SOLUTION OF MULTI-CENTER MOLECULAR INTEGRALS OF SLATER-TYPE ORBITALS

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Abstract. The troublesome multi-center molecular integrals of Slater type orbitals (STO) in molecular physics calculations can be evaluated by using the Fourier transform and proper coupling of the two center exchange integrals. A numerical integration procedure is then readily rendered to the final expression in which the integrand consists of well known special functions of arguments containing the geometrical arrangement of the nuclear centers and the exponents of the atomic orbitals. A practical procedure has been devised for the calculation of a general multi-center molecular integral coupling arbitrary Slater-type orbitals. Symmetry relations and asymptotic conditions are discussed. Explicit expressions of three-center one-electron nuclear attraction integrals and four-center two-electron Coulomb repulsion integrals for STO of principal quantum number n=2 are listed. A few numerical results are given for the purpose of comparison.

I. Introduction

Because the calculation of three and four-center integrals is one of the most complicated problems involved in the quantum theory of molecules and solids[1] , it has been a stumbling block to molecular ab initio calculation. The nature of the complications is due to the complicated angular dependence associated with different centers and the presence of square roots of radial dependence in describing relations between functions of different distances. In the past, two general procedures have been employed. The method of Barnett and Coulson[2] is based on a one-center expansion in which the numerical work commonly is very tedious and prone to error. The other method is based on the adoption of Gaussian orbitals either via expansion[3] or transformation[4] . Although the Gaussian type orbitals are computationally convenient, they are nevertheless inadequate because of poor radial dependence, e.g., the nonfulfillment of the cusp condition as well as the rapid falloff at long distances. Therefore, numerious Gaussian orbitals must be introduced in order to produce an accurate result. In the past, a few systematic investigations of molecular two center integrals over Slater-type orbitals (STO) led to general and explicit, but formal, solutions,[5] -[7] which commonly cannot be used efficiently for numerical calculations. Recently, instead of tackling the STO, which supposedly give a more accurate electronic distribution, Filter and Steinborn introduced the so called "B functions"[8]

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and "Λ functions"[9] which are closely related to the reduced Bessel functions and Laguerre functions, respectively. Linear transformations exist between the STO and these two types of functions. A general expression[10] has been given for the three-center nuclear attraction integral and the multicenter repulsion integral over the "B functions". However, the advantage of these functions is dubious both because the expression itself is still complicated, involving multiple numerical integration, and because additional effort is required to perform the summation to obtain the STO integral values. We have already suggested[11] that, by using the Fourier transform technique and properly coupling a pair of two-center exchange integrals, the multicenter molecular integrals can be handled in a straightforward manner. For example, a four-center two-electron Coulomb integral can be cast into a simple triple numerical integration with finite domain. As the complicated geometrical arrangement is connected vectorially and appears in the argument of the functions in the integrand, a simple numerical procedure can be directly applied. However, we recently noted that the polynomials appearing in the integrand are related to the modified Bessel functions.[15] Therefore, by means of their recurrence relations, the final compact expressions are readily obtained.

II. Basic integrals and procedure

A set of exchange integrals which are commonly applied to the atomic collisions of heavy

particles has the following form

$$I_{n_1,l_1,n_2,l_2}(a,b,c,d) = \int r_A^{n_1-2} r_B^{n_2-2} (p_1 \cdot r_A)(p_2 \cdot r_A)..(p_{l_1} \cdot r_A)$$

$$\cdot (q_1 \cdot r_B)(q_2 \cdot r_B)..(q_{l_2} \cdot r_B) \exp(-c\, r_A - d\, r_B + ia.r_A + ib.r_B)\, dr \tag{1}$$

where, as before[1,2], $p_1, p_2 .. p_{l_1}$ and $q_1, q_2 .. q_{l_2}$ are arbitrary constant vectors and, in

particular, can be set to unit normal vectors along the Cartesian axes; a and b are real

constant vectors. The constants c and d are real and positive. Integers n_1 and $n_2 \geq 1$ and

l_1 and $l_2 \geq 0$. The vectors r_A, r_B are the radius vectors of the electron measured from nucleus A

and B respectively. It has been shown[1,4] that Eq. (1) can be expressed as a simple one-

dimensional integral such as

$$I_{n_1,l_1,n_2,l_2}(a,b,c,d) = (-i)^{l_1+l_2} (p_1 \cdot \nabla_a)..(p_{l_1} \cdot \nabla_a)(q_1 \cdot \nabla_b)..(q_{l_2} \cdot \nabla_b)$$

$$(-\partial/\partial c)^{n_1-1} (-\partial/\partial d)^{n_2-1} I_{1,0,1,0}(a,b,c,d) \tag{2}$$

where $I_{1,0,1,0}(a,b,c,d) = 2\pi \int_0^1 \dfrac{\exp(i\,\beta.\mathbf{R} - \lambda R)}{\lambda} du$ (3)

$$\lambda^2 = u(1-u)[a^2 + b]^2 + uc^2 + (1-u)^2 d$$ (4)

$$\beta = ua-(1-u)b, \qquad \mathbf{R} = r_A - r_B$$ (5)

Also, the following differential operations can be easily established

$$\nabla_a \lambda = \nabla_b \lambda = u(1-u)(a+b)/\lambda$$ (6)

$$\partial\lambda/\partial c = uc/\lambda, \qquad \partial\lambda/\partial d = (1-u)\,d/\lambda$$ (7)

$$\nabla_a(\beta.\mathbf{R}) = u\mathbf{R}, \qquad \nabla_b(\beta.\mathbf{R}) = -(1-u)\mathbf{R}$$ (8)

$$\partial(\beta.\mathbf{R})/\partial c = 0, \qquad \partial(\beta.\mathbf{B})/\partial d = 0$$ (9)

In adopting this expression, we suggested[1][2] that the multi-center molecular integrals of STO can be constructed from these two-center exchange integrals. Although in the final expressions numerical integration still has to be performed, the troublesome multi-center nature is connected in a vectorial relation which appears only in the argument of the integrand. Thus, after the geometry and the orbitals are given, the integrals can be evaluated in a straight-forward manner. The method has been found to be expedient, and accurate results have been obtained. In this communication, we note that the parametric differentiation in Eq. (2) is commutative and associative. Therefore, if the solid harmonic operators are introduced, in relation to Eq.(1), we can further define another set of two-center exchange integrals such as

$$J_{n_1,l_1,m_1\,;n_2,l_2,m_2}(a,b,c,d) = \int r_A^{l_1} Y_{l_1,m_1}^{*}(\hat{r}_A)\, r_B^{l_2} Y_{l_2,m_2}(\hat{r}_B)$$

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$$r_A^{n_1, -l_1, -1} \; r_B^{n_2, -l_2, -1} \; \exp(-cr_A - dr_B + ia.r_A + ib.r_B) \, dr \tag{10}$$

