# Computation of Electron Repulsion Integrals Using the Rys Quadrature Method

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Following an earlier proposal to evaluate electron repulsion integrals over Gaussian basis functions by a numerical quadrature based on a set of orthogonal polynomials (Rys polynomials),

$$(\eta\eta\|\eta\eta) = 2(\rho/\pi)^{1/2} \sum_{\alpha=1,N} I_x(u_\alpha) I_y(u_\alpha) I_z(u_\alpha) W_\alpha$$

a computational procedure is outlined for efficient evaluation of the two-dimensional integrals $I_x$, $I_y$, and $I_z$. Compact recurrence formulas for the integrals make the method particularly fitted to handle high-angular-momentum basis functions. The technique has been implemented in the HONDO molecular orbital program.

## I. INTRODUCTION

The evaluation of the electron-repulsion integrals

$$(\eta_i\eta_j\|\eta_k\eta_l) = \iint \eta_i(1)\eta_j(1) \times (1/r_{12})\eta_k(2)\eta_l(2)d\tau_1 d\tau_2 \quad (1)$$

where $\eta_i$ ... are one-electron basis functions, constitutes one of the major computational tasks in *ab initio* molecular orbital theory. The necessary angular dependence of a basis function can be achieved explicitly through the use of spherical harmonics, or equivalently through use of integer powers of the Cartesian coordinates. When the latter are combined with a Gaussian radial factor, as suggested by Boys,[1] a primitive basis function takes the form

$$\eta = x^{n^x} y^{n^y} z^{n^z} \exp(-ar^2) \quad (2)$$

The sum of powers, $\lambda$,

$$\lambda = n^x + n^y + n^z \quad (3)$$

is closely related to the total angular momentum quantum number. The attractive feature of Gaussians resides in the fact that there exist practical closed-form solutions to the electron-repulsion integrals.[1,2] One is faced, however, with the increasing complexity of the analytical expression for the larger $\lambda$ values, and hence integral evaluation on a computer becomes expensive in terms of both execution time and core storage requirements.

We have proposed a method[3] based on the theory of orthogonal polynomials which yields a general formula for basis functions of arbitrarily high angular momentum:

$$(\eta_i\eta_j\|\eta_k\eta_l) = 2(\rho/\pi)^{1/2} \times \sum_{\alpha=1,N} I_x(u_\alpha) I_y(u_\alpha) I_z(u_\alpha) W_\alpha \quad (4)$$

By computing a large block of integrals concurrently, the same $I$ factors may be used for many different integrals. This method is computationally simple and numerically well behaved, and is part of the molecular program HONDO.[4]

In this article we describe the algorithm used in the calculation of the $I$ factors of eq. (4). The application of a Gaussian quadrature to the evaluation of electron-repulsion integrals is reviewed in Sec. II. Efficient recursion formulas for calculation of the $I$s are given in Sec. III.

## II. GAUSSIAN QUADRATURE AND TWO-ELECTRON INTEGRALS

It has been known since the early work of Boys that the two-electron integral over primitive

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Gaussian basis functions can be expressed in the form[1,2,5]

$$(\eta_i\eta_j\|\eta_k\eta_l) = \sum_{m=0}^{L} C_m F_m(X) \tag{5}$$

where

$$F_m(X) = \int_0^1 dt\, t^{2m} \exp(-Xt^2) \tag{6}$$

and

$$L = \lambda_i + \lambda_j + \lambda_k + \lambda_l \tag{7}$$

The value of $X$ depends upon the exponential parameters $a_i$, $a_j$, $a_k$, $a_l$, and the positions of the centers of the four Gaussians, but is independent of the angular momentum indices $n_x$, $n_y$, and $n_z$. It follows immediately that eq. (5) can be written

$$(\eta_i\eta_j\|\eta_k\eta_l) = \int_0^1 dt\, \exp(-Xt^2)P_L(t), \tag{8}$$

where $P_L(t)$ is a polynomial of degree $L$ in $t^2$ with coefficients $C_m$. The integral in eq. (8) can be evaluated exactly by an $N$-point quadrature formula.

