

GAUSSIAN GEMINALS APPLIED FOR THE MOLECULAR CORRELATION ENERGY CALCULATION*

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(Received June 14, 1977)

An algorithm for the calculation of the second-order molecular correlation energy using Gaussian geminals basis set is presented. A convenient graphical representation of many-electron integrals is introduced. The usefulness of this graphical technique for the reduction of many-electron integrals to simpler ones is illustrated.

1. Introduction

Among a variety of methods for the correlation energy calculation those using the explicitly correlated functions appear to be the most successful ones [1, 2]. The same applies also to the variation-perturbation theories leading to the concept of the so-called pair energies. The simplest pair theory is known as the Sinanoglu method and is based on the solution of the pair equations for the first-order perturbed pair functions [1]

$$G(1, 2) |u_{ij}(1, 2)\rangle = -\frac{Q(1, 2)}{r_{12}} |[\varphi_i\varphi_j]_{12}\rangle, \quad (1)$$

where

$$G(1, 2) = h(1) + h(2) - e_i - e_j,$$

$$h(1)\varphi_i(1) = e_i\varphi_i(1) \text{ is Hartree-Fock (HF) equation,}$$

$$Q(1, 2) = (1 - \sum_{i=1}^{2N} |\varphi_i(1)\rangle \langle \varphi_i(1)|) (1 - \sum_{i=1}^{2N} |\varphi_i(2)\rangle \langle \varphi_i(2)|),$$

$$[\varphi_i\varphi_j]_{12} = \frac{1}{\sqrt{2}} (\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)).$$

It is believed that even if the strong orthogonality conditions

$$Q(1, 2) u_{ij}(1, 2) = u_{ij}(1, 2) \quad (2)$$

* This research was supported by the Institute of Low Temperature and Structure Research of the Polish Academy of Sciences.

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are imposed on u_{ij} the Sinanoglu scheme is able to account for ca. 80 percent of the total correlation energy E_{corr} :

$$E_{\text{corr}} = \sum_{j>i}^{2N} e_{ij}^{(2)}$$

$$e_{ij}^{(2)} = \langle u_{ij}(1, 2) | \frac{Q(1, 2)}{r_{12}} | [\varphi_i \varphi_j]_{12} \rangle. \quad (3)$$

The success of this method is primarily determined by the quality of variational pair functions. As shown by Byron and Joachain [3] and Pan and King [1], the expansion of u_{ij} in terms of explicitly correlated two-electron basis functions $w_{k,ij}(1, 2)$ followed by optimization of non-linear parameters results in reasonably accurate values of the second order pair energies. For a given basis set of explicitly correlated functions $w_{k,ij}(1, 2)$ the most convenient way of the approximate solution of Eq. (1) is by the minimalization of the appropriate functional [1]. Furthermore, the separation of the spin part of geminals gives new pair equations for spinless pair functions. The efficiency of the Sinanoglu method and the computational aspect of the variation solution of Eq. (1) depend on the choice of both the orbital $\{\varphi_i\}$ and the geminal $\{w_{k,ij}\}$ basis sets. It was found that the so-called Gaussian geminals (GG)

$$w(1, 2) = \exp(-a_A r_{A1}^2 - a_B r_{B2}^2 - b r_{12}^2) \quad (4)$$

represent a satisfactory geminal basis set in atomic [1] and molecular [2] calculations. In the case of molecules a substantial reduction of the computational effort is achieved if the orbital basis set is composed of primitive Gaussians

$$g(1) = \exp(-a_A r_{A1}^2) \quad (5)$$

with variationally optimized exponents and origins.

For these so-called floating spherical Gaussian orbitals (FSGO) and Gaussian geminals of Eq. (4) a number of useful rules for the calculation of atomic and molecular integrals can be derived.

The basic problem in the computer application of the Sinanoglu method is to construct the following matrix elements

$$(QQQ)_{kl} = \langle w_k(1, 2) Q(1, 2) | h(1) + h(2) - e_i - e_j | Q(1, 2) w_l(1, 2) \rangle \quad (6)$$

and

$$(F)_k = \langle w_k(1, 2) | \frac{Q(1, 2)}{r_{12}} | \Phi_i(1) \Phi_j(2) \rangle \quad (7)$$

Φ_i is a space part of the spinorbital φ_i .