In Eq.(10) n_1 ,l_1 ,m_1 and n_2 ,l_2 ,m_2 are the quantum numbers of the orbitals. In connection with Eq. (2), we obtain

$$J_{n_1,l_1,m_1;n_2,l_2,m_2}(a,b,c,d) = (-i)^{l_1+l_2} \; y_{l_1,m_1}^*(\nabla_a) \, y_{l_2,m_2}(\nabla_b)$$

$$(-\partial/\partial c)^{n_1-l_1-1} \; (-\partial/\partial d)^{n_2-l_2-1} \; I_{2,0,2,0}(a,b,c,d)$$

$$= (-i)^{l_1+l_2} \; y_{l_1,m_1}^*(\nabla_a) \, y_{l_2,m_2}(\nabla_b) \, (-\partial/\partial c)^{n_1-l_1-1} \; (-\partial/\partial d)^{n_2-l_2-1}$$

$$2\pi \, cd \int_0^1 e^{i\beta.R} \, R^3 \, \kappa_2(\lambda R) u(1-u)/\lambda^2 \, du \tag{11}$$

where κ_n is the modified spherical Bessel function. Furthermore, the solid harmonic gradient operator $y_{l_1,m_1}(\nabla_a)$ introduced can be interpreted as in the Condon-Shortley convention , for example, $y_{1,1} = -(3/8\pi)^{1/2}(\partial/\partial a_x + i\partial/\partial a_y)$ etc. For practical purposes, the differential operations have to be performed under the integral sign in Eq.(11) which is straightforward but laborious. However, with the aid of Eq.(4)-Eq.(9) and the recurrence relations of κ_n , the procedure can be greatly simplified. The technique of solving the multicenter molecular integral by coupling a pair of two-center exchange integrals has already been suggested. To illustrate the idea and to demonstrate the simple operations, we write down the three-center nuclear attraction integral, denoted as L, and the four-center two-electron

Coulomb repulsion integral, denoted as M, coupling some STO, the numerical solutions of which are known to be difficult.

We write

$$L = \int \psi^*_{n_1,l_1,m_1}(\xi_A, r_A) \frac{1}{r_C} \psi_{n_2,l_2,m_2}(\xi_B, r_B)\, dr \qquad (12)$$

Using the identity and referring to Fig. 1, we have

$$1/r_C = 1/2\pi^2 \int e^{iq.(r_A - R_{AC})}/q^2\, dq$$

Eq.(12) can be written as

$$L = C_{n_1}(\xi_A) C_{n_2}(\xi_B) \int e^{-iq.R_{AC}}/2\pi^2 q^2\, dq$$

$$(-i)^{l_1+l_2}\, [(-\partial/\partial\xi_A)^{n_1-l_1-1}(-\partial/\partial\xi_B)^{n_2-l_2-1}\, y^*_{l_1,m_1}(\nabla_a) y_{l_2,m_2}(\nabla_b)$$

$$2\pi\xi_A^5\xi_B^5 \int_0^1 e^{i\beta.R_{AB}} R_{AB}^3 \kappa_2(\lambda R_{AB})/\lambda^2\, u(1-u)\, du]_{a=q,b=0} \qquad (13)$$

$$\text{where } \beta = ua - (1-u)b, \quad \lambda^2 = u(1-u)|a+b|^2 + u\xi_A^2 + (1-u)\xi_B^2 \qquad (14)$$

After performing the parametric differentiation, the angular parts of **q** are integrated analytically by utilizing the plane wave expansion $\exp[iq.(uR_{AB} - R_{AC})]$, and the radial parts of q and u are integrated numerically. The four-center two-electron Coulomb integral is defined as follows:

$$M = \int \psi^*_{n_1,l_1,m_1}(\xi_A, r_A) \psi_{n_2,l_2,m_2}(\xi_B, r_B) \frac{1}{r_{12}} \psi^*_{n_3,l_3,m_3}(\xi_C, r_C)$$

$$\psi_{n_4, l_4, m_4}(\xi_D, r_2\,_D)\, dr_1\, dr_2 \tag{15}$$

In Eq.(15), for example, the indices n_2 ,l_2 ,m_2 are the quantum numbers of the orbital; $r_1\,_B$

denotes the radius vector of electron number 1 referred to an atomic nucleus B as origin; ξ_B is

the exponent parameter of STO etc.

We replace $1/r_1\,_2$ by its Fourier transform

$$1/r_1\,_2 = 1/2\pi^2 \int e^{iq.r_1\,_2}/q^2\, dq = 1/2\pi^2 \int e^{iq.(R_{AC}+r_2\,_C - r_1\,_A)}/q^2\, dq \tag{16}$$

Notice that expressing $r_1\,_2$ as $R_{AC}+r_2\,_C - r_1\,_A$ is quite arbitrary and offers no advantage

over other choices as long as they form a vectorial relation.

$$M = C_{n_1}(\xi_A)\, C_{n_2}(\xi_B)\, C_{n_3}(\xi_C)\, C_{n_4}(\xi_D)/(2\pi^2 q^2)$$

$$\int r_1\,_A^{l_1}\, Y^*_{l_1, m_1}(\hat{r}_1\,_A)\, r_1\,_B^{l_2}\, Y_{l_2, m_2}(\hat{r}_1\,_B)\, r_2\,_C^{l_3}\, Y^*_{l_3, m_3}(\hat{r}_2\,_C)\, r_2\,_D^{l_4}\, Y_{l_4, m_4}(\hat{r}_2\,_D)$$

$$r_1\,_A^{n_1 -l_1 -1}\, r_1\,_B^{n_2 -l_2 -1}\, r_2\,_C^{n_3 -l_3 -1}\, r_2\,_D^{n_4 -l_4 -1}\, e^{-iq.r_1\,_A} e^{iq.r_2\,_C} e^{iq.R_{AC}}$$

$$e^{-\xi_A r_1\,_A -\xi_B r_1\,_B -\xi_C r_2\,_C -\xi_D r_2\,_D}\, dr_1\, dr_2\, dq \tag{17}$$

By using Eq.(10), we write Eq.(17) as

$$M = C_{n_1}(\xi_A)\, C_{n_2}(\xi_B)\, C_{n_3}(\xi_C)\, C_{n_4}(\xi_D) \int e^{iq.R_{AC}}/(2\pi^2 q^2)\, dq$$

$$(-i)^{l_1 +l_2 +l_3 +l_4}\, [(-\partial/\partial\xi_A)^{n_1 -l_1 -1}\, (-\partial/\partial\xi_B)^{n_2 -l_2 -1}\, y^*_{l_1, m_1}(\nabla_a)\, y_{l_2, m_2}(\nabla_b)$$

$$2\pi \xi_A \xi_B \int_0^1 e^{i\beta.R_{AB}}\, R_{AB}^3\, \kappa_2(\lambda R_{AB})/\lambda^2\, u(1-u)\, |_{a=-q, b=0}\, du$$