$$(\eta_i\eta_j\|\eta_k\eta_l) = \sum_{\alpha=1}^{N} W_\alpha P_L(t_\alpha) \tag{9}$$

where $N$ is any integer satisfying

$$N > L/2, \tag{10}$$

$t_\alpha$ is a positive zero of the $N$th polynomial $R_N(t,X)$

$$R_N(t_\alpha,X) = 0 \tag{11}$$

and $W_\alpha$ is a weight factor which depends upon the value of $X$. $R_N(t,X)$ is the member of degree $2N$ of a set of even polynomials in the variable $t$, orthonormal on the interval [0,1] with respect to the weight factor $\exp(-Xt^2)$; i.e.,

$$\int_0^1 \mathrm{dt}\, \exp(-Xt^2)R_N(t,X)R_M(t,X) = \delta_{NM} \tag{12}$$

Efficient computation of $t_\alpha$ and $W_\alpha$ for any given value of $X$ is discussed by King and Dupuis.[6] In HONDO the roots and weight factors are evaluated by low-order polynomial approximations valid over finite intervals of $X$.

Taketa[2] gives an explicit but complicated algebraic formula for the $C_m$ coefficients. In principle, one could compute the values of $X$, $C_m$, $t_\alpha$, and $W_\alpha$, then by substitution evaluate $P_L(t_\alpha)$ and use eq. (9) to obtain the desired integral. However, it would be more efficient to use eq. (5) directly. The quadrature formula is superior only because one can obtain numerical values of $P_L(t_\alpha)$ without computing the $C_m$ coefficients.

### The Polynomial $P_L(t)$

Express the Coulomb operator $r_{12}^{-1}$ as a Gaussian transform:

$$\frac{1}{r_{12}} = 2\pi^{-1/2} \int_0^\infty du\, \exp(-u^2r_{12}^2) \tag{13}$$

A change in order of integration (valid) leads to

$$(\eta_i\eta_j\|\eta_k\eta_l) = 2\pi^{-1/2} \times \int_0^\infty du\, (\eta_i\eta_j|\exp(-u^2r_{12}^2)|\eta_k\eta_l) \tag{14}$$

The integrand in eq. (14) factors into a product of three two-dimensional integrals associated with the three axes of a Cartesian coordinate system:

$$(\eta_i\eta_j|\exp(-u^2r_{12}^2)|\eta_k\eta_l) = I_x'I_y'I_z' \tag{15}$$

Of the 12 $n^x$, $n^y$, $n^z$ indices only the four $n^x$ values enter into the $I_x'$ factor:

$$I_x'(n_i,n_j,n_k,n_l,u) = \iint dx_1\, dx_2\, (x_1 - x_i)^{ni} \times (x_1 - x_j)^{nj}(x_2 - x_k)^{nk}(x_2 - x_l)^{nl}\, e^{-Q_x} \tag{16}$$

where

$$Q_x = a_i(x_1 - x_i)^2 + a_j(x_1 - x_j)^2 + a_k(x_2 - x_k)^2 + a_l(x_2 - x_l)^2 + u^2(x_1 - x_2)^2 \tag{17}$$

Here $x_i$ is the $x$ coordinate of the center of $\eta_i$, and $n_i$ is the corresponding $n^x$ index. Let us define some new quantities:

$$x_A = (a_ix_i + a_jx_j)/(a_i + a_j) \tag{18}$$

$$x_B = (a_kx_k + a_lx_l)/(a_k + a_l) \tag{19}$$

$$A = a_i + a_j \tag{20}$$

$$B = a_k + a_l \tag{21}$$

$$\rho = AB/(A + B) \tag{22}$$

$$D_x = \rho(x_A - x_B)^2 \tag{23}$$

$$G_x = a_ia_j(a_i + a_j)^{-1}(x_i - x_j)^2 + a_ka_l(a_k + a_l)^{-1}(x_k - x_l)^2 \tag{24}$$

In terms of these, $Q_x$ becomes

$$Q_x = G_x + A(x_1 - x_A)^2 + B(x_2 - x_B)^2 + u^2(x_1 - x_2)^2 \tag{25}$$

Let us make a change of variable from $u$ to $t$:

$$u^2 = \rho t^2/(1 - t^2) \tag{26}$$

$$t^2 = u^2/(\rho + u^2) \tag{27}$$

$$dt = \rho(\rho + u^2)^{-3/2}du \tag{28}$$

Note that as $u$ varies from zero to infinity, $t$ varies from zero to unity. Finally, we define a modified form of the two-dimensional integral

$$I_x = e^{D_x t^2}(1 - t^2)^{-1/2}I'_x \tag{29}$$

Similarly, $I_y$ is related to $I'_y$, and $I_z$ to $I'_z$. By substituting eq. (15) and eqs. (26)–(29) into eq. (14) one recovers eq. (8) where