In the next section a procedure for effective reduction of many electron integrals to elementary integrals with functions (4) and (5) is shown and a convenient graphical representation is introduced. An algorithm for the construction of matrix elements (6) and (7) from elementary one- and multi-electron integrals using their graphical representation is discussed in Section 3.

2. Reduction of many electron integrals to elementary integrals

Any FSGO of the form (5) can be unambiguously represented by a 4-dimension array $\bar{A} = \{a_A, A_X, A_Y, A_Z\}$. Let us denote this array by a symbol \bar{A} when the FSGO is a bra-function and by $\dot{\bar{A}}$ when it is a ket-function. Then the GG (4) as a bra can be given by a

graphical representation $\overline{\bar{A}} \text{---} b \text{---} \overline{\bar{B}}$ and the GG as a ket by $\overline{\dot{\bar{A}}} \text{---} b \text{---} \overline{\dot{\bar{B}}}$. Let us also introduce the following graphical symbols for one- and two-electron operators:

| operator | its graphical representation |
|--|--|
| kinetic energy | $x_K \text{---} \text{---} \text{---}$ |
| nuclear attraction | $x_N \text{---} \text{---} \text{---}$ |
| sum of kinetic energy and nuclear attraction | $x \text{---} \text{---} \text{---}$ |
| inter-electron repulsion | $\bullet \text{---} \text{---} \text{---}$ |

Thus a typical two-electron integral:

$$\langle \exp(-a_A r_{A1}^2 - a_B r_{B2}^2 - b_1 r_{12}^2) - \frac{A_1}{2} \exp(-a_C r_{C1}^2 - a_D r_{D2}^2 - b_2 r_{12}^2) \rangle$$

is represented by

$$x_K \text{---} \text{---} \overline{\bar{A}} \text{---} b_1 \text{---} \overline{\bar{B}} \\ \overline{\bar{C}} \text{---} b_2 \text{---} \overline{\bar{D}}$$

and the integral

$$\langle \exp(-a_A r_{A1}^2 - a_B r_{B2}^2 - a_C r_{C3}^2 - b_1 r_{12}^2) \frac{1}{r_{12}} \exp(-a_D r_{D1}^2 - a_E r_{E2}^2 - a_F r_{F3}^2 - b_2 r_{23}^2) \rangle$$

by

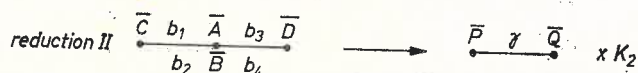
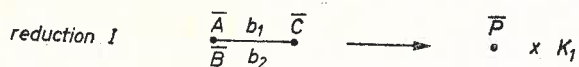
$$\overline{\bar{A}} \text{---} b_1 \text{---} \overline{\bar{B}} \text{---} \overline{\bar{C}} \\ \overline{\bar{D}} \text{---} \overline{\bar{E}} \text{---} b_2 \text{---} \overline{\bar{F}}$$

Let us define elementary integrals. Their graphical representation is given as follows:¹

$$\begin{array}{cc} \overline{\bar{A}} \text{---} \overline{\bar{B}} & \overline{\bar{A}} \text{---} b_1 \text{---} \overline{\bar{B}} \\ \overline{\bar{C}} \text{---} \overline{\bar{D}} & \overline{\bar{C}} \text{---} b_2 \text{---} \overline{\bar{D}} \\ a & b \\ & (8) \\ x \text{---} \overline{\bar{A}} & x_K \text{---} \overline{\bar{A}} \text{---} b_1 \text{---} \overline{\bar{B}} \\ & \overline{\bar{C}} \text{---} b_2 \text{---} \overline{\bar{D}} \\ c & d \end{array}$$

¹ Elementary integral d (8) cannot be reduced by direct integration over the coordinates of that electron on which the kinetic energy operator does not act. The reason is that the correlation factors which couple this electron with the electron in the $-\frac{A}{2}$ operator are on both sides of this operator. Using Green's theorem these factors can be joined and the reduction can be performed [4].