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$$\left[\left(-\partial/\partial\xi_C\right)^{n,\,-1,\,-1} \left(-\partial/\partial\xi_D\right)^{n_4,\,-1,\,-1} y_{1,\,m}^{*}(\nabla_a,) y_{1,\,m_4}(\nabla_b,) \right.$$

$$\tag{18}$$

$$2\pi\xi_C\xi_D \int_0^1 e^{i\beta'.R_{CD}} R_{CD}^3 \kappa_2 (\lambda'R_{AB})/\lambda'^2 \; u'(1-u') \; \big|_{a'=q,b'=0} du'$$

where β and λ are as defined before and

$$\beta' = u'a' - (1-u')b', \qquad \lambda'^2 = u'(1-u')|a'+b'|^2 + u'\xi_C^2 + (1-u')\xi_D^2 \tag{19}$$

Because the angles are generated via parametric differentiation with respect to the constant vectors **a**, **b**, **a'** and **b'**, it is necessary to invoke the conditions, **a** = -**q**, **b** = 0, **a'** = **q**, **b'** = 0 at the end of the differential operations. Then, the integrand consists of a finite sum of angular orbitals in variable **q**. By properly coupling the orbitals[1,7] and using the plane-wave expansion $\exp[i\mathbf{q}.(R_{AC} - uR_{AB} + u'R_{CD})]$, we can integrate analytically the angular part of **q**. Then the radial parts of **q**, u and u' integrations are calculated numerically in a straightforward manner, such as by Gaussian quadrature or other numerical means.

III. Symmetry relations

By inspection, there are simple symmetry relations that can be readily employed; in this way the number of independent integral expressions derived is reduced to the minimum.

Three-center Nuclear Attraction Integrals

Referring to Fig. 1, suppose we have an expression (see Appendix A) for the following

integral. For brevity, we write $i = n_1 ,l_1 ,m_1$, $j = n_2 ,l_2 ,m_2$ etc.

If the expression of the following integral is known

$$L_{i,j} = \int \psi_i^*(\xi_A, r_A) \frac{1}{r_C} \psi_j(\xi_B, r_B) dr \tag{20}$$

we consider the following integral

$$L'_{j,i} = \int \psi_j^*(\xi_A, r_A) \frac{1}{r_{C'}} \psi_i(\xi_B, r_B) dr \tag{21}$$

where $L'_{j,i}$ denotes the integral for which the nuclear center C has undergone an

inversion operation, i.e., if $r_C = |r - R_C|$, then $r_{C'} = |r + R_C|$. Furthermore, through the

inversion of the electronic coordinate which is equivalent to the operation taking r_A to $-r_B$,

r_B to $-r_A$, Eq.(21) becomes

$$L'_{j,i} = \int \psi_j^*(\xi_A, -r_B) \frac{1}{r_C} \psi_i(\xi_B, -r_A) dr$$

$$= (-1)^{l_1 + l_2} \int \psi_j^*(\xi_A, r_B) \frac{1}{r_C} \psi_i(\xi_B, r_A) dr$$

$$= (-1)^{l_1 + l_2} L_{i,j}^*(\xi_A \leftrightarrow \xi_B) \tag{22}$$

The interpretation of Eq.(22) is that the value of integral $L_{j,i}$ can be obtained by

taking the complex conjugate of the value derived by means of the expression of $L'_{i,j}$ in which

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the exponents are properly interchanged with the inverted nuclear coordinate C. Finally, a phase factor is multiplied to obtain the integral value.

Four-center Two-electron Coulomb Repulsion Integrals

Referring to Fig. 2, suppose we have

$$I_{i,j;k,l} = \int \psi_i^*(\xi_A, r_{1A}) \psi_j(\xi_B, r_{1B}) \frac{1}{r_{12}} \psi_k^*(\xi_C, r_{2C}) \psi_l(\xi_D, r_{2D}) dr_1 dr_2 \qquad (23)$$

and are interested in evaluating another integral of the following form

$$I_{k,l;i,j} = \int \psi_k^*(\xi_A, r_{1A}) \psi_l(\xi_B, r_{1B}) \frac{1}{r_{12}} \psi_i^*(\xi_C, r_{2C}) \psi_j(\xi_D, r_{2D}) dr_1 dr_2$$

$$(24)$$

The integral value of $I_{k,l;i,j}$ is, in general, different from that of $I_{i,j;k,l}$. Because the subscripts 1 and 2 are dummy indices, Eq.(24) can be easily rewritten as

$$I_{k,l;i,j} = \int \psi_k^*(\xi_A, r_{2A}) \psi_l(\xi_B, r_{2B}) \frac{1}{r_{12}} \psi_i^*(\xi_C, r_{1C}) \psi_j(\xi_D, r_{1D}) dr_1 dr_2$$

$$= I_{i,j;k,l} \{ A \leftrightarrow C, B \leftrightarrow D, \xi_A \leftrightarrow \xi_C, \xi_B \leftrightarrow \xi_D \} \qquad (25)$$

In Eq.(25), exchange of the nuclear center is implied, e.g., A to C, C to A etc., including the exchange of exponents in the expression of $I_{i,j;k,l}$. Essentially, the nuclear center is reordered.

Next, consider the following integral

$$I_{j,i;l,k} = \int \psi_j^*(\xi_A, r_1 A) \psi_i(\xi_B, r_1 B) \frac{1}{r_{12}} \psi_l^*(\xi_C, r_2 C) \psi_k(\xi_D, r_2 D) \, dr_1 \, dr_2$$

(26)

Comparing to Eq.(23), we immediately find that

$$I_{j,i;l,k} = I_{i,j;k,l}^*(A \leftrightarrow B, C \leftrightarrow D, \xi_A \leftrightarrow \xi_B, \xi_C \leftrightarrow \xi_D)$$

(27)

IV. Asymptotic Behavior and Nuclear Center Collapse

With this formulation, more information of the asymptotic behavior of the integral is easier to obtain, at least in a qualitative sense. For example, it is obvious that the integrand decreases exponentially as R_{AB} and R_{CD} increase linearly through κ_n. However, if R_{AB} and R_{CD} are kept finite, the integrand decreases in a dampened oscillatory fashion with respect to R_{AC} through j_n. In another words, the integral value varies to a smaller extent with respect to a change of R_{AC} than of R_{AB} and R_{CD}, as we would expect. The formula is equally valid if the nuclear centers are collapsed into three, two or one center by simply taking the nuclear distance to zero, e.g., $R_{AB} = 0$, or $R_{CD} = 0$, (three center), or $R_{AB} = R_{CD} = 0$ (two center), or $R_{AB} = R_{CD} = R_{AC} = 0$ (one center), respectively. We notice that $\kappa_n(x)$ goes to infinity at the origin, but of course, this does not necessarily mean that the integral is not finite. However, for $n \geq 2$, there is a much stronger singular point at the origin; the straightforward procedure by

