}^2/2 a_{\alpha\mathrm{B}}) \qquad (16)\\ &\quad \cdot \langle\varphi(\boldsymbol{n}_{\mathrm{A}}, \boldsymbol{a}_{\mathrm{A}}, \boldsymbol{b}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{A}}) | \varphi(\boldsymbol{n}_{\alpha\mathrm{B}} + 2\boldsymbol{u}_\alpha, \boldsymbol{a}_{\mathrm{B}}, \boldsymbol{b}_{\mathrm{B}}, \boldsymbol{r}_{\mathrm{B}})\rangle\}.\end{aligned}$$

In the course of the calculation we used the relation (14) and the formula for the derivatives of the H-polynomials

$$H_n^{(k)}(x) = \left(\frac{\partial}{\partial x}\right)^k H_n(x) = 2^k \frac{n!}{(n-k)!} H_{n-k}(x). \qquad (17)$$

e) Nuclear attraction and electron repulsion integrals

By using the expansion of the EHG function in terms of ordinary HG functions (10), the Coulombic type integrals are reduced to the known formulas. For example, the nuclear attraction of the nucleus N is described by integrals of the form

$$\langle \varphi(\boldsymbol{n}_\mathrm{A}, \boldsymbol{a}_\mathrm{A}, \boldsymbol{b}_\mathrm{A}, \boldsymbol{r}_\mathrm{A}) | 1/r_\mathrm{N} | \varphi(\boldsymbol{n}_\mathrm{B}, \boldsymbol{a}_\mathrm{B}, \boldsymbol{b}_\mathrm{B}, \boldsymbol{r}_\mathrm{B}) \rangle = \sum_{m_{x\mathrm{A}}} \dots \sum_{m_{z\mathrm{B}}} k(m_{x\mathrm{A}}, m_{y\mathrm{A}}, m_{z\mathrm{A}})\, k(m_{x\mathrm{B}}, m_{y\mathrm{B}}, m_{z\mathrm{B}}) \cdot |\langle f(\boldsymbol{n}_\mathrm{A}, \boldsymbol{d}_\mathrm{A}, \boldsymbol{r}_\mathrm{A}) | 1/r_\mathrm{N} | f(\boldsymbol{n}_\mathrm{B}, \boldsymbol{d}_\mathrm{B}, \boldsymbol{r}_\mathrm{B}) \rangle . \quad (18)$$

The later integrals are explicitly given in our earlier paper [9]. Analogously, the interelectronic potential energy integrals are expressed in terms of matrix elements

$$\langle \varphi(\boldsymbol{n}_\mathrm{A}, d_\mathrm{A}, \boldsymbol{r}_\mathrm{A})\, \varphi(\boldsymbol{n}_\mathrm{B}, d_\mathrm{B}, \boldsymbol{r}_\mathrm{B}) \cdot | 1/r_{12} | \varphi(\boldsymbol{n}_\mathrm{C}, d_\mathrm{C}, \boldsymbol{r}_\mathrm{C})\, \varphi(\boldsymbol{n}_\mathrm{D}, d_\mathrm{D}, \boldsymbol{r}_\mathrm{D}) \rangle .$$

The formulas presented in [9] can be then employed if some care regarding the sign is exercised as noticed by Golebiewski and Mrozek [13].

3. Discussion

The main result of the present analysis is that the matrix elements of the SCF Hamiltonian over the EHG functions are given in a form which is significantly simpler than the algorithm provided by Kartiel and Adam [29, 30]. Their procedure involves development of a product of the two HG functions centered at two different nuclei in a series of the complete set of the harmonic oscillator functions placed at the third center. It is well known that this kind of approach implies slow convergency in many instances, e.g., when two centers are far appart or when nonlinear parameters of the two considered HG functions are widely different. This drawback is circumvented in this work. We have dealt with the most general form of the EHG functions possessing a large number of variational degrees of freedom which should be advantageous in highly anisotropic chemical environments like, e.g., in linear systems where the calculations based on the EHG basis are certainly feasible. In most of other cases the use of spherical Gaussians could suffice. This would considerably simplify the formalism because the summation (8) is then redundant. In other words, all integrals can be expressed in closed analytical form if the $H_{n_{x\mathrm{A}}}(a_{x\mathrm{A}} x_\mathrm{A})\, H_{n_{y\mathrm{A}}}(a_{y\mathrm{A}} y_\mathrm{A})\, H_{n_{z\mathrm{A}}}(a_{z\mathrm{A}} z_\mathrm{A}) \exp(-b r_\mathrm{A}^2)$ basis set is employed. The most important feature of the EHG function is then still preserved, that is, the H-polynomials and the exponential function are differently scaled, which allows better fitting of the Roothaan-Hartree-Fock atomic orbitals. Additional flexibility is gained by the use of the addition theorem for the H-polynomials [34]:

$$2^{n/2} H_n(x+y) = \sum_{k=0}^{n} \binom{n}{k} H_k(\sqrt{2}\,x)\, H_{n-k}(\sqrt{2}\,y) . \quad (19)$$