All integrals obtained with GG's and FSGO's can be simply reduced to the integrals (8). The formulae for calculation of elementary integrals have been already published [4]. To perform any reduction it is necessary to know how to reduce the two elements from which all the many-electron integrals are constructed. The graphical representation of these elements and the way of reduction is the following (the integration is performed over the coordinates of that electron which occupies orbitals \bar{A} and \bar{B})



where

$$K_1 = \exp\left(-\frac{a_A a_B}{\gamma_1} r_{AB}^2 - \frac{a_C \delta}{a_C + \delta} r_{XC}^2\right) \left(\frac{\pi}{\alpha_1}\right)^{3/2}$$

$$K_2 = \exp\left(-\frac{a_A a_B}{\gamma_1} r_{AB}^2 - \frac{a_C \beta_1}{a_P} r_{XC}^2 - \frac{a_D \beta_2}{a_Q} r_{XD}^2\right) \left(\frac{\pi}{\alpha}\right)^{3/2}$$

$$\gamma_1 = a_A + a_B, \quad \beta_1 = b_1 + b_2, \quad \beta_2 = b_3 + b_4$$

$$\alpha_1 = \gamma_1 + \beta_1, \quad \alpha = \gamma_1 + \beta_1 + \beta_2,$$

$$\delta_1 = \frac{\gamma_1 \beta_1}{\alpha}, \quad \delta_2 = \frac{\gamma_1 \beta_2}{\alpha}, \quad \delta = \frac{\gamma_1 \beta_1}{\gamma_1 + \beta_1}, \quad \gamma = \frac{\beta_1 \beta_2}{\alpha},$$

$$\bar{X} = \frac{a_A \bar{A} + a_B \bar{B}}{\gamma_1}, \quad \bar{P} = \frac{a_C \bar{C} + \delta_1 \bar{X}}{a_P}, \quad \bar{Q} = \frac{a_D \bar{D} + \delta_2 \bar{X}}{a_Q},$$

$$a_P = \delta_1 + a_C, \quad a_Q = \delta_2 + a_D$$

Examples of the three-electron integral reductions are shown in Fig. 1.

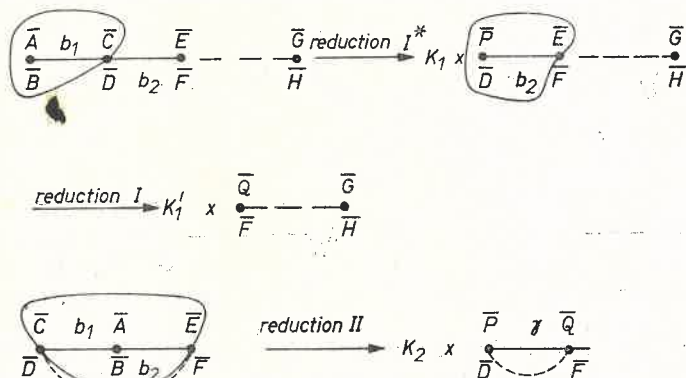


Fig. 1. Examples of the many-electron integral reductions to elementary integrals. Fragments of the integrals which take part in elementary reductions marked by arrows are encircled

* For the definitions of the reduction I and II see text.

