

An analytical algorithm for the evaluation of two-electron integrals in diatomics: A test calculation with an elliptical basis set

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Abstract. A purely analytical method designed to compute the two-electron integrals that appear in an *ab-initio* calculation of the electronic structures of diatomic molecules using elliptical basis set is presented. Test calculations are successfully carried out on LiH molecule.

Keywords. *Ab-initio* calculation; elliptical orbitals; two-centre two-electron integrals; charge distribution function; exponential integral; double precision arithmetic.

1. Introduction

In recent years, renewed interest has been shown in *ab-initio* calculations of electronic structures of various interstellar diatomic species (Hinkley *et al* 1972; Elitzur 1976; Wilson 1978; Wilson and Richards 1978). Standard programmes are available which perform SCF calculations using large extended basis sets of Slater orbitals and Gaussian orbitals. The use of a large basis set of STO's makes computation costly and cumbersome. It would therefore be worthwhile to switch over to some other basis functions having much larger variational flexibility. By an optimal choice of the variational degrees of freedom inherent in the basis functions one can then reduce the size of the basis set employed for the calculation. For the diatomics, the use of elliptical orbitals (EO) as basis set would probably be the best. They have much larger flexibility as compared to the others (the EO's contain five flexible parameters, n, j, ν, α, β). Moreover, EO's can account properly for the electronic charge distribution in the remote sites along the molecular axis, through the proper choice of the integral parameters n and j only. Coming to the evaluation of two-electron integrals, one notes that with a basis set of EO's, all the three types of two electron integrals—coulomb ($\chi_i \chi_l / \chi_m \chi_n$), exchange ($\chi_l \chi_m / \chi_i \chi_n$) and hybrid ($\chi_l \chi_l / \chi_i \chi_m$)—can be represented by a single formula leading to easier programming structure. Further, since the basis orbitals are symmetry-adopted, a small set of basis should hopefully provide a better description of bonding properties (Ebbing 1960; Hurley 1976).

As the evaluation of one-electron integrals is very simple and can easily be adopted from the existing literature (Ebbing 1960, Harris 1960), we are mainly concerned with the two-electron integrals and our observations are presented in this paper.

Regarding the evaluation of the two-electron integrals, there seems to be a general (mis) belief that the analytical methods are prone to the accumulation of very serious round-off errors and enormous time consumption due to the use of lengthy recurrence schemes. To bypass the difficulty one generally shifts to the use of numerical methods (Ebbing 1960; Harris 1960; Rüdénberg 1964; Mehler and Rüdénberg 1969). In this connection, it may be worthwhile to mention that the numerical technique developed by Mehler and Rüdénberg (1969) (the charge distribution or ‘ $f_{lm}(\xi)$ technique’) for the exchange integrals involving real STAO’s reduces the computation time quite efficiently. In this study we have demonstrated that a strictly analytical evaluation of all 2-electron integrals is possible using a basis set of EO’s and that numerical stability can be ensured by using double precision arithmetic throughout and adopting certain convergence ‘tricks’ while passing through lengthy recurrence schemes. Of particular interest in this respect is our manner of handling the exponential integrals.

2. Method

2.1 Orbital expression

The basis orbital is described by Harris (1960)

$$\chi_{n,j\nu} = (2\pi a^3)^{-1/2} \exp(-a\xi) \exp(-\beta\eta) \xi^n \eta^j \\ [(\xi^2 - 1)(1 - \eta^2)]^{1/2} |\nu| \exp(+i\nu\phi) \quad (1)$$

$(a = R/2);$

where n and j are positive integral parameters and $|\nu|$ determines the orbital angular momentum about the molecular axis while a and β are variationally determined parameters. ξ, η, ϕ are the three variables in elliptical co-ordinate system; R is the distance between the two nuclei, which are at the two foci.