Substituting $x = x_\mathrm{A}$ and $y = \mathrm{const}$ one obtains

$$H_n(x_\mathrm{A} + \mathrm{const}) = 2^{-n/2} \sum_{k=0}^{n} \binom{n}{k} H_{n-k}(\sqrt{2}\,\mathrm{const})\, H_k(\sqrt{2}\,x_\mathrm{A}) . \quad (20)$$

Hence, the H-polynomial can be shifted along the coordinate axes quite arbitrarily and still be expressed as a sum of the properly scaled H-polynomials centered on the atom A. This feature might be very useful in calculations of electric properties of molecules like, e.g., polarizabilities [35].

It is of some interest to disclose the relation between the HG and harmonic oscillator (or Hermite) functions. The latter were used in nuclear physics by Talmi [36] and in molecular quantum mechanics by Roberts [37] and by Moshinsky and Novaro [38]. One starts again from the addition theorem (19) which, by putting $x = 0$ yields

$$H_n(y) = 2^{-n/2} \sum_{k=0}^{n} \binom{n}{k} H_k(0)\, H_{n-k}(\sqrt{2y}) . \quad (21)$$

Multiplying by $\exp(-y^2)$ and taking into account that k runs only over even values one obtains

$$H_n(y) \exp(-y^2) = 2^{-n/2} \sum_{k=0}^{n} (-1)^{k/2} \frac{n!}{(n-k)!\,(k/2)!} H_{n-k}(\sqrt{2}y) \cdot \exp(-y^2) . \quad (22)$$

In other words, the HG function of the n-th order is a particular linear combination of all harmonic oscillator functions of the same parity up to the n-th order.

Finally, as a closing remark, it should be pointed out that basis sets employed in molecular quantum mechanics can be roughly classified in two large groups: (a) those consisting of atomic orbitals possessing some physical meaning and (b) sets comprised by functions which allow easy calculations of $1/r_{12}$ integrals. The former are usually approximate eigenfunctions of the atomic Hamiltonian or their linear combinations adapted to conform local symmetry of an atom in a chemical environment. The physical content of these atomic orbitals ensures relatively small basis sets but the resulting molecular integrals are rather intricate. Consequently, calculation of the integrals is usually time consuming. On the other hand, sets denoted by (b) offer very efficient treatment of all integrals. However, the basis set functions have little or no physical significance. They are introduced purely because of the mathematical convenience in computing required integrals, and consequently the number of basis set functions is large implying that an immense amount of molecular integrals has to be computed because this number is proportional to N_b^4. Here N_b denotes the number of basis set functions. The optimal basis sets probably lie somewhere in between groups (a) and (b). In this connection it should be pointed out that it is usually useful to follow the underlying physical picture of the problem in designing the basis set. A few examples will illustrate this point. It is well established by now that chemical bonding between less electronegative atoms is accompanied by an increase in electron density in the interatomic region. Hence use of bond functions centered at the middle of the chemical bonds has beneficial effects to the accuracy of the results. Further, the well known success of the Hall-Roothaan-Hartree-Fock method in describing basic properties of molecules by using MO-LCAO formalism can be traced down to the polycentric nature of the molecular charge density distributions. Atoms do retain their identities in molecules to a large extent [39]. On the contrary, the single-center ab initio method assumes expansion of the molecular electron density around a unique (heavy atom) center, being thus unrealistic. It is, therefore, not surprisng that the single-center method did not give satisfactory results in spite of considerably computational efforts, and that it was subsequently abandoned. Additional instructive examples are provided by the gauge invariant atomic basis sets (GIAO) which yield physically meaningful magnetic properties in a simple manner [40, 41] and by the already mentioned electric field variant AOs [35]. It is noteworthy that the HG basis belongs to the class (b). In contrast, the EHG set is shifted a bit toward the group (a) being better accomodated to the chemical environment. In particular, their "floating" ability is advantageous for the computation of electric properties [35]. Finally, it is interesting to mention that the basis set generated by the generalized gradient operator $\Delta^n y_{lm} \exp(-r^2)$ [42] leads to substantial simplifications of many-center molecular integrals. It seems, therefore, that the search for new and better systems of modified Gaussian functions is worth of further investigations.

Acknowledgements

I would like to thank the referee for useful comments. This work was completed during the author's stay at the Organisch-chemisches Institut der Universität Heidelberg. The financial support of the Alexander-von-Humboldt-Stiftung is gratefully acknowledged.

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