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Evaluation of Molecular Integrals in a Mixed Gaussian and Plane-Wave Basis by Rys Quadrature

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We report on the use of Rys numerical quadrature for the calculation of two-electron exchange integrals containing two Gaussians and two plane-wave functions, and two-electron integrals containing three Gaussians and one plane-wave function. Generally, the Rys polynomials for this mixed basis set are complex. We present formulas for obtaining their roots and weights that are also generally complex. Rys numerical quadrature provides an alternative method for calculation of integrals of this type that are encountered in the electron–molecule scattering theory.

Key Words: two-electron integrals; Rys numerical quadrature; mixed plane-wave-Gaussian basis sets.

I. INTRODUCTION

Hybrid two-electron integrals in a mixed Gaussian and plane-wave basis set are needed in calculations of electron scattering by polyatomic molecules [1]. A product of a Gaussian and a plane-wave function may be expressed as a product of two Gaussians, one real function and the other one centered on a point in the complex plane, multiplied by an pre-exponential factor

$$e^{-\alpha(\mathbf{r}-\mathbf{A})^2}e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{A}}e^{-k^2/2\alpha}e^{(-\alpha/2)(\mathbf{r}-\mathbf{A})^2}e^{(-\alpha/2)(\mathbf{r}-\mathbf{A}-i(\mathbf{k}/\alpha))^2}, \tag{1}$$

and also as single Gaussian

$$e^{-\alpha(\mathbf{r}-\mathbf{A})^2}e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{A}}e^{-k^2/4\alpha}e^{-\alpha(\mathbf{r}-\mathbf{A}-i(\mathbf{k}/2\alpha))^2}. \tag{2}$$

Hybrid integrals therefore may be calculated as is usual in the electronic structure theory for calculation of two-electron integrals over Gaussians, except that complex arguments must

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be used in incomplete gamma functions [2, 3]. However, calculation of hybrid integrals in this way has not been used much in practice. Instead, Watson and McKoy [4] developed a method based on a partial wave expansion of plane-wave functions. We thought, however, it might be profitable to examine for this purpose the use of the Rys numerical quadrature [5], developed for effective calculation of two-electron integrals in the electronic structure theory [6, 7]. We consider two types of integrals, exchange free–free integrals and integrals with three Gaussians and one plane-wave function.

II. RELATION TO INTEGRALS OVER GAUSSIANS

The purpose of this section is to obtain the integrals in a form amenable to treatment by the Rys numerical quadrature and to express all quantities needed in this method [7]. Using Eq. (1) we rewrite the exchange free–free integral in the form

$$\begin{aligned}
&\iint e^{-i\mathbf{k}'\cdot\mathbf{r_1}}(x_1 - A_x)^{m^x}(y_1 - A_y)^{m^y}(z_1 - A_z)^{m^z} e^{-\alpha(\mathbf{r_1}-\mathbf{A})^2}\left(\frac{1}{r_{12}}\right)e^{i\mathbf{k}\cdot\mathbf{r_2}} \\
&\quad\times (x_2 - B_x)^{n^x}(y_2 - B_y)^{n^y}(z_2 - B_z)^{n^z} e^{-\beta(\mathbf{r_2}-\mathbf{B})^2}\, d\mathbf{r_1}\, d\mathbf{r_2} \\
&= e^{-i\mathbf{k}'\cdot\mathbf{A}} e^{-k'^2/4\alpha} e^{i\mathbf{k}\cdot\mathbf{B}} e^{-k^2/4\beta} \iint (x_1 - A_x)^{m^x}(y_1 - A_y)^{m^y}(z_1 - A_z)^{m^z} e^{-\alpha(\mathbf{r_1}-\mathbf{A}+i\mathbf{k}'/2\alpha)^2} \\
&\quad\times \left(\frac{1}{r_{12}}\right)(x_2 - B_x)^{n^x}(y_2 - B_y)^{n^y}(z_2 - B_z)^{n^z} e^{-\beta(\mathbf{r_2}-\mathbf{B}-i\mathbf{k}/2\beta)^2}\, d\mathbf{r_1}\, d\mathbf{r_2}.
\end{aligned} \tag{3}$$