2.2 Choice of basis set

Along with the unique flexibility, the EO’s (many of which differ only in n, j and not in a, β) can provide much computational saving which will be discussed in § 3.3. So designing a ‘reasonable basis’ is of tremendous importance both in the sense of qualitative reliability and of economic ability. Moreover, it was observed that if overlap integral between two EO’s exceeds 0.95, basis set is no longer linearly independent. Inclusion of such EO’s may lead to (i) ill-determination of at least one M.O., (ii) divergence in SCF calculation. So, computational utility and linear independence are two essential features that should be incorporated in optimising the flexible parameters to set up a “reasonable basis”. In this connection we would like to mention that greater flexibility is achieved by inclusion of inner orbital splitting (Shull and Löwdin 1956), whenever possible. A few examples of reasonable basis sets are given below:

$$S_1 : (1\sigma_a^i, 1\sigma_b^i)_N; \quad i = 4, N = 8.$$

$$S_2 : (1\sigma_a^i, 1\sigma'_a{}^i, 1\sigma_b^j, 1\sigma'_b{}^j, 2\sigma_a^j, 2\sigma_b^j, 2\pi_{\pm a}^j, 2\pi_{\pm b}^j)_N \quad i=1, j=4, N=28,$$

$$S_3 : (1\sigma_a^i, 1\sigma'_a{}^i, 1\sigma_b^j, 1\sigma'_b{}^j, 2\sigma_a^j, 2\sigma_b^j, 2\pi_{\pm a}^j, 2\pi_{\pm b}^j, 3\sigma_a^k, 3\sigma_b^k, 3\pi_{\pm a}^k, 3\pi_{\pm b}^k)_N$$

$$i = 1, j = 2, k = 4, N = 40$$

(a and b are two foci of the elliptical co-ordinate system; σ, σ' are obtained from inner orbital splitting; i, j, k indicates that a number of orbitals differ only in integral parameter, N is total number of orbitals).

2.3 Integral expression

The general expression for two-electron integrals is:

$$I = \int \chi_i^* (1) \chi_j (1) \frac{1}{r_{12}} \chi_k^* (2) \chi_l (2) dv_1 dv_2, \quad (2)$$

$\chi_i, \chi_j, \chi_k, \chi_l$ are elliptical orbitals. From now onwards, for the sake of notational simplicity we omit the characteristic quantum numbers of EO's in equation (1)

$$= \int \Omega (1) \frac{1}{r_{12}} \bar{\Omega} (2) dv_1 dv_2, \quad (3)$$

$$\text{where } \Omega (1) = \chi_i^* (1) \chi_j (1), \quad (4)$$

$$\bar{\Omega} (2) = \chi_k^* (2) \chi_l (2). \quad (5)$$

Expressing r_{12}^{-1} by the Neumann expansion, (Rüdenberg 1951),

$$\frac{1}{r_{12}} = \frac{4}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^l (-1)^m \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|} (\xi_-) Q_l^{|m|} (\xi_+),$$

$$P_l^{|m|} (\eta_1) P_l^{|m|} (\eta_2) \exp(im\phi_1) \exp(-im\phi_2), \quad (6)$$

where ξ_- is the smaller and ξ_+ the greater of ϕ_1 and ϕ_2 , and performing some transformation, one finally obtains (Ebbing 1960)

$$I = \frac{R^5}{16} \sum_{l=0}^{\infty} \sum_{m=-l}^l \int_1^{\infty} d\xi \frac{1}{(\xi^2-1) [P_l^{|m|}(\xi)]^2} \int_1^{\xi} P_l^{|m|}(x) W_l^{|m|}(x) dx$$

$$\int_1^{\xi} P_l^{|m|}(y) \bar{W}_l^{|m|}(y) dy \quad (7)$$

$$W_i^{l m_1}(\xi_1) = \int_{-1}^{+1} d\eta_1 \int_0^{2\pi} \Omega(1) (\xi_1^2 - \eta_1^2) P_i^{m_1}(\eta_1) \exp(im\phi_1) d\phi_1 \quad (8)$$

$$\text{and } \bar{W}_i^{l m_1}(\xi_2) = \int_{-1}^{+1} d\eta_2 \int_0^{2\pi} \bar{\Omega}(2) (\xi_2^2 - \eta_2^2) P_i^{m_1}(\eta_2) \exp(-im\phi_2) d\phi_2 \quad (9)$$

