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Note

New Method to Evaluate Atomic Electron-Repulsion Integrals

1. INTRODUCTION

In atomic electronic structure calculations by orbital methods, the electron-repulsion integrals over orbitals a, b, c, and d may be expressed as [1]:

$$\langle a(1)\, c(1)|\, r_{12}^{-1}\, |b(2)\, d(2)\rangle$$

$$= \sum_k c^k(l_a, m_a; l_c, m_c)\, c^k(l_d, m_d; l_b, m_b)\, R^k(ac/bd), \tag{1}$$

where the c^ks are Condon–Shortley coupling coefficients and the radial integrals $R^k(ac/bd)$ are given by

$$R^k(ac/bd) = \int_0^\infty dr_1 r_1^2 R_a(r_1)\, R_c(r_1) \int_0^\infty dr_2 r_2^2 R_b(r_2)\, R_d(r_2) r_<^k / r_>^{k+1} \tag{2}$$

The term $r_<^k / r_>^{k+1}$ in the right side of (2) originates in Legendre's expansion for the reciprocal of the inter-electronic distance, r_{12}^{-1}.

$R^k(ac/bd)$ integrals can be obtained analytically for a variety of radial orbitals. In particular, accurate and efficient formulas for calculating (2) using Slater-type radial functions,

$$R_a = N_a r^{n_a - 1} e^{-Z_a r} \tag{3}$$

$$N_a = (2Z_a)^{1/2 + n_a} [(2n_a)!]^{-1/2}, \tag{4a}$$

have been given [2], although their use for high values of n_a and Z_a must be approached with some care because of arithmetic overflows and underflows that may occur in the evaluation of the normalization constant N_a and in calculating the R^k integrals (2) before normalization. In what follows, Eq. (4a) will be generalized

$$N_a = (2Z_a)^{1/2 + n_a} [\Gamma(2n_a + 1)]^{-1/2} \tag{4b}$$

to account for non-integer quantum numbers n_a.

The right side of (2) can also be evaluated by means of a Gauss–Laguerre numerical quadrature. All radial integrals arising from a given set of Slater-type or related radial orbitals can be evaluated close to full accuracy (14 figures) using a unique set of 80 Gauss–Laguerre quadrature points [3] in the r_1 axis obtained by

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considering the position of the maxima and inflexion points of the various base functions; between 3 and 5 quadrature points in the r_2 axis are needed for each point in the r_1 axis.

In this article we discuss an alternative numerical method which gives comparatively accurate results using only about 40 basis-set-independent integration points, and which is particularly useful when the traditional Legendre representation of r_{12}^{-1} is substituted by a physically more meaningful Taylor-series expansion [4]. A Taylor-series expansion of r_{12}^{-1} may be written as

$$r_{12}^{-1} = \sum_{m=0} G_m(r_1, r_2; q)(q - \cos\theta_{12})^m, \tag{5}$$

$$G_m(r_1, r_2; q) = [(r_1 - r_2)^2 + 2(1-q)\, r_1 r_2]^{-1/2} f_m\, y^m, \tag{6}$$

$$f_m = (-1)^m\, (2m-1)!!/(2^m m!), \tag{7}$$

$$y = 2r_1 r_2/[(r_1 - r_2)^2 + 2(1-q)\, r_1 r_2]. \tag{8}$$

Equation (5) can be generalized by taking different q_i values for corresponding intervals $[a_i, b_i]$ defining a particular range of $\cos\theta_{12}$.

