

An Algorithm for Evaluation of Two-Electron Integrals by Numerical Integration Method*

Evaluation of integrals is a critical step in quantum mechanical calculations of molecular electronic structures. Among them, the two-electron integrals are especially difficult to evaluate. While a great deal of literature has been compiled for analytic evaluation of one- and two-electron integrals between certain types of basis functions, namely, the Slater-type functions and Gaussian-type functions, no analytic method can be developed for functions of arbitrary forms. The latter usually arise in perturbational calculations of small systems. The only solution to this problem is the method of numerical integration. In this note, we present an algorithm for computing two-electron integrals based on a special choice of coordinate system. An important feature of this algorithm is the disappearance of the troublesome r_{12} (the interelectronic distance) factor in the denominator of the integrand which is the usual cause of convergence problems in other methods [1]. Therefore, the accuracy can be improved by directly increasing the number of quadrature points. The method is also simple and easy to program on a digital computer.

The coordinate system used here is a combination of perimetric and one-center coordinates [2]. The perimetric coordinates are defined as

$$u = r_{2a} - r_{1a} + r_{12}, \quad 0 \leq u < \infty, \quad (1)$$

$$v = r_{1a} - r_{2a} + r_{12}, \quad 0 \leq v < \infty, \quad (2)$$

$$w = 2(r_{1a} + r_{2a} - r_{12}), \quad 0 \leq w < \infty, \quad (3)$$

where r_{1a} and r_{2a} are the distances from the first and second electrons to center A and r_{12} is the distance between the two electrons. The volume element (Fig. 1)

$$d\tau_1 d\tau_2 = r_{1a} r_{2a} r_{12} dr_{1a} dr_{2a} dr_{12} \sin \theta_{1a} d\theta_{1a} d\chi d\varphi, \quad (4)$$

may be expressed in terms of perimetric coordinates as follows:

$$d\tau_1 d\tau_2 = (\pi/128)(u + v)(2u + w)(2v + w) du dv dw \sin \theta_{1a} d\theta_{1a} d\chi, \quad (5)$$

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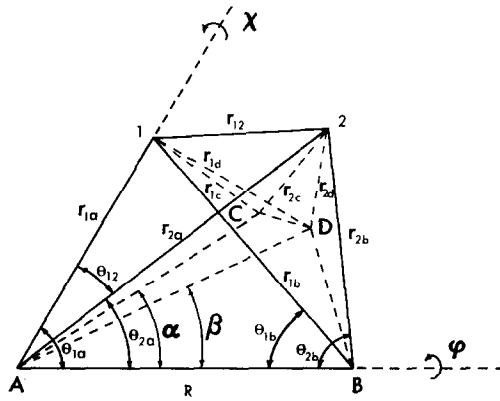


FIG. 1. The coordinate system.

where, for simplicity, the φ integration has been carried out. For a typical two-electron integral I , with no φ dependence, we have

$$\begin{aligned}
 I &= \int \int \phi_a^*(\mathbf{r}_1) \phi_b(\mathbf{r}_1) r_{12}^{-1} \phi_a^*(\mathbf{r}_2) \phi_b(\mathbf{r}_2) d\tau_1 d\tau_2 \\
 &= (\pi/64) \iiint_{u,v,w=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\chi=0}^{2\pi} \phi_a^*(1) \phi_b(1) \phi_a^*(2) \phi_b(2) (2u+w) \\
 &\quad \times (2v+w) du dv dw \sin \theta_{1a} d\theta_{1a} d\chi.
 \end{aligned}
 \tag{6}$$

In this work, we have used the Gauss-Laguerre quadratures for u, v, w integrations and the Gauss-Legendre quadratures for angular integrations. After a change of variables, Eq. (6) becomes

$$\begin{aligned}
 I &= (\pi^3/128) \iiint_{u,v,w=0}^{\infty} \iint_{\theta',\chi'=-1}^{+1} \phi_a^*(1) \phi_b(1) \phi_a^*(2) \phi_b(2) (2u+w)(2v+w) du dv dw \\
 &\quad \times \cos(\theta'_{1a}(\pi/2)) d\theta'_{1a} d\chi',
 \end{aligned}
 \tag{7}$$

where

$$\theta'_{1a} = (2\theta_{1a}/\pi) - 1,
 \tag{8}$$

$$\chi' = (\chi/\pi) - 1.
 \tag{9}$$

To illustrate the use of the method, we have computed some exchange integrals

arising from the calculation of the diatomic electronic wave functions. For such calculations, the following relationships are useful:

$$r_{2b} = \{r_{2a}^2 + R^2 - 2Rr_{2a} \cos \theta_{2b}\}^{1/2}, \quad (10)$$

$$\cos \theta_{2b} = -\cos \theta_{12}(\cos \theta'_{12})^{-1} \sin(\theta'_{1a}\pi/2 - \theta'_{12}), \quad (11)$$

$$\theta'_{12} = \tan^{-1}\{-\tan \theta_{12} \cos(\chi'\pi)\}, \quad (12)$$

where r_{2b} is the distance from the second electron to center B . In Table I, we list some of the integrals computed by the present method along with the "exact" values obtained analytically. At least two points should be noted. First, since the integrand is not symmetric with respect to the exchange of centers there is a considerable difference in the accuracy of the final result when the two centers are interchanged. This is especially so when the two functions at a and b extend very differently in space. The convergence is always better when the more contractive function is centered at a . For example, the second integral in Table I will be 0.00278 if $1s_a$ and $1s_b$ are interchanged. Second, the quadrature points are a complicated function of the integrand. They have to be determined by trial and error. The present choice of $n_1 = n_2 = n_3$ and $n_4 = n_5$ is only for the sake of convenience; it is by no means the most efficient one.