Substitution of the orbitals (1) into (2) and integrating over ϕ_1 and ϕ_2 leads to the requirement

$$\nu_i - \nu_j + \nu_k - \nu_l = 0, \quad (10)$$

for nonvanishing integrals and following Rüdénberg (1951) the final expression of the integral becomes

$$\begin{aligned} I = & \frac{4}{R} \sum_{l=M}^{\infty} \int_1^{\infty} d\xi \frac{1}{(\xi^2 - 1) [P_l^M(\xi)]^2} \left\{ B_{j\bar{Q}}^{Ml}(\beta) \int_1^{\xi} dx P_l^M(x) (x^2 - 1)^{M/2+Q} \right. \\ & \left. \exp(-ax) x^{n+2} - B_{(j+2)\bar{Q}}^{Ml}(\beta) \int_1^{\xi} dx P_l^M(x) (x^2 - 1)^{M/2+Q} \exp(-ax) x^n \right\} \\ & \left\{ B_{\bar{j}\bar{Q}}^{Ml}(\bar{\beta}) \int_1^{\xi} dy P_l^M(y) (y^2 - 1)^{M/2+\bar{Q}} \exp(-\bar{a}y) y^{\bar{n}+2} - B_{(\bar{j}+2)\bar{Q}}^{Ml}(\bar{\beta}) \right. \\ & \left. \int_1^{\xi} dy P_l^M(y) (y^2 - 1)^{M/2+\bar{Q}} \exp(-\bar{a}y) y^{\bar{n}} \right\} \quad (11) \end{aligned}$$

$$\text{where } a = a_i + a_j, \quad \bar{a} = a_k + a_l,$$

$$\beta = \beta_i + \beta_j, \quad \bar{\beta} = \beta_k + \beta_l,$$

$$n = n_i + n_j, \quad \bar{n} = n_k + n_l,$$

$$j = j_i + j_j, \quad \bar{j} = j_k + j_l,$$

$$M = |\nu_i - \nu_j|, \quad \bar{M} = |\nu_k - \nu_l|,$$

$$Q = \frac{1}{2} \{ |\nu_i| + |\nu_j| - M \}, \quad \bar{Q} = \frac{1}{2} \{ |\nu_k| + |\nu_l| - \bar{M} \}.$$

Utilising the condition (10) and Rüdberg's procedure (1951) one can derive the general computable form of (11) as

$$\begin{aligned}
 I = & \frac{4}{R} \sum_{l=m}^{\infty} \{ B_{jQ}^{Ml}(\beta) B_{j\bar{Q}}^{Ml}(\bar{\beta}) \phi_{(n+2)Q, \bar{n}\bar{Q}}^{Ml}(a, \bar{a}) \\
 & - B_{jQ}^{Ml}(\beta) \cdot B_{(j+2)\bar{Q}}^{Ml}(\bar{\beta}) \cdot \phi_{(n+2)Q, \bar{n}\bar{Q}}^{Ml}(a, \bar{a}) \\
 & - B_{(j+2)Q}^{Ml}(\beta) \cdot B_{j\bar{Q}}^{Ml}(\bar{\beta}) \cdot \phi_{nQ, \bar{n}\bar{Q}}^{Ml}(a, \bar{a}) \\
 & + B_{(j+2)Q}^{Ml}(\beta) \cdot B_{(j+2)\bar{Q}}^{Ml}(\bar{\beta}) \cdot \phi_{nQ, \bar{n}\bar{Q}}^{Ml}(a, \bar{a}) \}. \quad (13)
 \end{aligned}$$

Thus, for the basis orbitals with $\nu = 0, 1$, using the condition $(ij | kl) = (kl | ij) = (lk | ji) = (ji | lk) \neq (ij | lk) = (lk | ij) = (kl | ji) = (ji | kl)$, etc. the problem leads to the evaluation of the following four types of distinct and nonvanishing integrals which are to be stored during the calculation:

$$\begin{aligned}
 \text{Type } A & : Q = 0, \quad \bar{Q} = 0, \quad M = 0; \\
 \text{Type } B & : Q = 1, \quad \bar{Q} = 0, \quad M = 0; \\
 \text{Type } C & : Q = \bar{Q} = 0, \quad M = 1; \\
 \text{Type } D & : Q = \bar{Q} = 1, \quad M = 0 \quad (14)
 \end{aligned}$$