A new method [4, 5] for atomic electronic structure calculations seeking to overcome the convergence problem of configuration interaction calculations makes use of well-defined truncations of expansion (5) about several values of the parameter q. If the series (5) is truncated at $m = n$, the new (truncated) Taylor series may be rewritten in terms of Legendre polynomials as

$$(r_{12}^{-1})_n = \sum_{k=0}^{n} H_k(r_1, r_2; n; q)\, P_k(\cos\theta_{12}), \tag{9}$$

$$H_k(r_1, r_2; n; q) = [(r_1 - r_2)^2 + 2(1-q)\, r_1 r_2]^{-1/2} \sum_{m=k}^{n} T(k, m)\, f_m\, y^m, \tag{10}$$

$$T(k, m) = \sum_{i=0}^{m} (-1)^i \binom{m}{i} D(k, i) q^{(m-i)}, \tag{11}$$

where the $D(k, i)$ are expansion coefficients for the powers of $\cos\theta_{12}$ in terms of Legendre polynomials,

$$\cos^i\theta_{12} = \sum_{k=\mathrm{mod}(i,2)(\,,2)}^{i} D(k, i)\, P_k(\cos\theta_{12}), \tag{12}$$

and f_m and y are given by (7) and (8), repectively; $(\ ,2)$ means that the corresponding running index has a stride of two.

In Eq. (1), the traditional R^k radial integrals may now be replaced by T^k integrals given by

$$T^k(ac/bd) = \int_0^\infty dr_1 r_1^2 R_a(r_1)\, R_c(r_1) \int_0^\infty dr_2 r_2^2 R_b(r_2) \times R_d(r_2)\, H_k(r_1, r_2; n; q), \tag{13}$$

where the regular function $H_k(r_1, r_2; n; q)$ replaces the physically ill-behaved term $r_<^k / r_>^{k+1}$.

Equation (1) may be generalized [6],

$$\langle a(1)\, c(1)|\, r_{12}^{-1}\, |b(2)\, d(2)\rangle = \sum_k c^k(l_a, m_a; l_c, m_c) \times c^k(l_d, m_d; l_b, m_b)\, I^k(ac/bd), \tag{14}$$

$$I^k(ac/bd) = \int_0^\infty dr_1 r_1^2 R_a(r_1)\, R_c(r_1) \int_0^\infty dr_2 r_2^2 R_b(r_2)\, R_d(r_2) \times \frac{(2k+1)}{2} \int_{-1}^{1} P_k(x)\, r_{12}^{-1}\, dx, \tag{15}$$

where the integration variable x is for $\cos\theta_{12}$. Equations (14)–(15) open new interesting possibilities [6].

In particular, Eq. (5)–(8) may now be used for N_q intervals $[a_i, b_i]$ and corresponding q_i parameters spanning the full range of x between -1 and 1 in (15), yielding

$$I^k(ac/bd) = \sum_{i=1}^{N_q} \sum_{m=0}^{k} I_i^m(ac/bd)\, A_{km}(q_i), \tag{16}$$

$$I_i^m(ac/bd) = \int_0^\infty dr_1 r_1^2 R_a(r_1\, R_c(r_1) \times \int_0^\infty dr_2 r_2^2 R_b(r_2)\, R_d(r_2)\, G_m(r_1, r_2; q_i), \tag{17}$$

$$A_{km}(q_i) = \frac{(2k+1)}{2} \int_{a_i}^{b_i} P_k(x)(q_i - x)^m\, dx. \tag{18}$$

Similar equations are obtained when (9)–(11) are replaced in (15) instead of (5)–(8). In both cases the basic numerical method is identical to the one to be used to evaluate Eq. (2).

The numerical method is discussed in Section 2. Results for the traditional radial integrals R^k are given in Section 3. The evaluation of the new radial integrals I^k is taken up in Section 4 and conclusions are given in Section 5.