3. Graphical form of matrix elements

If the advantage of the equality

$$\langle \Phi_k(1) | h(1) | \Phi_i(1) \rangle = \delta_{ki} e_k \quad (9)$$

is taken the matrix elements (6) and (7) can be developed to²

$$\begin{aligned} (QGQ)_{kl} &= \langle w_k(1, 2) Q(1, 2) | h(1) + h(2) - e_i - e_j | Q(1, 2) w_l(1, 2) \rangle \\ &= \langle w_k(1, 2) | h(1) + h(2) - e_i - e_j | w_l(1, 2) \rangle \\ &\quad + \sum_{n=1}^N \left[\begin{aligned} &\langle w_k(1, 2) \Phi_n(3) | \Phi_n(1) w_l(3, 2) \rangle (e_i + e_j) \\ &+ \langle w_k(1, 2) \Phi_n(3) | w_l(1, 3) \Phi_n(2) \rangle (e_i + e_j) \\ &- \langle \Phi_n(1) w_k(3, 2) | h(1) | w_l(1, 2) \Phi_n(3) \rangle \\ &- \langle w_k(1, 3) \Phi_n(2) | h(2) | w_l(1, 2) \Phi_n(3) \rangle \\ &- \langle w_k(1, 2) \Phi_n(3) | h(1) | \Phi_n(1) w_l(3, 2) \rangle \\ &- \langle w_k(1, 2) \Phi_n(3) | h(2) | w_l(1, 3) \Phi_n(2) \rangle \\ &- \langle w_k(1, 2) \Phi_n(3) | h(1) | w_l(1, 3) \Phi_n(2) \rangle \\ &- \langle w_k(1, 2) \Phi_n(3) | h(2) | \Phi_n(1) w_l(3, 2) \rangle \end{aligned} \right] \\ &\quad + \sum_{m,n=1}^N \left[\begin{aligned} &- \langle w_k(1, 2) | \Phi_m(1) \Phi_n(2) \rangle \langle \Phi_m(1) \Phi_n(2) | w_l(1, 2) \rangle (e_m + e_n - e_i - e_j) \\ &+ \langle w_k(1, 2) | \Phi_m(1) \Phi_n(2) \rangle \langle \Phi_m(1) \Phi_n(2) | h(1) + h(2) | w_l(1, 2) \rangle \\ &+ \langle w_k(1, 2) | h(1) + h(2) | \Phi_m(1) \Phi_n(2) \rangle \langle \Phi_m(1) \Phi_n(2) | w_l(1, 2) \rangle \end{aligned} \right] \end{aligned} \quad (10)$$

$$\begin{aligned} (F)_k &= \langle w_k(1, 2) | \frac{1}{r_{12}} | \Phi_i(1) \Phi_j(2) \rangle \\ &\quad - \sum_{n=1}^N \langle w_k(3, 2) \Phi_n(1) | \frac{1}{r_{12}} | \Phi_i(1) \Phi_j(2) \Phi_n(3) \rangle \\ &\quad + \sum_{n=1}^N - \langle w_k(1, 3) \Phi_n(2) | \frac{1}{r_{12}} | \Phi_i(1) \Phi_j(2) \Phi_n(3) \rangle \\ &\quad + \sum_{m,n=1}^N \langle w_k(1, 2) | \Phi_m(1) \Phi_n(2) \rangle \langle \Phi_m(1) \Phi_n(2) | \frac{1}{r_{12}} | \Phi_i(1) \Phi_j(2) \rangle \end{aligned} \quad (11)$$

² Pan and King [1] took advantage of HF equation

$$h(1) \Phi_k = e_k \Phi_k. \quad (9a)$$

But it is justified only in this case when h is a HF operator. When the first order function correction is outside the space spanned by the basis functions used in the SCF calculation, one should use Eq. (9) rather than Eq. (9a).