Hereafter we will follow closely the notation of the paper by Rys and collaborators [7]. Hence, in accordance with their paper we define

$$x_i = A_x \tag{4}$$

$$x_j = A_x - i\frac{k'}{\alpha} \tag{5}$$

$$x_k = B_x \tag{6}$$

$$x_l = B_x + i\frac{k_x}{\beta} \tag{7}$$

$$a_i = \frac{\alpha}{2} \tag{8}$$

$$a_j = \frac{\alpha}{2} \tag{9}$$

$$a_k = \frac{\beta}{2} \tag{10}$$

$$a_l = \frac{\beta}{2} \tag{11}$$

$$x_A = A_x - i\frac{k'_x}{2\alpha} \tag{12}$$

$$x_B = B_x + i\frac{k_x}{2\beta} \tag{13}$$

$$A = \alpha \tag{14}$$

$$B = \beta \tag{15}$$

$$\rho = \frac{\alpha\beta}{\alpha+\beta} \tag{16}$$

$$D_x = \rho(x_A - x_B)^2 \tag{17}$$

$$G_x = -\frac{k_x'^2}{4\alpha} - \frac{k_x^2}{4\beta}. \tag{18}$$

The number of points in the numerical quadrature is given by the condition

$$N > \frac{m^x + m^y + m^z + n^x + n^y + n^z}{2}. \tag{19}$$

The respective Nth Rys polynomial

$$R_N(t_\alpha, X) = 0 \tag{20}$$

is of degree $2N$ in the variable t and the parameter X is obtained as

$$X = D_x + D_y + D_z \tag{21}$$

The roots t_α and weight factor W_α of $R_N(t, X)$ depend on the value of X. Once the roots and weights are determined, the integral from Eq. (2) is obtained by numerical quadrature,

$$\begin{aligned}\iint &(x_1 - A_x)^{m^x}(y_1 - A_y)^{m^y}(z_1 - A_z)^{m^z} e^{-\alpha(\mathbf{r_1}-\mathbf{A}+i\mathbf{k}'/2\alpha)}\left(\frac{1}{r_{12}}\right)(x_2 - B_x)^{n^x}(y_2 - B_y)^{n^y} \\ &\times (z_2 - B_z)^{n^z} e^{-\beta(\mathbf{r_2}-\mathbf{B}-i\mathbf{k}/2\beta)^2}\, d\mathbf{r_1}\, d\mathbf{r_2} = 2\left(\frac{\rho}{\pi}\right)^{1/2} \sum_{\alpha=1,N} I_x(t_\alpha) I_y(t_\alpha) I_z(t_\alpha) W_\alpha,\end{aligned} \tag{22}$$

following the usual procedure. The only difference is that we have to pass to complex arithmetics. The integrals I_x, I_y, I_z are obtained as described [7] in the original procedure for real Gaussians, except that x_A, x_B, X, and Rys polynomials R_N are now complex, and that only integrals of the type $I(n_i, 0, n_k, 0)$ are calculated. The problem thus reduces to an efficient computation of complex t_α and W_α for any given value of complex X. This will be discussed in the following sections. The integrals I_x, I_y, and I_z contain the factor $\exp(-G)$. This factor in its original expression [7] is independent of the positions of the electrons and so can be taken outside the integral and collected together with other factors standing before the integral in Eq. (2).

The integrals with three Gaussians may be expressed as

$$\begin{aligned}\iint &(x_1 - A_x)^{m^x}(y_1 - A_y)^{m^y}(z_1 - A_z)^{m^z} e^{-\alpha(\mathbf{r_1}-\mathbf{A})^2}(x_1 - B_x)^{n^x}(y_1 - B_y)^{n^y}(z_1 - B_z)^{n^z} \\ &\times e^{-\beta(\mathbf{r_1}-\mathbf{B})^2}(1/r_{12})(x_2 - C_x)^{l^x}(y_2 - C_y)^{l^y}(z_2 - C_z)^{l^z} e^{-\gamma(\mathbf{r_2}-\mathbf{C})^2} e^{i\mathbf{k}\cdot\mathbf{r_2}}\, d\mathbf{r_1}\, d\mathbf{r_2} \\ = e^{i\mathbf{k}\cdot\mathbf{C}} e^{-k^2/2\gamma} &\iint (x_1 - A_x)^{m^x}(y_1 - A_y)^{m^y}(z_1 - A_z)^{m^z} e^{-\alpha(\mathbf{r_1}-\mathbf{A})^2} \\ &\times (x_1 - B_x)^{n^x}(y_1 - B_y)^{n^y}(z_1 - B_z)^{n^z} e^{-\beta(\mathbf{r_1}-\mathbf{B})^2}(1/r_{12})(x_2 - C_x)^{l^x}(y_2 - C_y)^{l^y} \\ &\times (z_2 - C_z)^{l^z} e^{-(\gamma/2)(\mathbf{r_2}-\mathbf{C})^2} e^{-(\gamma/2)(\mathbf{r_2}-\mathbf{C}-i\mathbf{k}/\gamma)^2}\, d\mathbf{r_1}\, d\mathbf{r_2}.\end{aligned} \tag{23}$$