2. Method

If the variables r_1 and r_2 (each ranging from 0 to ∞) are substituted by circular coordinates ρ and α (also known as hyperspherical coordinates [7]),

$$r_1 = \rho \cos\alpha$$

$$r_2 = \rho \sin\alpha$$

$$dr_1\, dr_2 = \rho\, d\rho\, d\alpha,$$

the radial integral R^k in (2) is given by

$$R^k(ac/bd) = N_a N_c N_b N_d \left\{ \int_0^{\pi/4} d\alpha \cos^{n_{ac}-k-1}\alpha \sin^{n_{bd}+k}\alpha + \int_{\pi/4}^{\pi/2} d\alpha \cos^{n_{ac}+k}\alpha \sin^{n_{bd}-k-1}\alpha \right\} \times \int_0^{\infty} \rho^{(n_{ac}+n_{bd})} e^{-[Z_{ac}\cos\alpha + Z_{bd}\sin\alpha]\rho}\, d\rho, \tag{19}$$

in a basis of Slater-type radial orbitals, where $n_{ac} = n_a + n_c$, $n_{bd} = n_b + n_d$, $Z_{ac} = Z_a + Z_c$, and $Z_{bd} = Z_b + Z_d$. Notice that the principal quantum numbers in Eq. (3) only need to satisfy $n_a \geqslant 0$, viz., $0s$, $0p$, etc., orbitals are allowed, which is not possible in the conventional approach using r_1 and r_2 coordinates without recurring to the complicated exponential integrals $E_n(r)$. After integrating over ρ, R^k becomes

$$R^k(ac/bd) = N_a N_c N_b N_d \Gamma(n_{ac}+n_{bd}+1) \left\{ \int_0^{\pi/4} d\alpha \frac{\cos^{n_{ac}-k-1}\alpha \sin^{n_{bd}+k}\alpha}{[Z_{ac}\cos\alpha + Z_{bd}\sin\alpha]^{(n_{ac}+n_{bd}+1)}} + \int_{\pi/4}^{\pi/2} d\alpha \frac{\cos^{n_{ac}+k}\alpha \sin^{n_{bd}-k-1}\alpha}{[Z_{ac}\cos\alpha + Z_{bd}\sin\alpha]^{(n_{ac}+n_{bd}+1)}} \right\}, \tag{20}$$

which can be evaluated to various accuracies by using a Gauss–Legendre quadrature in each of the intervals $[0, \pi/4]$ and $[\pi/4, \pi/2]$ for a wide range of principal quantum numbers n_a and orbital exponents Z_a, as discussed in the next section.

In practice, however, straightforward use of (20) leads to arithmetic underflows and overflows due to the product of the four normalization constants $N_a N_c N_b N_d$ (large values of principal quantum numbers and orbital exponents) and to the occurrence of $\Gamma(n_{ac}+n_{bd}+1)$ (large principal quantum numbers). In order to circumvent this problem, the definitions and scaling factors needed are

$$\bar{\Gamma}(n) = \Gamma(n)^{1/8}; \qquad \bar{N}_a = N_a^{1/4}; \qquad \bar{N}_{ac} = \bar{N}_a \bar{N}_c; \qquad \bar{N}_{bd} = \bar{N}_b \bar{N}_d$$

$$\eta = \bar{N}_{ac} \bar{\Gamma}(n_{ac}+n_{bd}+1)\, \bar{N}_{bd}, \tag{21}$$

$$\chi = \sqrt{\eta}, \tag{22}$$

whence the first integrand I_1 of (20) may be expressed, in Fortran, as

$$I_1 = (T1 * T2 * T2) ** 2, \tag{23}$$

where

$$T1 = \eta \cos^{(n_{ac}-k-1)/2}\alpha \sin^{(n_{bd}+k)/2}\alpha, \tag{24}$$

$$T2 = \chi/(Z_{ac}\cos\alpha + Z_{bd}\sin\alpha)^{(n_{ac}+n_{bd}+1)/4}, \tag{25}$$

and analogously for the second integrand. In this way, using standard floating point numbers of magnitudes between 10^{-37} and 10^{37}, up to azimuthal quantum number $l=12$, principal quantum numbers $n=13$ and orbital exponents Z between 0.001 and 100 can be used. For $l<12$, the allowed range of n and Z values is even greater than that.