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directly taking e.g., $R_{AB} \to 0$ would certainly lead to some numerical problems. Fortunately, by close inspection, we find that, at all times, the term $R^m \kappa_n(\lambda R)$, $m \geq n+1$ appears in the integrand. Using the series representation[1,*] of κ_n

$$\kappa_n(x) = e^{-x}/x \, [1 + \frac{(n+1)!}{1! \, \Gamma(n)} (2x)^{-1} + \frac{(n+2)!}{2! \, \Gamma(n-1)} (2x)^{-2} + \ldots.]$$

$$= e^{-x}/x \sum_0^n (n+\frac{1}{2}, k) (2x)^{-k} \tag{28}$$

where the Hankel's symbol $(n, k) = \dfrac{\Gamma(1/2+n+k)}{k! \, \Gamma(1/2+n-k)}$.

we therefore, obtain

$$\lim_{R \to 0} R^m \kappa_n(\lambda R) = 0 \, , m > n+1 \tag{29}$$

$$= \frac{(2n)!}{2^n \lambda^{n+1} n!} \, , m = n+1 \tag{30}$$

i.e., for the collapsed center case, Eqs.(29) and (30) can be used in the integrand to avoid any numerical difficulties.

V. Numerical Example

In order to test this method, a simple Gaussian quadrature integration scheme has been applied to the derived formulas for the two electron multicenter integrals for the methane molecule. The results are listed in Table I along with the well known published results of Shavitt and Karplus[4], and the results computed using the Barnett-Coulson[2] method. We used the identical

parameters and the same notation as reported by Shavitt and Karplus, which are summarized in

Table I.

Table I. Some multi-center-two electron integrals for methane

	x	y	z	Orbital	Symbol	Exp.
C	0.0	0.0	0.0	$1s(C)$	c	5.700
H_1	0.0	0.0	-2.0	$2p(C)$	x,y,z	1.625
H_2	1.8856180	0.0	0.6666667	$1s(H_i)$	h_i	1.000
H_3	-0.94280904	1.63299316	0.6666667			
H_4	-0.94280904	-1.63299316	0.6666667			

Results, according to number of quadrature points

	This method		Shavitt-Karplus		Barnett-Coulson
Integral	12x12x16	20x20x24	12x12x16	20x20x24	
$(h_1\ h_2\ ;h_3\ h_4)$	0.03068148	0.03068213	0.03068196	0.03068187	0.03068247
$(h_1\ h_2\ ;h_1\ h_3)$	0.03569343	0.03569397	0.03569398	0.03569368	
$(h_1\ h_1\ ;h_2\ h_3)$	0.09569741	0.09570521	0.09570384	0.09570556	
$(c\ h_1\ ;h_3\ h_4)$	0.01298606	0.01274316	0.01286213	0.01271293	0.01274093
$(x\ h_1\ ;h_3\ h_4)$	-0.00752578	-0.00752560	-0.00752573	-0.00752559	-0.00752559
$(z\ h_1\ ;h_3\ h_4)$	-0.04765937	-0.04766222	-0.04766145	-0.04766277	-0.04766263

$(c\,h_1\,;c\,h_2\,)$	0.01191481	0.01121649	0.01191464	0.01121651	
$(c\,h_1\,;x\,h_2\,)$	0.02017340	0.01981324	0.02018282	0.01980944	0.01980903
$(c\,h_1\,;z\,h_2\,)$	0.00602142	0.00588692	0.00602480	0.00588562	0.00588522
$(x\,h_1\,;x\,h_2\,)$	0.03557018	0.03556931	0.03556692	0.03556880	0.03556858
$(x\,h_1\,;z\,h_2\,)$	0.00149034	0.00148956	0.00148892	0.00148937	0.00148940
$(y\,h_1\,;y\,h_2\,)$	0.02231921	0.02231975	0.02231903	0.02231976	0.02231959
$(z\,h_1\,;x\,h_2\,)$	-0.07790808	-0.07791435	-0.07791088	-0.07791394	-0.07791452
$(z\,h_1\,;z\,h_2\,)$	0.00855243	0.00854907	0.00854768	0.00854864	0.00854849
$(c\,c\,;h_1\,h_2\,)$	0.16644702	0.16654179	0.16864892	0.16656439	
$(x\,c\,;h_1\,h_2\,)$	0.00236735	0.00237118	0.00236900	0.00237002	0.00237004
$(z\,c\,;h_1\,h_2\,)$	-0.00167397	-0.00167668	-0.00167514	-0.00167586	-0.00167581
$(x\,x\,;h_1\,h_2\,)$	0.14192876	0.14192778	0.14192799	0.14192784	0.141927
$(x\,z\,;h_1\,h_2\,)$	-0.00143553	-0.00143592	-0.00143598	-0.00143598	-0.00143579
$(y\,y\,;h_1\,h_2\,)$	0.13676011	0.13675834	0.13675888	0.13675864	0.136758
$(z\,z\,;h_1\,h_2\,)$	0.14091369	0.14091243	0.14091270	0.14091244	0.140912
$(x\,x\,;z\,h_1\,)$	-0.22143208	-0.22142793	-0.22142658		
$(x\,z\,;x\,h_1\,)$	-0.01062253	-0.01062202	-0.01062207		
$(z\,z\,;z\,h_1\,)$	-0.25503541	-0.25502346	-0.25502024		

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VI. Conclusion

Using the integral transform technique, we have derived explicit expressions for one-electron three-center nuclear attraction molecular integrals coupling the n=2 atomic Slater orbitals which are listed in Appendix A. Using Eq. (20) and similar expressions given in Appendix A, we can write the expressions for two-electron four-center Coulomb repulsion integrals, which are considered among the most difficult molecular integrals to evaluate. It is neither necessary nor feasible to list all the expressions; however, we give in Appendix B, a representative set. These expressions contain well behaved and well known special functions to which numerical procedures can be easily applied. Although the development is parallel to what was reported earlier,[1],[2] the recognition of the modified Bessel functions in the integrand and the gradient operators introduced allow us to write directly the integral expression coupling any arbitrary orbitals in a much more compact form. As pointed out earlier, the merit of this approach lies in the fact that the complicated geometrical nature of a multi-center integral is properly handled by means of the vectorial relations and is manifested in the integrand through the argument of special functions in a natural way. Therefore, it may have better numerical behavior than most aforementioned methods. For a small set of molecular integrals, we have encountered no numerical difficulties as clearly borne out by our numerical example. However, a more thorough investigation will be conducted in the future. By means of a simple symmetry

argument, the number of independent integral expressions can be greatly reduced. We also have shown the asymptotic behavior of the integral with respect to the internuclear distance and expect no numerical difficulties if provisions are properly taken to treat the collapsed center case. With perseverance, other integral expressions involving either higher orbitals or other operators can be equally well deduced. Despite the fact that this method cannot be easily generalized, i.e., explicit expressions have to be developed for each particular integral, this method, nevertheless, offers indeed a simple and compact solution to this notoriously difficult molecular problem. With further refinement and efficient numerical procedures, we believe this approach will make a contribution to the field of molecular calculation. We also point out that this formulation is quite suitable for a small computer, as was demonstrated in our numerical example. A typical run of a set of integrals on a IBM PC AT is of the order of a few minutes.