As with exchange free–free integrals we define

$$x_i = A_x \tag{24}$$

$$x_j = B_x \tag{25}$$

$$x_k = C_x \tag{26}$$

$$x_l = C_x + i\frac{k_x}{\gamma} \tag{27}$$

$$a_i = \alpha \tag{28}$$

$$a_j = \beta \tag{29}$$

$$a_k = \frac{\gamma}{2} \tag{30}$$

$$a_l = \frac{\gamma}{2} \tag{31}$$

$$x_A = \frac{\alpha A_x + \beta B_x}{\alpha + \beta} \tag{32}$$

$$x_B = C_x + i\frac{k_x}{2\gamma} \tag{33}$$

$$A = \alpha + \beta \tag{34}$$

$$B = \gamma \tag{35}$$

$$\rho = \frac{(\alpha + \beta)\gamma}{\alpha + \beta + \gamma} \tag{36}$$

$$G_x = \alpha\beta(\alpha + \beta)^{-1}(A_x - B_x)^2 - \frac{k_x^2}{4\gamma} \tag{37}$$

$$N > \frac{l^x + l^y + l^z + m^x + m^y + m^z + n^x + n^y + n^z}{2}. \tag{38}$$

The value of X is obtained from Eqs. (17) and (21) and the numerical quadrature is the same as in Eq. (22) for exchange free–free integrals. The terms I_x needed for the evaluation of the integral are of the type $I_x(n_i, n_j, n_k, 0)$ and they are obtained by recurrence formulas [7]. [As suggested by the referee, the transfer of factors $(x_i - x_j)$ to center i, used in these recurrence formulas, may be done by the PRISM algorithm of the GAUSSIAN code.]

III. COMPLEX RYS POLYNOMIALS

By a complex Rys polynomial we mean a Rys polynomial according to the original definition [5],

$$R_n(t, X) = \sum_{k=0}^{n} C_{kn}(X)t^{2k}, \tag{39}$$

but with complex C_{kn} coefficients, complex parameter X, and complex variable t. For a given X the coefficients are obtained from the orthogonality condition [5]

$$C_{mm}\sum_{k=0}^{n} C_{kn}F_{m+k} = \delta_{mn}, \qquad m \le n, \tag{40}$$

where F elements are incomplete gamma functions for complex arguments X. The computation of $F_n(X)$ is discussed separately [8]. The values of t_α were obtained by root search in the complex plane, basically in the same way as is done in one dimension by routines contained in the HONDO package [9]. The weight factors were calculated by using the formula [5]

$$W_\alpha^{-1} = \sum_{i=0}^{n-1} R_i(t_\alpha)^2. \tag{41}$$

In the asymptote $\operatorname{Re} z \to -\infty$ it holds [8]

$$\lim_{\operatorname{Re} z \to -\infty} F_m(z) = \lim_{\operatorname{Re} z \to -\infty} F_0(z). \tag{42}$$

For $R_l(t, X)$ the root is given [5] by

$$t_\alpha = (F_1/F_0)^{1/2}, \tag{43}$$

which implies the asymptote

$$\lim_{\operatorname{Re} x \to -\infty} t_\alpha = 1. \tag{44}$$

The same asymptote also holds for higher Rys polynomials $R_n(t, X)$. This tendency may be seen in Figs. 1 and 2.