It is noteworthy that, for $Q = \bar{Q} = 0$,

$$\begin{aligned}
 B_{j0}^{Ml}(\beta) &= B_j^{Ml}(\beta); \quad B_{j\bar{0}}^{Ml}(\bar{\beta}) = B_j^{Ml}(\bar{\beta}), \\
 \phi_{n0, \bar{n}0}^{Ml}(a, \bar{a}) &= \phi_{nn}^{Ml}(a, \bar{a}). \quad (15)
 \end{aligned}$$

It is a relatively simple matter to extend the scheme of Rüdberg (1951) for the calculation of two electron integrals, for nonvanishing Q and \bar{Q} , all of which can be expressed in terms of $B_j^{Ml}(\beta)$, $B_j^{Ml}(\bar{\beta})$, $\phi_{nn}^{Ml}(a, \bar{a})$. We are giving the details of only three factors, as the rest also follow the same:

$$\begin{aligned}
 B_{jQ}^{Ml}(\beta) &= \int_{-1}^{+1} P_l^M(\eta) (1 - \eta^2)^{1/2} \eta^{M+1} \eta^j \exp(-\beta\eta) d\eta \\
 (\text{for } Q = 1) & \\
 &= \int_{-1}^{+1} P_1^M(\eta) (1 - \eta^2)^{M/2} \eta^j \exp(-\beta\eta) d\eta - \\
 &\quad \int_{-1}^{+1} P_1^M(\eta) (1 - \eta^2)^{M/2} \eta^{j+2} \exp(-\beta\eta) d\eta \\
 \text{i.e.,} \quad B_{jQ}^{Ml}(\beta) &= B_j^{Ml}(\beta) - B_{j+2}^{Ml}(\beta), \quad (16)
 \end{aligned}$$

(for $Q = 1$)

$$\text{and } B_{j\bar{Q}}^{Ml}(\bar{\beta}) = B_j^{Ml}(\bar{\beta}) - B_{j+2}^{Ml}(\bar{\beta}). \quad (17)$$

(for $\bar{Q} = 1$)

Similarly,

$$\phi_{nQ, \bar{n}\bar{Q}}^{Ml}(a, \bar{a}) = \int_1^\infty d\xi \frac{1}{[(\xi^2 - 1)] [P_l^M(\xi)]^2} \int_1^\xi dx P_l^M(x) (x^2 - 1)^{1/2M+1} \exp(-ax) x^n$$

$$\begin{aligned} \text{(for } Q = 1, \bar{Q} = 1) \quad & \int_1^\xi dy P_l^M(y) (y^2 - 1)^{1/2M+1} \exp(-\bar{a}y) y^{\bar{n}} \\ & = \phi_{(n+2), (\bar{n}+2)}^{Ml}(a, \bar{a}) - \phi_{(n+2), \bar{n}}^{Ml}(a, \bar{a}) \\ & \quad - \phi_{n, (\bar{n}+2)}^{Ml}(a, \bar{a}) + \phi_{n\bar{n}}^{Ml}(a, \bar{a}). \end{aligned} \quad (18)$$

For basis orbitals with $\nu > 1$, the types of integrals increase, but the same technique is again useful.

2.4 Recurrence schemes for $B_j^{Ml}(\beta)$

If β is not very small,

$$B_{j+1}^{Ml}(\beta) = a_M(l) B_j^{Ml(-1)}(\beta) + a_M(l+1) B_j^{M(l+1)}(\beta) \quad (l \geq 1), \quad (19)$$

$$\text{where, } a_M(l) = a_0(l) [1 - (M/l^2)]^{1/2}, \quad (20)$$

$$a_0(l) = 1/(4 - 1/l^2)^{1/2}, \quad (21)$$

$$B_0^{Ml}(\beta) = \frac{1}{\beta^M} \left[\frac{(l+M)!}{(l-M)!} \right]^{1/2} B_0^{0l}(\beta), \quad (22)$$

$$B_0^{0l}(\beta) = [2(2l+1)]^{1/2} b_j^l(\beta), \quad (23)$$

$$b_0^l(\beta) = \frac{1}{2} \int_{-1}^{+1} dt P_l(t) \exp(\beta t), \quad (24)$$