$$P_L(t) = 2(\rho/\pi)^{1/2}I_x I_y I_z \tag{30}$$

and using $y$ and $z$ analogs of eq. (23) one obtains

$$X = D_x + D_y + D_z \tag{31}$$

To obtain the working formula for the two-electron Coulomb repulsion integral simply substitute eq. (30) into eq. (9) giving

$$(\eta_i\eta_j\|\eta_k\eta_l) = \sum_{\alpha=1,N} I_x(u_\alpha)I_y(u_\alpha)I^*_z(u_\alpha) \tag{32}$$

where

$$I^*_z(u_\alpha) = 2(\rho/\pi)^{1/2}I_z(u_\alpha)W_\alpha \tag{33}$$

The strategy used for an efficient implementation of this algorithm has been described previously.[3] In the next section we focus on the evaluation of the two-dimensional integrals $I_x$. One could work out algebraic formulas but an alternative approach has proven more desirable. It used recurrence relations which are given below.

## III. RECURRENCE RELATIONS

An efficient procedure for obtaining values of $I_x$ [and thereby $P_L(t)$] is crucial to the success of the quadrature formula eq. (9). We start by defining the function

$$g_{n,m}(x_1,x_2) \equiv (x_1 - x_i)^n(x_2 - x_k)^m \times \exp[-A(x_1 - x_A)^2 - B(x_2 - x_B)^2 - u^2(x_1 - x_2)^2] \tag{34}$$

Let $G_{n,m}$ be given by the two-dimensional integral

$$G_{n,m} \equiv \iint_{-\infty}^{+\infty} dx_1\,dx_2\,g_{n,m}(x_1,x_2) \tag{35}$$

Then $G_{n,m}$ is related to $I'_x$ of eq. (16) by placing the polynomial factors of the $\eta_j$ and $\eta_l$ primitives on center $i$ and $k$; i.e.,

$$G_{n,m}\exp(-G_x) = I'_x(n_i + n_j,0,n_k + n_l,0,u) \tag{36}$$

Differentiation of $g_{n,m}$ with respect to $x_1$ and integration over all values of $x_1$ and $x_2$ using

$$\iint_{-\infty}^{+\infty} dx_1\,dx_2\frac{\partial g_{n,m}}{\partial x_1} = 0 \tag{37}$$

leads to

$$\frac{n}{2}G_{n-1,m} + [A(x_A - x_i) + u^2(x_k - x_i)]G_{n,m} - (A + u^2)G_{n+1,m} + u^2G_{n,m+1} = 0 \tag{38}$$

Similarly, differentiation with respect to $x_2$ and integration leads to

$$\frac{m}{2}G_{n,m-1} + [B(x_B - x_k) + u^2(x_i - x_k)]G_{n,m} - (B + u^2)G_{n,m+1} + u^2G_{n+1,m} = 0 \tag{39}$$

Eliminating $G_{n,m+1}$ between eqs. (38) and (39) gives

$$G_{n+1,m} = nB_{10}G_{n-1,m} + mB_{00}G_{n,m-1} + C_{00}G_{n,m} \tag{40}$$

where the coefficients as a function of $t$ are given by

$$C_{00} = (x_A - x_i) + \frac{B(x_B - x_A)}{A + B}t^2 \tag{41}$$

$$B_{00} = \frac{1}{2(A + B)}t^2 \tag{42}$$

$$B_{10} = \frac{1}{2A} - \frac{B}{2A(A + B)}t^2 \tag{43}$$

Eliminating $G_{n+1,m}$ gives

$$G_{n,m+1} = mB'_{01}G_{n,m-1} + nB_{00}G_{n-1,m} + C'_{00}G_{n,m} \tag{44}$$

where

$$C'_{00} = (x_B - x_k) + \frac{A(x_A - x_B)}{A + B}t^2 \tag{45}$$

and

$$B'_{01} = \frac{1}{2B} - \frac{A}{2B(A + B)}t^2 \tag{46}$$

Furthermore, $G_{00}$ is given explicitly by

$$G_{00} = \exp(-D_x t^2)(1 - t^2)^{1/2}\frac{\pi}{(AB)^{1/2}} \tag{47}$$

Combining eqs. (29), (36), and (47) it is easily verified that the recurrence relations eqs. (40) and (44) generate an $I_x(n_i + n_j,0,n_k + n_l,0)$, which is an even polynomial in $t$ as is required. It is shown below that shifting centers to provide the final