Complex Rys polynomials constructed as described in this section have the same properties, necessary for numerical quadrature, as the usual real Rys polynomials [5]. They are orthogonal with respect to the complex weight factor $\exp(-Xt^2)$,

$$\int_0^1 R_i(t, X) R_j(t, X) \exp(-Xt^2)\, dt = \delta_{ij}, \tag{45}$$

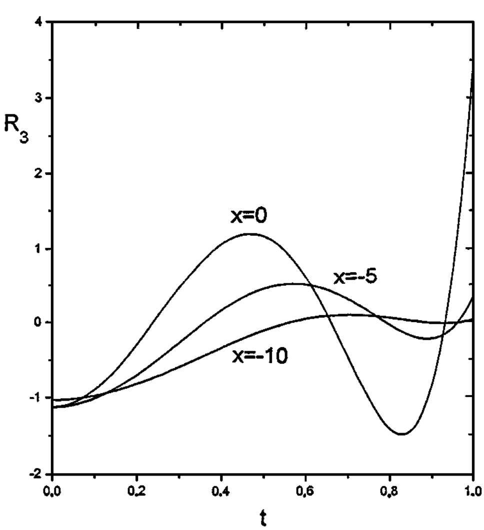

FIG. 1. Rys polynomials $R_3(t, x)$ for three different parameters x.

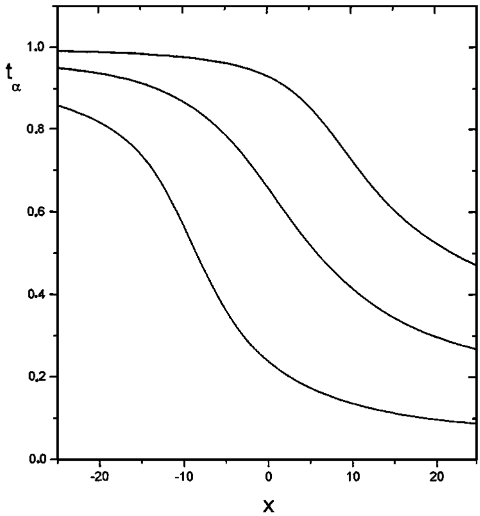

FIG. 2. Dependence of roots t_α of $R_3(t, x)$ on the value of the parameter x.

and they are also orthogonal under summation,

$$\sum_{\alpha=1}^{n} R_i(t_\alpha, X) R_j(t_\alpha, X) W_\alpha(t_\alpha) = \delta_{ij}, \tag{46}$$

where $2n > i + j$, $t_\alpha(X)$ is a root of R_n with a positive real part, and W_α is the appropriate weight.

IV. DETERMINATION OF ROOTS AND WEIGHTS

Widespread use of the Rys numerical quadrature in the electronic structure theory is due to the circumstance that the roots t_α and weight factors W_α may be calculated accurately

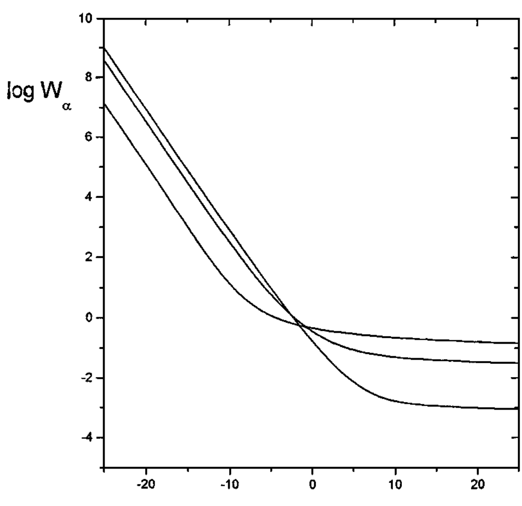

FIG. 3. Dependence of weight factors W_α of $R_3(t, x)$ on the value of the parameter x.

and efficiently [5] for any given n and X. In this section we present the results of our experimentation with complex Rys polynomials $R_n(t, z)$. Optimum calculation of t_α and W_α requires the use of different formulas depending on n and $z = x + iy$. We report several distinct cases.

For the imaginary part of z we may estimate the upper limit for a range of its absolute value which is met in practical calculations. For exchange integrals the value of z is given by Eqs. (4)–(17) and (21). Assume for simplicity that only x components of the vectors $\mathbf{A}$, $\mathbf{B}$, $\mathbf{k}$, and $\mathbf{k}'$ are nonvanishing, and that $\mathbf{k} = \mathbf{k}'$ and $\alpha = \beta$. Then the imaginary part of z is

$$\operatorname{Im} z = -(A_x - B_x)k_x. \tag{47}$$

The largest interatomic distance in the molecule of benzene, for example, is about 10 a.u., and the electron energy of 1000 eV corresponds to $k = 8.6\,\text{a.u.}^{-1}$. This gives $|\operatorname{Im} z| = 86$. Under the same assumption we arrive at a similar estimate for integrals with three Gaussians and one plane-wave function. We considered it there sufficient to limit our experimentation for the region given by $|\operatorname{Im} z| < 400$.