$b_0^l(\beta)$'s were determined using the scheme of Corbató (1956). For very small values of β , $B_j^{Ml}(\beta)$ can be obtained by the Taylor expansion as suggested by Rüdberg (1951):

$$B_j^{Ml}(\beta) = \sum_{k=0}^{\infty} (-1)^k \frac{\beta^k}{k!} B_{j+k}^{Ml}(0). \quad (25)$$

2.5 Recurrence schemes for $\phi_{nn}^{M^i}(a, \bar{a})$

The sequence of calculation may be represented as

$$\begin{array}{cccc} \phi_{00}^{00}(a, \bar{a}) & \rightarrow & \phi_{nn}^{00}(a, \bar{a}) & \rightarrow & \phi_{nn}^{01}(a, \bar{a}) & \rightarrow & \phi_{nn}^{M^i}(a, \bar{a}). \\ \text{(i)} & & \text{(ii)} & & \text{(iii)} & & \text{(iv)} \end{array} \quad (26)$$

The recursion formulas used are:

$$\begin{aligned} \text{(i)} \quad \phi_{00}^{00}(a, \bar{a}) &= (1/a\bar{a}) \{ \exp(-a) G_0(\bar{a}) \\ &+ \exp(-\bar{a}) G_0(a) - G_0(a + \bar{a}) \}, \end{aligned} \quad (27)$$

$$\text{where, } G_0(x) = \exp(-x) \epsilon(x) \quad (28)$$

$$\epsilon(x) = \frac{1}{2} \{ C + \log 2x - \exp(2x) Ei(-2x) \} \quad (29)$$

$C = 0.5772156649$, the constant of Euler.

Ei functions were calculated using the polynomial quotient (Abramowitz 1965)

$$Ei(y) = (1/y e^y) \frac{y^4 + a_1 y^3 + a_2 y^2 + a_3 y + a_4}{y^4 + b_1 y^3 + b_2 y^2 + b_3 y + b_4} + \epsilon(y) \quad (30)$$

for $1 \leq y < \infty$

Here, $|\epsilon(y)| < 2 \times 10^{-8}$

$$\begin{aligned} a_1 &= 8.57332, 87401, & a_3 &= 8.63476, 08925, \\ a_2 &= 18.05901, 69730, & a_4 &= 0.26777, 37343 \end{aligned} \quad (31)$$

$$\begin{aligned} b_1 &= 9.57332, 23454, & b_3 &= 21.09965, 30827, \\ b_2 &= 25.63295, 61486, & b_4 &= 3.95849, 69228. \end{aligned} \quad (32)$$

Recently Amos (1980), published a recursive procedure to handle $Ei(y)$ where $\epsilon(y) \sim 10^{-14}$, but it is presumed that time required to compute these functions would be much higher than the time required by our method.

$$\begin{aligned} \text{(ii)} \quad \phi_{nn}^{00}(a, \bar{a}) &= (1/a\bar{a}) \{ \bar{a} n \phi_{(n-1)\bar{n}}^{00}(a, \bar{a}) \\ &+ a \bar{n} \phi_{n(n-1)}^{00}(a, \bar{a}) - n\bar{n} \phi_{(n-1)(\bar{n}-1)}^{00}(a, \bar{a}) \\ &+ \exp(-a) G_n^-(\bar{a}) + \exp(-\bar{a}) G_n(a) - G_{n+\bar{n}}(a+\bar{a}) \} \end{aligned} \quad (33)$$

where $G_n(x)$ was determined using the following recursion formulas.