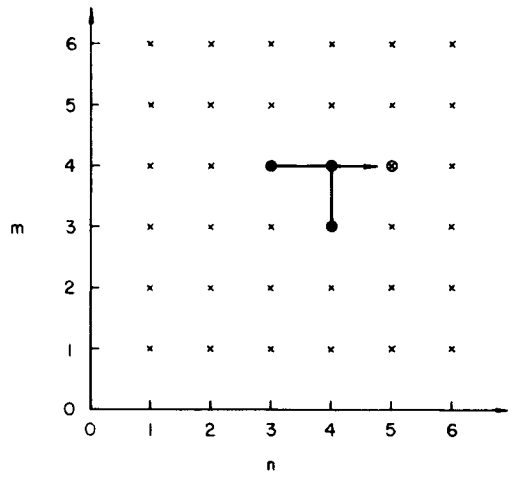


**Figure 1.** Diagrammatic representation of recurrence relations for two-dimensional integrals.

quantity $I_x(n_i,n_j,n_k,n_l)$ does not change the polynomial nature of $I_x$.

To produce the list of desired $I_x$ values for each $t_\alpha$ in the quadrature formula [eq. (32)], one first starts with special cases of eqs. (40) and (44):

$$G_{n+1,0} = nB_{10}G_{n-1,0} + C_{00}G_{n,0}, \quad (48)$$

$$G_{0,m+1} = mB'_{01}G_{0,m-1} + C_{00}G_{0,m} \quad (49)$$

Then one uses the two-term relations

$$G_{n,1} = nB_{00}G_{n-1,0} + C_{00}G_{n,0} \quad (50)$$

$$G_{1,m} = mB_{00}G_{0,m-1} + C_{00}G_{0,m} \quad (51)$$

Finally, the three-term relation of eq. (40) yields $G_{n,m}$. The process is represented diagramatically in Figure 1. The full list of $I_x(n_i,n_j,n_k,n_l)$ is generated by a two-step process involving the "transfer" equations

$$I_x(n_i,n_j,m,0) = I_x(n_1 + 1,n_j - 1,m,0) + (x_i - x_j)I_x(n_i,n_j - 1,m,0) \quad (52)$$

$$I_x(n_i,n_j,n_k,n_l) = I_x(n_i,n_j,n_k + 1,n_l - 1) + (x_k - x_l)I_x(n_i,n_j,n_k,n_l - 1) \quad (53)$$

For a given value of $m$ (i.e., $k,l$ pair), eq. (52) transfers a factor of $x_1 - x_i$ in eq. (34) to center $j$. Figure 2 illustrates the procedure. Asterisks indicate multiplication by $x_i - x_j$. The $(n_i,n_j)$ pairs enclosed in the rectangle are those ultimately required in the quadrature scheme. Eq. (53) is applied to each of these $(n_i,n_j)$ pairs, generating each time the appropriate $(n_k,n_l)$ pairs completing the list of $I_x$ integrals.

In eq. (34), one could equally as well have chosen center $j$ instead of $i$, or center $l$ instead of $k$. In practice it is most efficient to choose the centers which minimize the number of "transfers" which must be done according to either eq. (52) or eq. (53). For example, the block of integrals resulting from the four shells $(PS\|SP)$ is more efficiently generated by using centers $i$ and $l$ than by using $i$ and $k$. Therefore, instead of "switching" the four shells into a standard order such as $(PS\|SP)$, one merely has to make the proper selection of centers to be used in the recurrence and "transfer" equations.

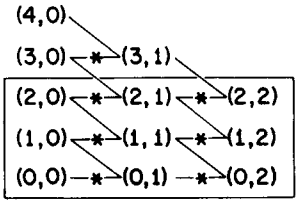


**Figure 2.** Diagrammatic illustration of the use of the "transfer equations."

## IV. CONCLUSION

Following an earlier proposal[3] that two-electron-repulsion integrals be computed via a numerical quadrature [eq. (32)] based on the set of orthogonal Rys polynomials, we present efficient and compact recurrence formulas to calculate the two-dimensional integrals which enter the quadrature formula. The simplicity of the recurrence formulas is responsible for the ease with which the original computer code[4] has been extended to handle $f$- and $g$-type Gaussian functions.[7] The Rys quadrature method has also proven to be a key factor allowing the efficient computation of the first and second derivatives of integrals with respect to nuclear coordinates.[8-10]

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