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Appendix A

Three-center nuclear attraction integrals

We list only the integrands with the argument of the functions omitted wherever possible. The full expression should be interpreted in the following sense, for example:

$$L_4 = <2p_0 \, A \, \frac{1}{r_C} \, 1sB>$$

$$= 2/\sqrt{\pi} \; \xi_A \xi_B C_2 \, (\xi_A) C_1 \, (\xi_B) \int_0^\infty \int_0^1 \; [-j_1 \, (q\omega) \, \kappa_3 \, (\lambda R_{AB}) \, R_{AB}^4 \, u^2 \, (1-u)^2 \, q$$

$$Y_{1,0} \, (\hat{\omega})/\lambda^3 \; + j_0 \, (q\omega) \, \kappa_2 \, (\lambda R_{AB}) \, R_{AB}^4 \, u^2 \, (1-u) \, Y_{1,0} \, (\hat{R}_{AB}) /\lambda^2 \;] \, du \, dq$$

We further substitute $q = \tan(v)$ to use v as an integration variable with the limit from 0 to $\pi/2$. In the above equation, we have

$$\omega = u R_{AB} - R_{AC}, \quad R_{AB} = R_B - R_A, \quad R_{AC} = R_C - R_A$$

and λ is the positive root of $\lambda^2 = u(1-u)q^2 + u\xi_A^2 + (1-u)\xi_B^2$

$$C_n(\xi) = (2\xi)^{(2n+1)/2} \sqrt{(2n)!}$$

$$L_1 = <1sA \, \frac{1}{r_C} \, 1sB> = \xi_A \xi_B C_1 \, (\xi_A) C_1 \, (\xi_B) u(1-u) j_0 \, R_{AB}^3 \kappa_2 \, /\lambda^2 \, /\pi \tag{A1}$$

$$L_2 = <2sA \, \frac{1}{r_C} \, 1sB> = \xi_B \, C_2 \, (\xi_A) C_1 \, (\xi_B) j_0 \, [\, R_{AB}^4 u^2 \, (1-u)^2 \xi_A \kappa_3 \, /\lambda^3 \, -R_{AB}^3 u(1-u)\kappa_2 \, /\lambda^2 \,]/\pi$$

$$\tag{A2}$$

$$L_3 = <2sA \frac{1}{r_C} 2sB> = C_2(\xi_A)C_2(\xi_B)j_0 [R_{AB}^5 u^2 (1-u)^2 \xi_A^2 \xi_B^2 \kappa_4/\lambda^4 - R_{AB}^3 \kappa_3/\lambda^3$$

$$(u\xi_A^2 + (1-u)\xi_B^2)u(1-u) + R_{AB}^3 u(1-u)\kappa_2/\lambda^2]/\pi \tag{A3}$$

$$L_4 = <2p_0 A \frac{1}{r_C} 1sB> = 2/\sqrt{\pi}\xi_A\xi_B C_2(\xi_A)C_1(\xi_B)R_{AB}^4 u^2(1-u)[-j_1\kappa_3(1-u)q$$

$$Y_{1,0}(\hat{\omega})/\lambda^3 + j_0\kappa_2 Y_{1,0}(\hat{R}_{AB})/\lambda^2] \tag{A4}$$

$$L_5 = <2p_{\pm 1} A \frac{1}{r_C} 1sB> = 2/\sqrt{\pi}\xi_A\xi_B C_2(\xi_A)C_1(\xi_B)u^2(1-u)R_{AB}^4[-j_1\kappa_3(1-u)q$$

$$Y_{1,\pm 1}^*(\hat{\omega})/\lambda^3 + j_0\kappa_2 Y_{1,\pm 1}^*(\hat{R}_{AB})/\lambda^2] \tag{A5}$$

$$L_6 = <2p_0 A \frac{1}{r_C} 2sB> = 2/\sqrt{\pi}C_2(\xi_A)C_2(\xi_B)\xi_A[-R_{AB}^5 u^2(1-u)^3 \kappa_4 q j_1 \xi_B^2 Y_{1,0}(\hat{\omega})/\lambda^4$$

$$+R_{AB}^5 j_0\kappa_3 u^2(1-u)^2 \xi_B^2 Y_{1,0}(\hat{R}_{AB})/\lambda^3 + u^2(1-u)^2\kappa_3 R_{AB}^4 j_1 q$$

$$Y_{1,0}(\omega)/\lambda^3 - u^2(1-u)\kappa_2 R_{AB}^4 Y_{1,0}(\hat{R}_{AB})j_0/\lambda^2] \tag{A6}$$

$$L_7 = <2p_{\pm 1} A \frac{1}{r_C} 2sB> = 2/\sqrt{\pi}C_2(\xi_A)C_2(\xi_B)\xi_A[-R_{AB}^5 u^2(1-u)^3 \kappa_4 q j_1 \xi_B^2 Y_{1,\pm 1}^*(\hat{\omega})/\lambda^4$$

$$+R_{AB}^5 j_0\kappa_3 u^2(1-u)^2 \xi_B^2 Y_{1,\pm 1}^*(\hat{R}_{AB})/\lambda^3 + u^2(1-u)^2\kappa_3 R_{AB}^4 j_1 q$$

$$Y_{1,\pm 1}^*(\hat{\omega})/\lambda^3 - u^2(1-u)\kappa_2 R_{AB}^4 Y_{1,\pm 1}^*(\hat{R}_{AB})j_0/\lambda^2] \tag{A7}$$

$$L_8 = <2p_0 A \frac{1}{r_C} 2p_0 B> = 4\xi_A\xi_B C_2(\xi_A)C_2(\xi_B)[\kappa_4^2 q^2 R_{AB}^5 u^3(1-u)^3/\lambda^4 \{j_2(1/5\pi)^{1/2}$$

$$Y_{2,0}(\hat{\omega})-j_0/4\pi \}-j_1\kappa_3 R_{AB}^5 q u^2(1-u)^2(2u-1)Y_{1,0}(\hat{R}_{AB})Y_{1,0}(\hat{\omega})$$