$$G_n(x) = G_{n-2}(x) - A_{n-2}(x), \quad (34)$$

$$x \cdot A_n(x) = n A_{n-1}(x) + \exp(-x), \quad (35)$$

which start from

$$A_0(x) = (1/x) \exp(-x), \quad (36)$$

$$G_0(x) = 1/2 \exp(-x) \{C + \log 2x - \exp(2x) Ei(-2x)\}, \quad (37)$$

$$G_1(x) = 1/2 \exp(-x) \{C + \log 2x + \exp(2x) Ei(-2x)\}. \quad (38)$$

(iii) $\phi_{nn}^{0l}(\alpha, \bar{\alpha})$ or ϕ_{nn}^{l-} are calculated using the following formulas:

$$\phi_{nn}^{00} = \varphi_{nn}^0, \quad (39)$$

$$\phi_{nn}^l = [(2l-1)/l^2] \varphi_{nn}^l, \quad (l \geq 1), \quad (40)$$

$$\varphi_{nn}^l = (b_{l-2}/b_{l-1}) \varphi_{nn}^{(l-2)} + \psi_{nn}^{(l-1)}, \quad l \geq 2, \quad (41)$$

$$\begin{aligned} \psi_{nn}^l &= \psi_{nn}^{l-2} + b_l \varphi_{(n+1)(\bar{n}+1)}^l + b_{l-2} \varphi_{(n+1)(\bar{n}+1)}^{l-2} \\ &\quad - b_{l-1} \{ \varphi_{(n+2)\bar{n}}^{l-1} + \varphi_{n(\bar{n}+2)}^{l-1} \}. \quad l \geq 2, \end{aligned} \quad (42)$$

$$\text{where } b_0 = 1, b_l = 4 - (1/l^2), l \geq 1. \quad (43)$$

For $l = 0, 1$, the following relations are to be added:

$$\varphi_{nn}^1 = \psi_{nn}^0, \quad (44)$$

$$\begin{aligned} \psi_{nn}^1 &= 3 \varphi_{(n+1)(\bar{n}+1)}^1 + \varphi_{nn}^1 - \varphi_{(n+1)(\bar{n}+1)}^0 - \varphi_{(n+2)\bar{n}}^0 \\ &\quad - \varphi_{n(\bar{n}+2)}^0 + A_n(\alpha) A_{\bar{n}+1}(\bar{\alpha}) + A_{n+1}(\alpha) A_{\bar{n}}(\bar{\alpha}), \end{aligned} \quad (45)$$

$$\psi_{nn}^0 = \varphi_{(n+1)(\bar{n}+1)}^0 - A_n(\alpha) A_{\bar{n}}(\bar{\alpha}) - A_{nn}^0(\alpha, \bar{\alpha}), \quad (46)$$

$$A_{nn}^- = (1/(\alpha + \bar{\alpha})) \{n A_{(n-1)\bar{n}} + \bar{n} A_{n(\bar{n}-1)} + A_n(\alpha) A_{\bar{n}}(\bar{\alpha})\}, \quad (47)$$

$$A_{00} = (1/(\alpha + \bar{\alpha})) A_0(\alpha) A_0(\bar{\alpha}). \quad (48)$$

(iv) The final recursion formula is:

$$\begin{aligned} \phi_{nn}^{(M+1)l} = & \phi_{(n+1)(n+1)}^{Ml} - [(l+M)/(2l+1)] \phi_{nn}^{M(l-1)} \\ & - [(l+1-M)/(2l+1)] \phi_{nn}^{M(l+1)}, \quad l \geq 1. \end{aligned} \quad (49)$$

3. Results and discussion

The numerical implementation of this scheme requires careful handling of the stability and convergence problem.

3.1 Numerical stability

In the calculation of $\phi_{nn}^{Ml}(\alpha, \bar{\alpha})$ which involves a lot of recurrence relations, significant digits may be lost at a random rate. This is a general drawback of the analytical method. This was avoided by keeping l the running symbol in equation (13), to a certain value (discussed in subsequent section), so that ϕ_{nn}^{Ml} 's remain positive throughout. However, not only the lengthy recursive procedure but the lack of desired degree of accuracy in the exponential function $Ei(y)$ (equation (30)); which are the building units of ϕ_{nn}^{Ml} is also responsible for the numerical chaos involved in the process. We have avoided this by using a different expression for $Ei(y)$ (equation (30)), which is useful up to π orbitals. For integrals with δ orbitals which require larger values of l for convergence, one has to generate a new expression for $Ei(y)$ involving higher terms in the polynomials (equation (30)). Regarding the numerical stability of $B_j^{Ml}(\beta)$'s, we have used the Corbató's (1956) scheme in calculating the starting integrals $b_0^l(\beta)$ (equation (24)) instead of the Rüdberg's (1951) formulations.