3. Accuracy for the Evaluation of $R^k(ac/bd)$ Integrals

In Table I we show the accuracy of selected $R^k(ac/bd)$ integrals involved in single-configuration self-consistent field calculations of neutral Ar as a function of the number of Gauss–Legendre quadrature points. It is seen that 16-point quadrature formulas in $[0, \pi/4]$ and $[\pi/4, \pi/2]$ are adequate for orbital exponent optimizations, and 20-point formulas should be considered a safe compromise. In general, final results could always be obtained by using, say, 32-point Gauss–Legendre quadratures.

4. Evaluation of $I^k(ac/bd)$ Integrals

The evaluation of $I^k(ac/bd)$ integrals of Eq. (16) requires the computation of quantities $I_i^m(ac/bd)$, Eq. (17), and $A_{km}(q_i)$, Eq. (18). In order to evaluate $I_i^m(ac/bd)$ one follows a similar procedure as for $R^k(ac/bd)$ integrals, Eq. (20), but now integrands such as I_1, defined by Eq. (23), must be multiplied by a factor F which is equal to the value of the regular function $G_m(\rho, \alpha; q_i)=G_m(r_1, r_2; q_i)$ after

TABLE I

Accuracy of Various $R^k(ac/bd)$ Integrals as a Function of the Number of Gauss–Legendre Quadrature Points Using Eq. (20) as a Starting Point

$R^k(ac/bd)$	Full value	12	16	20	24	28
$(1s1s/1s1s)$	11.25	15	17	17	17	17
$(1s1s/2s2s)$	2.970703125	7	10	14	17	17
$(1s2s/1s2s)$	0.43505859375	13	17	17	17	17
$(3s3s/3s3s)$	0.7744140625	10	16	17	17	17
$(1s2p/1s2p)$	0.449661480468480	13	17	17	17	17
$(2s3p/2s3p)$	0.0407867431640625	11	16	17	17	17
$^0(2p2p/3p3p)$	0.035282439634886999	11	16	17	17	17
$^2(2p2p/3p3p)$	0.017915435669528113	12	17	17	17	17
$^0(3p3p/3p3p)$	0.516276041666666667	10	15	16	16	17
$^2(3p3p/3p3p)$	0.272526041666666667	11	15	16	16	16

Note. The orbital exponents are $Z_{1s}=18$, $Z_{2s}=16$, $Z_{3s}=3$, $Z_{2p}=7$, $Z_{2p}=2$. The number of significant figures achieved is under the columns marked 12, 16, 20, 24, and 28, denoting the number of quadrature points in $[0, \pi/4]$ and in $[\pi/4, \pi/2]$.

integration over ρ and for given values of α and q_i. These factors F are basis-set-independent and hence they are evaluated only once for the whole calculation.

Also, in order to keep arithmetic within bounds, it is necessary to multiply y in Eq. (8) by $(a_i - q_i)$ and, correspondingly, to divide $(q_i - x)$ by the same quantity in Eq. (18). In this way, the evaluation of (18) with a 12-point Gauss–Legendre quadrature offers no problems.

5. Conclusions

Radial electron-repulsion integrals $R^k(ac/bd)$ can be accurately evaluated by integrating the right side of (20) with 20-point Gauss–Legendre quadratures in each of the intervals $[0, \pi/4]$, $[\pi/4, \pi/2]$, and introducing auxiliary scaling factors given by Eqs. (21)–(22) and used in Eqs. (23)–(25). For $l = 12$, up to $n = 13$ principal quantum numbers and orbital exponents between 0.001 and 100 can be handled in usual floating point Fortran. The new method allows the introduction of non-integer principal quantum numbers and, also, principal quantum numbers smaller than $l + 1$, which might be useful in atomic structure calculations beyond Hartree–Fock. The main motivation, however, was to obtain accurate quadratures to evaluate electron repulsion integrals when using various types of representations of r_{12}^{-1}, as exemplified by Eq. (5). Also, novel correlation factors, such as any reasonable function depending upon $\cos\theta_{12}$, can be introduced through Eq. (18) at no extra computational cost.

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