TABLE I

Some Two-center Exchange Integrals Computed by the Present Algorithm^a

R	Integral	Exponents	n_1	n_2	n_3	n_4	n_5^b	I^c	I_{Exact}^d
1.0	$[1s_a 1s_b / 1s_a 1s_b]$	2.189, 1.183; 2.189, 1.183	12	12	12	8	8	0.35116	0.35115
2.022	$[1s_a 1s_b / 1s_a 1s_b]$	5.7, 1.2; 5.7, 1.2	6	6	6	8	8	0.00862	0.00862
2.022	$[2s_a 1s_b / 2s_a 1s_b]$	1.625, 1.2; 1.625, 1.2	10	10	10	10	10	0.16737	0.16731
2.022	$[2p_{\sigma a} 1s_b / 2p_{\sigma a} 1s_b]$	1.625, 1.2; 1.625, 1.2	8	8	8	8	8	0.20129	0.20160
2.022	$[2p_{\sigma a} 1s_b / 1s_a 1s_b]$	1.625, 1.2; 1.625, 1.2	8	8	8	8	8	0.02141	0.02148
2.022	$[2p_{\sigma a} 1s_b / 2s_a 1s_b]$	1.625, 1.2; 1.625, 1.2	10	10	10	10	10	0.17531	0.17512

^a Both distances and integrals are in atomic unit.

^b n_1, n_2, n_3 are the number of the Gauss-Laguerre quadratures and n_4, n_5 are the number of the Gauss-Legendre quadratures.

^c Integrals computed by the present method.

^d Integrals computed analytically.

The present method is not restricted to two-center electronic integrals. It can be extended to three- and four-center integrals easily when more relationships like Eqs. (10)–(12) are derived for the coordinates involving the other centers. Let the other centers be designated by C and D , we have the relations

$$r_{1c} = \{r_{1a}^2 + AC^2 - 2r_{1a}AC \cos \theta_{1ac}\}^{1/2}, \quad (13)$$

$$r_{1d} = \{r_{1a}^2 + AD^2 - 2r_{1a}AD \cos \theta_{1ad}\}^{1/2}, \quad (14)$$

$$\cos \theta_{1ac} = \cos \alpha \cos \theta_{1a} + \sin \alpha \sin \theta_{1a} \cos \varphi, \quad (15)$$

$$\cos \theta_{1ad} = \cos \beta \cos \theta_{1a} + \sin \beta \sin \theta_{1a} \cos(\varphi + \eta), \quad (16)$$

$$r_{2c} = \{r_{12}^2 + r_{1c}^2 - 2r_{12}r_{1c} \cos \theta_{21c}\}^{1/2}, \quad (17)$$

$$r_{2d} = \{r_{12}^2 + r_{1d}^2 - 2r_{12}r_{1d} \cos \theta_{21d}\}^{1/2}, \quad (18)$$

$$\begin{aligned} \cos \theta_{21c} = & (r_{12}^2 + r_{1c}^2 - r_{2a}^2)(r_{1c}^2 + r_{1a}^2 - AC^2)/(4r_{12}r_{1c}r_{1a}^2) \\ & + [(1 - \cos^2 \theta_{1ac})^{1/2}(r_{2a}AC)/(r_{12}r_{1c})] \cos(\chi - \gamma), \end{aligned} \quad (19)$$

$$\begin{aligned} \cos \theta_{21d} = & (r_{12}^2 + r_{1d}^2 - r_{2a}^2)(r_{1d}^2 + r_{1a}^2 - AD^2)/(4r_{12}r_{1d}r_{1a}^2) \\ & + [(1 - \cos^2 \theta_{1ad})^{1/2}(r_{2a}AD)/(r_{12}r_{1d})] \cos(\chi - \delta), \end{aligned} \quad (20)$$

where η is the angle between plane ACB and ADB , and r_{1c} , r_{1d} , r_{2c} , and r_{2d} are the distances between the electrons and the other centers; γ is the angle between plane $A12$ and $A1C$ and δ is the angle between plane $A12$ and $A1D$. Other quantities are defined in Fig. 1. The expressions for the other angles can be obtained by a relationship among the related angles similar to that in Eqs. (15) and (16). When this is done, the integration for a typical four-center integral can be carried out as follows:

$$\begin{aligned} I = & (\pi^3/256) \iiint_{u,v,w=0}^{\infty} \iiint_{\theta',\chi',\varphi'=-1}^{+1} \phi_a^*(1) \phi_b(1) \phi_c^*(2) \phi_d(2)(2u+w)(2v+w) \\ & \times du dv dw \cos(\theta'_{1a}\pi/2) d\theta'_{1a} d\chi' d\varphi', \end{aligned} \quad (21)$$

where $\varphi' = (\varphi/\pi) - 1$.

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