Roots and Weights for $R_1(t, z)$

$x > 33$ *and any* y. In this region we may apply the limiting expression derived [5] for real $R_1(t, x)$ and the root and weight is obtained directly as

$$t = (2z)^{-1/2} \tag{48}$$

and

$$W = \frac{1}{2}(\pi/z)^{1/2}. \tag{49}$$

$15 < x < 33$ *and any* y. As with the real $R_1(t, x)$, the limiting expression, augmented by the Q-type correction [5, 9], may be applied,

$$W = \frac{1}{2}(\pi/z)^{1/2} + e^{-z} Q_w \tag{50}$$

and

$$Q_w = (0.1962326414943/z - 0.4969524146449)/z - 0.60156581186481 \times 10^{-4}. \tag{51}$$

For the root we have

$$t = (F_1/F_0)^{1/2}, \tag{52}$$

and

$$F_0 = W, \tag{53}$$

$$F_1 = (F_0 - e^{-z})/2z. \tag{54}$$

$10 < x < 15$ *and* $|y| < 8$. The root and weight are calculated again by means of Eqs. (50)–(52), but the Q-type correction contains four terms [9].

$10 < x < 15$ *and* $|y| > 8$ *and* $-25 < x < 10$ *and any* y. F_0 is calculated explicitly [8] and used in Eqs. (52)–(54).

$x < -25$ *and any* y. F_0 is calculated by means of the asymptotic expansion [8] protecting the calculation against overflow. The weight is obtained from Eq. (53) as W/e^{-z} and the term e^{-z} is shifted to the pre-exponential factor (see Eqs. (1) and (2)). F_1 is also obtained as F_1/e^{-z} from Eq. (54) and root t from Eq. (52).

Roots and Weights for $R_2(t, z)$

$x > 40$ *and any* y. Roots and weights may be obtained directly from limiting expressions derived [5, 9] for real R_2,

$$t_\alpha = z^{-1/2} r_{\alpha n}, \tag{55}$$

$$W_\alpha = z^{-1/2} w_{\alpha n}, \tag{56}$$

where $r_{\alpha n}$ is a positive root of Hermite polynomial H_{2n} and $W_{\alpha n}$ is the corresponding weight factor for the $2n$-point Gauss–Hermite quadrature formula [5, 9].

$33 < x < 40$ *and any* y; $15 < x < 33$ *and* $|y| < 15$; $10 < x < 15$ *and* $|y| < 5$. Roots and weights may be obtained directly by means of the limiting expressions containing Q_r and Q_w corrections [5, 9],

$$t_\alpha = z^{-1/2} r_{\alpha n} + e^{-z} Q_r \tag{57}$$

$$W_\alpha = z^{-1/2} w_{\alpha n} + e^{-z} Q_w. \tag{58}$$

$15 < x < 33$ *and* $|y| > 15$; $10 < x < 15$ *and* $|y| > 5$; $-25 < x < 10$ *and any* y. For a given z we select an optimum way of calculation for F_0, F_1, F_2, and F_3 functions [8]. Squares of roots t_1^2 and t_2^2 are found from the solution of the quadratic equation representing the R_2 polynomial

$$(F_0 F_2 - F_1^2)v^2 + (F_1 F_2 - F_0 F_3)v + F_1 F_3 - F_2^2 = 0 \tag{59}$$

and for the weight factors we have

$$W_1 = \left(F_1 - t_2^2 F_0\right) / \left(t_1^2 - t_2^2\right) \tag{60}$$

and

$$W_2 = F_0 - W_1. \tag{61}$$

$x < -25$ *and any* y. Again we use Eqs. (59)–(61) but the F_n functions are obtained from the asymptotic expansion [8].

Roots and Weights for $R_3(t, z)$

$x \geq 0$ *and* $y = 0$. The roots and weights are obtained by the standard procedure [5, 9].

$-18 < x < 0$ and $y = 0$. This region was broken into several smaller ones and within each we obtained the Chebyshev polynomial approximation for t_α and W_α, following closely the original procedure used for positive x arguments [5].

$-25 < x < -18$ and any y; $-18 < x < 33$ and any $y \neq 0$; $33 < x < 100$ and $|y| > 50$. First we evaluate the coefficients of the R_3 polynomial,

$$R_3(t, z) = C_{03} + C_{13}t^2 + C_{23}t^4 + C_{33}t^6, \tag{62}$$

from the functions F_0 to F_6 by the $C^T FC$ orthogonalization [5].