$$/\lambda^3 + 3j_0\kappa_3^4 R_{AB}^4 u^2(1-u)^2/\lambda^3 /4\pi$$

$$-j_0 \kappa_2 R_{AB}^5 u^2 (1-u)^2 Y_{1,0}(\hat{R}_{AB}) Y_{1,0}(\hat{R}_{AB})/\lambda^2] \tag{A8}$$

$$L_9 = <2p_0 A \frac{1}{r_C} 2p_{\pm 1} B> = 4\xi_A \xi_B C_2(\xi_A) C_2(\xi_B)[q^2 \kappa_4 R_{AB}^5 u^3 (1-u)^3 /\lambda^4 (3/20\pi)^{1/2} j_2$$

$$Y_{2,\pm 1}(\hat{\omega}) - j_1 \kappa_3 R_{AB}^5 q u^2 (1-u)^2 \{u Y_{1,0}(\hat{R}_{AB}) Y_{1,\pm 1}(\hat{\omega}) -$$

$$(1-u) Y_{1,0}(\hat{\omega}) Y_{1,\pm 1}(\hat{R}_{AB})\}/\lambda^3 \tag{A9}$$

$$-j_0 \kappa_2 R_{AB}^5 u^2 (1-u)^2 Y_{1,0}^*(\hat{R}_{AB}) Y_{1,\pm 1}(\hat{R}_{AB})/\lambda^2]$$

$$L_{10} = <2p_{\pm 1} A \frac{1}{r_C} 2p_{\pm 1} B> = 4\xi_A \xi_B C_2(\xi_A) C_2(\xi_B)[\kappa_4 R_{AB}^5 q^2 u^3 (1-u)^3 /\lambda^4$$

$$(-j_0 /4\pi - (1/20\pi)^{1/2} j_2 Y_{2,0}(\hat{\omega})) \tag{A10}$$

$$+j_1 \kappa_3 R_{AB}^5 q u^2 (1-u)^2 \{(1-u) Y_{1,\pm 1}(\hat{R}_{AB}) Y_{1,\pm 1}^*(\hat{\omega})$$

$$-u Y_{1,\pm 1}(\hat{\omega}) Y_{1,\pm 1}^*(\hat{R}_{AB})\}/\lambda^3 -j_0 R_{AB}^5 u^2 (1-u)^2 \kappa_2$$

$$Y_{1,\pm 1}^*(\hat{R}_{AB}) Y_{1,\pm 1}(\hat{R}_{AB})/\lambda^2 +3j_0 \kappa_4 R_{AB}^4 u^2 (1-u)^2 /\lambda^3 /4\pi]$$

Appendix B

Four-center two-electron repulsion integrals

We list only the integrands and suppress the argument of the functions wherever possible. The full expression should be interpreted in the following sense, for example:

$$M_{10} = <2p_{\pm1} \, A \, 1sB \, \frac{1}{r_{12}} \, 2sC \, 1sD>$$

$$= \xi_A \xi_B C_2(\xi_A) C_1(\xi_B) C_1(\xi_C) C_1(\xi_D)/\sqrt{\pi} \int_0^\infty \int_0^1 \int_0^1 \, [-j_1(q\omega) \, \kappa_3 \, (\lambda R_{AB}) \, R_{AB}^4$$

$$u^2(1-u)^2 \, q \, Y_{1,\pm1}^*(\hat{\omega})/\lambda^3 + j_0(q\omega) \, \kappa_2 \, (\lambda R_{AB}) \, R_{AB}^4 \, u^2(1-u)Y_{1,\pm1}^*(\hat{R}_{AB})/\lambda^2 \,]$$

$$[R_{CD}^4 \, \kappa_3' \, (\lambda' R_{CD}) u'^2(1-u')\xi_C \xi_D/\lambda'^3 - R_{CD}^3 \, \kappa_2' \, (\lambda' R_{CD}) u'(1-u')\xi_D/\lambda'^2 \,] \, du \, du' \, dq$$

We further substitute $q = \tan(v)$ to use v as an integration variable with the limits from 0 to $\pi/2$. In the above equation, we have

$$\omega = R_{AC} - uR_{AB} + u'R_{CD}, \quad R_{AB} = R_B - R_A, \quad R_{AC} = R_C - R_A, \quad R_{CD} = R_D - R_C$$

$$\lambda^2 = u(1-u)q^2 + u\xi_A^2 + (1-u)\xi_B^2, \quad \lambda'^2 = u'(1-u')q^2 + u'\xi_C^2 + (1-u)\xi_D^2$$

$$C_n(\xi) = (2\xi)^{(2n+1)/2}\sqrt{(2n)!}$$

$$M_1 = <1sA \, 1sB \, \frac{1}{r_{12}} \, 1sC \, 1sD> = C_1(\xi_A) C_1(\xi_B) C_1(\xi_C) C_1(\xi_D)\xi_A \xi_B \xi_C \xi_D \, j_0 \, /(2\pi)$$

$$u(1-u)\kappa_2 \, /\lambda^2 \, R_{AB}^3 \, u'(1-u')\kappa_2' \, R_{CD}^3 \, /\lambda'^2 \tag{B1}$$

$$M_2 = <2sA \, 1sB \, \frac{1}{r_{12}} \, 1sC \, 1sD> = C_2(\xi_A) C_1(\xi_B) C_1(\xi_C) C_1(\xi_D) \, j_0 \, /(2\pi)$$

$$[R_{AB}^4 \, \kappa_3 \, u^2(1-u)^2\xi_A \xi_B/\lambda^3 - R_{AB}^3 \, \kappa_2 \, u(1-u)\xi_B/\lambda^2 \,][u'(1-u')\xi_C \xi_D \, \kappa_2' \, R_{CD}^3 \, /\lambda'^2 \,] \tag{B2}$$

$$M_3 = <2sA\ 1sB\ \frac{1}{r_{12}}\ 2sC\ 1sD> = C_2\ (\xi_A)C_1\ (\xi_B)C_2\ (\xi_C)C_1\ (\xi_D)\ j_o\ /(2\pi)$$

$$[R_{AB}\kappa_3\ u^4\ (1-u)\xi_A^2\xi_B^2/\lambda^3\ -R_{AB}\kappa_2\ u(1-u)\xi_B^3/\lambda^3\ ]$$

$$[R_{CD}\kappa_3'\ u'^4\ (1-u')\xi_C^2\xi_D^2/\lambda'^3\ -R_{CD}\kappa_2'\ u'(1-u')\xi_D^3/\lambda'^3\ ] \tag{B3}$$