3.2 Convergence test

The infinite summation of the right side of equation (13) obviously needs truncation. Usually, the truncation point is chosen as the point where the current term does not differ from its value at just the previous step by more than a pre-assigned positive number (*i.e.*, $\text{abs}(\text{sum}_{l+1} - \text{sum}_l) \leq \epsilon$). This straightforward checking of convergence of the sum led to difficulties in the present case. We had to adopt a different strategy for this purpose, which is based on a detailed study of the convergence behaviour of the summation in equation (13) over a wide range of values of the parameters α and β . The general pattern of convergence is illustrated in figure 1. A number which is allowed to vary only at the turning points (*e.g.*, B , C etc.), is generated and as the iterations cross the point C , the process is terminated. If iterations are continued beyond the point D , erroneous results are obtained. The reliability of this technique of checking convergence is clearly demonstrated in table 1 where some representative values of two-electron integrals for HF molecule calculated by our procedure have been compared with available literature values (Pople and Beveridge 1970). Moreover, the results of complete SCF calculation on LiH molecule reported in table 2 using the two-electron integrals computed by the present method compared favourably with the existing literature data (Ebbing 1960).

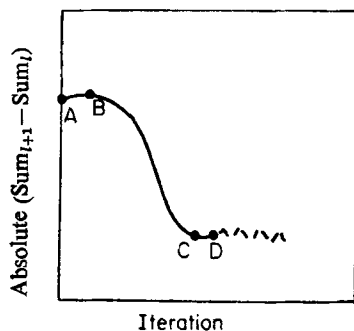


Figure 1. General pattern of convergence.

Table 1. Comparison of the values of some two electron integrals of HF molecule

Integrals	Present values	Literature values (Pople 1970)
(11 11)	5.437497	5.4375
(61 11)	0.194781	0.19478
(61 61)	0.008252	0.00825
(66 11)	0.526932	0.52693
(66 61)	0.029386	0.02939
(66 66)	0.625000	0.62500

(1 and 6 in the parenthesis in the 1st column are $1s$ sro orbitals centred on F atom and on H atom respectively. In calculating these integrals a transformation from cartesian co-ordinate system to elliptical co-ordinate system was performed.)

Table 2. Comparison of the results of scf calculation of LiH molecule:

n	j	Orbitals ν a		β	Present values*		Literature (Ebbing 1960) value*	
					1st two orbital energies	SCF energy	1st two orbital energies	SCF energy
0	0	0	3.42	3.51				
0	0	0	4.92	5.05	$\epsilon_1 =$		$\epsilon_1 =$	
1	1	0	4.17	4.28	-2.4263007		-2.42629	
0	0	0	1.08	0.98		$E =$		$E =$
0	1	0	1.08	0.98		-7.9817230		-7.98168
0	0	0	1.50	-1.50	$\epsilon_2 =$		$\epsilon_2 =$	
1	1	0	1.50	-1.50	-0.2920908		-0.29209	
0	0	± 1	4.7	4.7				
0	0	± 1	1.6	-1.6				
1	0	± 1	1.6	-1.6				

*The results are in atomic unit.

3.3 Time requirement

One may presume that in computing two-centre two-electron integrals ($ij|kl$), the technique adopted by Mehler and Rudenberg (1969) with N^2 operation, may be much faster than the method developed by us, for which number of operations is theoretic-