For any t close to a root t_α we obtain the following approximate expression from the truncated Taylor expansion:

$$R_3(t) = R_3'(t_\alpha)(t - t_\alpha). \tag{63}$$

For the root t_α we have

$$t_\alpha = t - R_3(t)/R_3'(t_\alpha). \tag{64}$$

Equation (64) is solved iteratively for t_1 by using a suitable guess for t_1 in both R_3 and R_3'. Convergence is good for an educated guess and the precision to 10^{-11} is achieved in several steps. We found that the number of points used for a guess may be limited to a set listed in Table 1.

The other two roots may be obtained by using the properties of the cubic equation

$$a + bv + cv^2 + v^3 = 0 \tag{65}$$

$$\left(v - t_1^2\right)\left(v - t_2^2\right)\left(v - t_3^2\right) = 0 \tag{66}$$

TABLE 1
Roots and Weights of $R_3(t, z)$ for Several Values of z

x	y	α	t_α	W_α
0	0	1	0.2386191861 +0.0*i*	0.4679139346 +0.0*i*
		2	0.6612093865 +0.0*i*	0.3607615730 +0.0*i*
		3	0.9324695142 +0.0*i*	0.1713244924 +0.0*i*
−25	0	1	0.8608284718 +0.0*i*	0.0002077080 +0.0*i*
		2	0.9517421873 +0.0*i*	0.0056630601 +0.0*i*
		3	0.9914385577 +0.0*i*	0.0145560467 +0.0*i*
0	100	1	0.0292290031 +0.3435130055*i*	−0.0002148267 +0.000052316*i*
		2	0.0493015410 −0.0517897788*i*	0.0628828727 −0.0627221449*i*
		3	0.9998428610 −0.0049973347*i*	−0.0025555275 +0.0043027389*i*
33	50	1	0.0496122630 −0.0266995959*i*	0.0824406699 −0.0443667042*i*
		2	0.1519787400 −0.0817896766*i*	0.0178694536 −0.0096167198*i*
		3	0.2674269042 −0.1439198667*i*	0.0005153764 −0.0002773578*i*
33	200	1	0.0233543649 −0.0198167738*i*	0.0388079835 −0.0329294981*i*
		2	0.0715421285 −0.0607053187*i*	0.0084119249 −0.0071376007*i*
		3	0.1258879315 −0.1068191141*i*	0.00024261606 −0.0002058542*i*

$$a \equiv C_{03}/C_{33} = -t_1^2 t_2^2 t_3^2 \tag{67}$$

$$b \equiv C_{13}/C_{33} = t_1^2 t_2^2 + t_2^2 t_3^2 + t_1^2 t_3^2 \tag{68}$$

$$c \equiv C_{23}/C_{33} = -t_1^2 - t_2^2 - t_3^3. \tag{69}$$

Since t_1 is already known, the roots t_2 and t_3 are obtained as

$$v = t_\alpha^2$$

from the quadratic equation

$$v^2 + (c + t_1^2)v - a/t_1^2 = 0 \tag{70}$$

The weights are obtained from Eq. (41).

$x < -25$ and any y. As is seen from Fig. 1, the curve for R_3 becomes flat as x decreases and the determination of roots becomes troublesome. In this region of x the calculation of F_n functions is fast [8], and it is therefore preferable to reorganize the right-hand side of Eq. (22) as

$$2\left(\frac{\rho}{\pi}\right)^{1/2} \sum_{\alpha=1,N} I_x(t_\alpha) I_y(t_\alpha) I_z(t_\alpha) W_\alpha = \sum_m \sum_\alpha C_m t_\alpha^{2m} W_\alpha \tag{71}$$

and next, using the properties of roots and weights of Rys polynomials [5], as

$$2\left(\frac{\rho}{\pi}\right)^{1/2} \sum_{\alpha=1,N} I_x(t_\alpha) I_y(t_\alpha) I_z(t_\alpha) W_\alpha = \sum_m C_m F_m, \tag{72}$$

which corresponds to the traditional calculation method of two-electron integrals in the electronic structure theory [10]. We do not claim, however, that the Rys numerical quadrature cannot be applied in this region. We only do not know to determine the roots and weights effectively and with sufficient precision for $x < -25$.

$x > 100$ and any y; $x > 50$ and $|y| < 50$. t_α and W_α may be calculated directly from the limiting expressions (55) and (56).