$$M_4 = <2sA\ 2sB\ \frac{1}{r_{12}}\ 1sC\ 1sD> = C_2\ (\xi_A)C_2\ (\xi_B)C_1\ (\xi_C)C_1\ (\xi_D)\ j_o\ /(2\pi)$$

$$[R_{AB}\kappa_4\ u^5\ (1-u)^2\ \xi_A^2\xi_B^2/\lambda^4\ -R_{AB}\kappa_3\ (u\xi_A^2+(1-u)\xi_B^2)$$

$$u(1-u)/\lambda^3\ +R_{AB}u(1-u)\kappa_2\ /\lambda^3\ ][u'(1-u')\xi_C^3\xi_D\ \kappa_2'\ R_{CD}/\lambda'^2\ ] \tag{B4}$$

$$M_5 = <2sA\ 2sB\ \frac{1}{r_{12}}\ 2sC\ 1sD> = C_2\ (\xi_A)C_2\ (\xi_B)C_2\ (\xi_C)C_1\ (\xi_D)\ j_o\ /(2\pi)$$

$$[R_{AB}\kappa_4\ u^5\ (1-u)^2\ \xi_A^2\xi_B^2/\lambda^4\ -R_{AB}\kappa_3\ (u\xi_A^2+(1-u)\xi_B^2)u(1-u)/\lambda^3\ +R_{AB}u(1-u)\kappa_2\ /\lambda^2\ ]$$

$$[R_{CD}\kappa_3'\ u'^4\ (1-u')\xi_C^2\xi_D/\lambda'^3\ -R_{CD}\kappa_2'\ u'(1-u')\xi_D^3/\lambda'^3\ ] \tag{B5}$$

$$M_6 = <2sA\ 2sB\ \frac{1}{r_{12}}\ 2sC\ 2sD> = C_2\ (\xi_A)C_2\ (\xi_B)C_2\ (\xi_C)C_2\ (\xi_D)\ j_o\ /(2\pi)$$

$$[R_{AB}\kappa_4\ u^5\ (1-u)^2\ \xi_A^2\xi_B^2/\lambda^4\ -R_{AB}\kappa_3\ (u\xi_A^2+(1-u)\xi_B^2)u(1-u)/\lambda^3\ +R_{AB}u(1-u)\kappa_2\ /\lambda^2\ ]$$

$$[R_{CD}\kappa_4'\ u'^5\ (1-u')^2\ \xi_C^2\xi_D^2/\lambda'^4\ -R_{CD}\kappa_3'\ (u'\xi_C^2+(1-u')\xi_D^2)$$

$$u'(1-u')/\lambda'^3\ +R_{CD}u'(1-u')\kappa_2'\ /\lambda'^2\ ] \tag{B6}$$

$$M_7 = <2p_0\ A\ 1sB\ \frac{1}{r_{12}}\ 1sC\ 1sD> = C_2\ (\xi_A)C_1\ (\xi_B)C_1\ (\xi_C)C_1\ (\xi_D)\xi_A\xi_B\xi_C\xi_D/\sqrt{\pi}$$

$$[\kappa_3\ qR_{AB}j_1\ u^4\ (1-u)^2\ Y_{1\ o}\ (\hat{\omega})/\lambda^3\ +j_o\ \kappa_2\ R_{AB}u^2\ (1-u)Y_{1\ o}\ (\hat{R}_{AB})/\lambda^2\ ][u'(1-u')\kappa_2'\ R_{CD}/\lambda'^2\ ]$$

$$\tag{B7}$$

$$M_8 = <2p_{\pm1}\ A\ 1sB\ \frac{1}{r_{12}}\ 1sC\ 1sD> = C_2\ (\xi_A)C_1\ (\xi_B)C_1\ (\xi_C)C_1\ (\xi_D)\xi_A\xi_B\xi_C\xi_D/\sqrt{\pi}$$

$$[\kappa_3 \, qR_{AB}^4 j_1 \, u^2 (1-u)^2 \, Y_{1 \, \pm 1}^* (\hat{\omega})/\lambda^3 + j_0 \, \kappa_2 \, R_{AB}^4 u^2 (1-u) Y_{1 \, \pm 1}^* (\hat{R}_{AB})/\lambda^2][u'(1-$$

$$u')\kappa_2' \, R_{CD}^3/\lambda'^2] \tag{B8}$$

$$M_9 = <2p_0 \, A \, 1sB \frac{1}{r_{12}} \, 2sC \, 1sD> = C_2 \, (\xi_A)C_1 \, (\xi_B)C_2 \, (\xi_C)C_1 \, (\xi_D)\xi_A \xi_B /\sqrt{\pi}$$

$$[\kappa_3 \, qR_{AB}^4 j_1 \, u^2 (1-u)^2 \, Y_{1 \, 0} (\hat{\omega})/\lambda^3 + j_0 \, \kappa_2 \, R_{AB}^4 u^2 (1-u) Y_{1 \, 0} (\hat{R}_{AB})/\lambda^2] \tag{B9}$$

$$[R_{CD}^4 \kappa_3' \, u'^2 (1-u')\xi_C \xi_D/\lambda'^3 - R_{CD}^3 \kappa_2' \, u'(1-u')\xi_D/\lambda'^2]$$

$$M_{10} = <2p_{\pm 1} \, A \, 1sB \frac{1}{r_{12}} \, 2sC \, 1sD> = C_2 \, (\xi_A)C_1 \, (\xi_B)C_1 \, (\xi_C)C_1 \, (\xi_D)\xi_A \xi_B /\sqrt{\pi}$$

$$[\kappa_3 \, qR_{AB}^4 j_1 \, u^2 (1-u)^2 \, Y_{1 \, \pm 1}^* (\hat{\omega})/\lambda^3 + j_0 \, \kappa_2 \, R_{AB}^4 u^2 (1-u) Y_{1 \, \pm 1}^* (\hat{R}_{AB})/\lambda^2] \tag{B10}$$

$$[R_{CD}^4 \kappa_3' \, u'^2 (1-u')\xi_C \xi_D/\lambda'^3 - R_{CD}^3 \kappa_2' \, u'(1-u')\xi_D/\lambda'^2]$$

$$M_{11} = <2p_0 \, A \, 1sB \frac{1}{r_{12}} \, 2sC \, 2sD> = C_2 \, (\xi_A)C_1 \, (\xi_B)C_2 \, (\xi_C)C_2 \, (\xi_D)\xi_A \xi_B /\sqrt{\pi}$$

$$[\kappa_3 \, qR_{AB}^4 j_1 \, u^2 (1-u)^2 \, Y_{1 \, 0} (\hat{\omega})/\lambda^3 + j_0 \, \kappa_2 \, R_{AB}^4 u^2 (1-u) Y_{1 \, 0} (\hat{R}_{AB})/\lambda^2 \tag{B11}$$