$$\begin{aligned}
 (QQQ)_{kl} &= -(e_i + e_j) \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{C} \cdot b_l \cdot \bar{D}} + (1 + P_{AB} P_{CD}) X \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{C} \cdot b_l \cdot \bar{D}} \\
 &+ (1 + P_{AB} P_{CD}) \sum_{XY} D_{XY} \left[\frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{D} \cdot b_l \cdot \bar{C}} + X \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{D} \cdot b_l \cdot \bar{C}} + X \frac{\bar{C} \cdot b_l \cdot \bar{D}}{\bar{X}} \frac{\bar{Y}}{\bar{B} \cdot b_k \cdot \bar{A}} \right. \\
 &\quad \left. + 2 \frac{\bar{X}}{\bar{Y}} \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{C} \cdot b_l \cdot \bar{D}} - \frac{\bar{C} \cdot b_l \cdot \bar{D}}{\bar{X}} \frac{\bar{Y}}{\bar{B} \cdot b_k \cdot \bar{A}} \right. \\
 &\quad \left. + (e_i + e_j) \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{D} \cdot b_l \cdot \bar{C}} \right] \\
 &+ (1 + P_{AB} P_{CD}) \sum_{XYZW} \left[2D_{XY} D_{WZ} D_{XW} D_{YZ} X \frac{\bar{X}}{\bar{Y}} \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{W}} \frac{\bar{Z} \cdot \bar{X}}{\bar{D} \cdot b_l \cdot \bar{C}} + \frac{\bar{C} \cdot b_l \cdot \bar{D}}{\bar{W}} \frac{\bar{Z}}{\bar{B} \cdot b_k \cdot \bar{A}} \right. \\
 &\quad \left. - D_{XY} D_{WZ} (2 \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{W}} \frac{\bar{Z}}{\bar{D} \cdot b_l \cdot \bar{C}} - \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{W}} \frac{\bar{Y}}{\bar{X}} - \frac{\bar{Y}}{\bar{C} \cdot b_l \cdot \bar{D}}) \right. \\
 &\quad \left. + \frac{\bar{X}}{\bar{Y}} \right] \\
 &+ \sum_{mn}^N \left[(-e_m - e_n - e_i - e_j) A_{mnk} A_{mnl} + A_{mnk} (B_{mnl} + C_{mnl}) + A_{mnl} (B_{mnk} + C_{mnk}) \right] \\
 (F)_k &= \sum_{XY} c_{iX} c_{jY} \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{D} \cdot b_l \cdot \bar{C}} + \sum_{mn}^N A_{mnk} \sum_{XYZW} c_{mX} c_{nY} c_{iW} c_{jZ} \frac{\bar{X}}{\bar{W}} - \frac{\bar{Y}}{\bar{Z}} \\
 &\quad - \sum_{XYZW} D_{WY} (c_{iX} c_{jZ} + P_{AB} c_{iZ} c_{jX}) \frac{\bar{W}}{\bar{Z}} - \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{Y}} \\
 A_{mnk} &= \sum_{XY} c_{mX} c_{nY} \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{Y}} \\
 B_{mnk} &= \sum_{XY} \left[c_{mX} c_{nY} X \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{Y}} + \sum_{WZ} (2D_{WZ} c_{mX} c_{nY} - D_{WZ} c_{mZ} c_{nZ}) \frac{\bar{W}}{\bar{Z}} - \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{Y}} \right] \\
 C_{mnk} &= \sum_{XY} \left[c_{mX} c_{nY} X \frac{\bar{B} \cdot b_k \cdot \bar{A}}{\bar{Y}} \frac{\bar{X}}{\bar{X}} + \sum_{WZ} (2D_{WZ} c_{mX} c_{nY} - D_{WZ} c_{mZ} c_{nZ}) \frac{\bar{W}}{\bar{Z}} - \frac{\bar{B} \cdot b_k \cdot \bar{A}}{\bar{Y}} \frac{\bar{X}}{\bar{X}} \right]
 \end{aligned}$$

Fig. 2. Graphical representation of matrix elements $(QQQ)_{kl}$ and $(F)_k$. All summations over X, Y, W, Z run up to dimension of FSGO basis set. D_{XY} is an element of the density matrix $D_{XY} = \sum_{i=1}^N c_{iX} c_{iY}$. $\bar{A}, \bar{B}, \bar{C}, \bar{D}$ are used for orbital factors in geminals. P_{AB} permutes indices A and B

Using the explicit form of h operator the final algorithm is obtained. In the introduced graphical representation it can be expressed as shown in Fig. 2.

It is easy to see that the elementary reductions required to calculate different integrals in the matrix elements (6) and (7) are identical. This simplifies the calculations since for instance the reduction which has been done for the integral

$$X \frac{\bar{A} \cdot b_k \cdot \bar{B}}{\bar{X}} \frac{\bar{Y}}{\bar{D} \cdot b_l \cdot \bar{C}}$$

of Fig. 2 can be also applied for the integral

$$\frac{\bar{W}}{\bar{Z}} \text{ --- } \frac{\bar{A} \ b_k \ \bar{B}}{\bar{X} \ \bar{D} \ b_l \ \bar{C}}$$

of Fig. 2. Our computer program for the variation solution of the Sinanoglu equation for molecules takes advantage of this possibility.

4. Conclusions

Gaussian geminals have been applied for computing the second order energy correction in Sinanoglu method. If HF equations are solved in the FSGO basis set, then the algorithm of the correlation correction is simple and easy for programming. Substantial inconvenience of the Sinanoglu method is that using correlated functions as many as four-electron integrals have to be computed, even for the two-electron problem. It results from the strong orthogonality condition (2). However the reduction of many electron integrals to elementary integrals runs smoothly. Calculations for LiH and BH [5] show that even a minimal basis set for correlation energy calculation, that means one optimized Gaussian geminal for each electron pair, gives about 60 percent of correlation energy.

The author would like to thank Dr A. J. Sadlej without whose help the present paper could not be prepared. Also the author is deeply indebted to Professor W. Zielenkiewicz for his kind attitude towards this work.

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