$33 < x < 50$ and $|y| < 50$. Equations (57) and (58) may be used for direct calculation of t_α and W_α.

Roots and Weights for $R_4(t, z)$

$x \geqq 0$ and $y = 0$. For real nonnegative z the roots and weights are calculated by the standard procedure [5, 9].

$x > 47$ and any y. Use may be made of Eqs. (55) and (56) with $r_{\alpha n}$ and $w_{\alpha n}$ determined for real R_4 polynomials [5, 9].

$35 < x < 47$ and $|y| < 50$; $20 < x < 35$ and $|y| < 5$. In this region roots and weights may be calculated from $r_{\alpha n}$ and $w_{\alpha n}$ values and Q corrections [5, 9] by means of Eqs. (57) and (58).

$-25 < x < 20$ *and any* y; $20 < x < 35$ *and* $|y| > 5$; $35 < x < 47$ *and* $|y| > 50$. We first evaluate F_1 to F_{10} functions [8]. Then the $R_4(t, z)$ polynomial is determined from the C$^{\mathrm{T}}$FC orthogonalization [5], and its roots are obtained by means of an iterative procedure, similar to that used for $R_3(t, z)$ polynomials. Again, we use a truncated Taylor expansion

$$R_4(t) = R_4'(t_\alpha)(t - t_\alpha) \tag{73}$$

and starting with two different educated guesses for two different roots, we obtain two values of t_α in several steps from

$$t_\alpha = t - R_4(t)/R_4'(t_\alpha). \tag{74}$$

This iterative procedure works well if the guesses for t_1 and t_2 are close to the two roots. We keep therefore the values of the guess in two arrays of size 288×400 internally stored in the program. The grid is 0.85 and each array spans the region $-25 \leqq x \leqq 47$ and $0 \leqq y \leqq 100$. Values for $y = 100$ may be used as a guess for determination of roots with $y > 100$.

The other two roots, t_3 and t_4, are obtained from the quadratic equation as $v = t_\alpha^2$,

$$v^2 + \left(d + t_1^2 + t_2^2\right)v + a/t_1^2 t_2^2 = 0, \tag{75}$$

which was derived from the following manipulation with $R_4(t, z)$:

$$R_4(t, z) = C_{04} + C_{14}t^2 + C_{24}t^4 + C_{34}t^6 + C_{44}t^8 \tag{76}$$

$$a + bv + cv^2 + dv^3 + v^4 = 0 \tag{77}$$

$$\left(v - t_1^2\right)\left(v - t_2^2\right)\left(v - t_3^2\right)\left(v - t_4^2\right) = 0 \tag{78}$$

$$a \equiv C_{04}/C_{44} = t_1^2 t_2^2 t_3^2 t_4^2 \tag{79}$$

$$b \equiv C_{14}/C_{44} = -t_1^2 t_2^2 t_3^2 - t_1^2 t_2^2 t_4^2 - t_2^2 t_3^2 t_4^2 - t_1^2 t_3^2 t_4^2 \tag{80}$$

$$c \equiv C_{24}/C_{44} = t_1^2 t_2^2 + t_1^2 t_3^2 + t_2^2 t_3^2 + t_1^2 t_4^2 + t_2^2 t_4^2 + t_3^2 t_4^2 \tag{81}$$

$$d \equiv C_{34}/C_{44} = -t_1^2 - t_2^2 - t_3^2 - t_4^2. \tag{82}$$

The weights are obtained from Eq. (41).

$x < -25$ *and any* y. For large negative x it is difficult to maintain in the determination of roots and weights the required numerical precision, and therefore it is preferable to derive explicit formulas for the C_m coefficients appearing in Eq. (71) and to evaluate the particular integral from the F_m functions in the traditional way. Still it is certainly desirable to develop such a procedure which could evaluate roots and weights in this region of z effectively and with sufficient precision.

V. SUMMARY

We suggested the Rys numerical quadrature as a method for the calculation of two-electron integrals in a mixed Gaussian and plane-wave function basis set. In contrast to the original use of the Rys numerical quadrature for integrals in Gaussian basis sets, the roots and weights of Rys polynomials $R_n(t, z)$ given by mixed basis sets are generally complex.

Their accurate and efficient computation requires different approaches for different regions of z. Our experimentation in this respect is presented for $R_n(t, z)$ polynomials with $n \leqq 4$.

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