ally $N^4/8$ for real basis (as $1 \leq i \leq j \leq N$, $1 \leq k \leq l \leq N$) and $N^4/2$ for complex basis (as $1 \leq i \leq j \leq N$, $1 \leq (k, l) \leq N$) (N is the dimension of the basis). But, in our procedure, the effective number of operations can be cut down by a certain arrangements of basis functions into groups (e.g. by incorporating those which have same a but different n, j, β into one group); each group in its turn may be split into subgroups (each subgroup having same n but different j, β). The effectiveness is clearly evident from the fact that the major time-consuming functions are $\phi_{nm}^{Ml}(a, \bar{a})$. These functions appear only once for a lot of integrals arising from the orbitals χ_i 's with same a_i 's, and are stored once and for all. In this connection, it should, however be emphasised that with the EO's, use of the method of Mehler and Rüdénberg (1969) will not appear so straightforward as it is for real STAO's because of multiple reasons: (a) complex EO's will make the expansion coefficients W_{ik}^m complicated unlike those for real STAO's (b) while in the EO's, integral parameters n, j (equation (1)) are concerned with the flexibility of the orbital, regarding STAO's they are merely by-product of the coordinate transformation; and (c) finally, k (in the expansion of $f_{lm}(\xi)$) being a running symbol leads to losing the advantage of grouping of the EO's and of expressing integrals with nonvanishing Q in terms of those with vanishing Q (equations (13), (16), (17) and (18)). Efficiency of the present programme is reflected in the required time (12.8 min only) in evaluating 15379 distinct integrals (i.e., an average of 6.6×10^{-4} min per integral). In order to compare the efficiency of the present method with that of the method available (Mehler and Rüdénberg 1969) we have listed the time required by the two methods in table 3. However, it should be pointed out that the time required to calculate the *two-centre* two-electron *exchange* integrals in STAO basis was only reported by Mehler and Rüdénberg (1969) while we have tabulated the time required to evaluate *all* two-electron integrals that include direct, exchange and hybrid types. Thus, we may conclude that our method is certainly faster than that of the Mehler and Rüdénberg's technique for a reasonable choice of basis EO's.

Table 3. Computation time in Burroughs 6700 computer system for all types (Coulomb, exchange, hybrid) of integrals arising from complex EO basis and comparison with Mehler and Rüdénberg's (1969) time:

Basis set	No. of EO's (χ_i 's) in the basis	No. of distinct a_i 's	Total No. of integrals reqd. for SCF calculation (with EO's)	Average time per integral (in min)	Total no. of <i>exchange integrals</i> from real STAO basis of same symmetry	Average time per integral (in min)
1s (STAO)	1	1	1	0.03	1	0.05
S ₁	8	2	2,304	$p \times 10^{-3}$	1	0.05
S ₂	28	8	3,18,304	$p \times 10^{-4}$	325	3×10^{-4}
S ₃	40	12	13,12,000	$p \times 10^{-5}$	3321	9.6×10^{-4}

(p , a factor which depends upon a_i 's, has values in the order of unity).

References

- Abramowitz M and Stegun I A 1965 *Handbook of mathematical functions with formulas, graphs and mathematical tables* (New York: Dover), pp. 231, 239
- Amos D A 1980a *ACM Trans. Math. Software* **6** 365, 420
- Corbató F J 1956 *J. Chem. Phys.* **24** 452
- Ebbing D D 1960 Electronic Structure of the ground state of the LiH molecule, Indiana University, Theoretical Chem. Laboratory, September
- Elitzur M 1976 *Astrophys. J.* **203** 123
- Harris F E 1960 *J. Chem. Phys.* **32** 3
- Hinkley R K, Walker T E H and Richards W G 1972 *J. Phys.* **B5** 2016
- Hurley A C 1976 *Introduction to electron theory of small molecules* (New York: Academic Press) p. 130
- Mehler E L and Rüdénberg K 1969 *J. Chem. Phys.* **50** 2575
- Pople J A and Beveridge D L 1970 *Approximate molecular orbital theory* (New York: McGraw-Hill) p. 48
- Rüdénberg K 1951 *J. Chem. Phys.* **19** 1445
- Rüdénberg K 1964 *Molecular orbitals in chemistry, physics and biology* (New York: Academic Press) p. 215
- Shull H and Löwdin P O 1956 *J. Chem. Phys.* **25** 1035
- Wilson I D L 1978 *J. Mol. Spectrosc.* **70** 394
- Wilson I D L and Richards W G 1978 *Nature* (London) **271** 137