$$[R_{CD}^5 \kappa_4' \, u'^2 (1-u')^2 \, \xi_C^2 \xi_D^2 /\lambda'^4 - R_{CD}^4 \kappa_3' (u'\xi_C + (1-u')\xi_D)$$

$$u'(1-u')/\lambda'^3 + R_{CD}^3 u'(1-u')\kappa_2' \, /\lambda'^2]$$

$$M_{12} = <2p_{\pm 1} \, A \, 1sB \frac{1}{r_{12}} \, 2sC \, 2sD> = C_2 \, (\xi_A)C_1 \, (\xi_B)C_2 \, (\xi_C)C_2 \, (\xi_D)\xi_A \xi_B /\sqrt{\pi}$$

$$[\kappa_3 \, qR_{AB}^4 j_1 \, u^2 (1-u)^2 \, Y_{1 \, \pm 1}^* (\hat{\omega})/\lambda^3 + j_0 \, \kappa_2 \, R_{AB}^4 u^2 (1-u) Y_{1 \, \pm 1}^* (\hat{R}_{AB})/\lambda^2] \tag{B12}$$

$$[R_{CD}^5 \kappa_4' \, u'^2 (1-u')^2 \, \xi_C^2 \xi_D^2 /\lambda'^4 - R_{CD}^4 \kappa_3' (u'\xi_C + (1-u')\xi_D)$$

$$u'(1-u')/\lambda'^3 + R_{CD}^3 u'(1-u')\kappa_2' \, /\lambda'^2]$$

$$M_{13} = <2p_0 \, A \, 2p_0 \, B \frac{1}{r_{12}} \, 1sC \, 1sD> = 2\xi_A' \xi_B \xi_C \xi_D C_2 \, (\xi_A)C_2 \, (\xi_B)C_1 \, (\xi_C)C_1 \, (\xi_D)$$

$$[\kappa_4 \, R_{AB}^5 q^2 u^3 (1-u)^3 /\lambda^4 \{j_2 \, (1/5\pi)^{1/2} \, Y_{2 \, 0} (\hat{\omega}) - j_0 \, /4\pi\}$$

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$$+j_1 \kappa_3 R_{AB}^5 q^2 u^2 (1-u)^2 (uY_{1,o}(\hat{R}_{AB})Y_{1,o}(\hat{\omega})$$

$$-(1-u)Y_{1,o}(\hat{\omega})Y_{1,o}(\hat{R}_{AB}))/\lambda^3 +3j_0 \kappa_3 R_{AB}^4 u^2 (1-u)^3/\lambda^2 /4\pi \qquad (B13)$$

$$-j_0 \kappa_2 R_{AB}^5 u^2 (1-u)^2 Y_{1,o}(\hat{R}_{AB}))Y_{1,o}(\hat{R}_{AB})/\lambda^2] u'(1-u')\kappa_2' R_{CD}^3/\lambda'^2$$

$$M_{1,4} = <2p_o A 2p_{\pm'} \frac{1}{r_{1,2}} 1sC 2sD> = 2\xi_A \xi_B C_2 (\xi_A)C_2 (\xi_B)C_1 (\xi_C)C_2 (\xi_D)$$

$$[q^2 \kappa_4 R_{AB}^5 u^3 (1-u)^3/\lambda^4 j_2 (3/20\pi)^{1/2} Y_{2,\pm'}(\hat{\omega})+$$

$$j_1 \kappa_3 R_{AB}^5 q u^2 (1-u)^2 (uY_{1,o}(\hat{R}_{AB})Y_{1,\pm'}(\hat{\omega})-(1-u)Y_{1,o}(\hat{\omega})Y_{1,\pm'}(\hat{R}_{AB}))/\lambda^3$$

$$-j_0 \kappa_2 R_{AB}^5 u^2 (1-u)^2 Y_{1,o}(\hat{R}_{AB})Y_{1,o}(\hat{R}_{AB})/\lambda^3]$$

$$[R_{CD}^4 \kappa_3' u'^2 (1-u')^2 \xi_C \xi_D/\lambda'^3 -R_{CD}^3 \kappa_2' u'(1-u')\xi_D/\lambda'^2] \qquad (B14)$$

$$M_{1,5} = <2p_{\pm'} A 2p_{\pm'} B \frac{1}{r_{1,2}} 2sC 2sD> = 2\xi_A \xi_B C_2 (\xi_A)C_2 (\xi_B)C_2 (\xi_C)C_2 (\xi_D)$$

$$[\kappa_4 R_{AB}^5 q^2 u^3 (1-u)^3/\lambda^4 (j_0 /4\pi+(1/20\pi)^{1/2} j_2 Y_{2,o}(\hat{\omega}))$$

$$-j_1 \kappa_3 R_{AB}^5 q u^2 (1-u)^2 \{(1-u)Y_{1,\pm'}(\hat{R}_{AB})Y_{1,\pm'}^*(\hat{\omega})$$

$$-u Y_{1,\pm'}(\hat{\omega})Y_{1,\pm'}^*(\hat{R}_{AB})\}/\lambda^3 -j_0 R_{AB}^5 u^2 (1-u)^2 \kappa_2$$

$$Y_{1,\pm'}^*(\hat{R}_{AB})Y_{1,\pm'}(\hat{R}_{AB})/\lambda^3 +3j_0 \kappa_3 R_{AB}^4 u^2 (1-u)^3/\lambda^2 /4\pi]$$

$$[R_{CD}^5 \kappa_4' u'^2 (1-u')^2 \xi_C^2 \xi_D^2 /\lambda'^4 -R_{CD}^4 \kappa_3' (u'\xi_C^2+(1-u')\xi_D^2)$$

$$u'(1-u')/\lambda'^3 +R_{CD}^3 u'(1-u')\kappa_2' /\lambda'^2] \qquad (B15)$$

$$M_{1,6} = <2p_o A 2p_o B \frac{1}{r_{1,2}} 2p_o C 1sD> =4\xi_A \xi_B \xi_C \xi_D C_2 (\xi_A)C_2 (\xi_B)C_2 (\xi_C)C_1 (\xi_D)\sqrt{\pi}$$

$$[\kappa_3' R_{CD}^4/\lambda'^3 u'^2 (1-u')^2 \{-\kappa_4 R_{AB}^5/\lambda^4 u^3 (1-u)^3 q^3 \{(27/28)^{1/2} (1/5\pi) j_3 Y_{3,o}(\hat{\omega})$$

$$-(9/20\pi)j_1 Y_{1,o}(\hat{\omega})\}+\kappa_3 R_{AB}^5/\lambda^3 q^2 u^2 (1-u)^2 (2u-1)\{j_0 /4\pi-(1/5\pi)^{1/2} j_2 Y_{2,o}(\hat{\omega})\}$$

$$Y_{1\,0}(\hat{R}_{AB}) + q\,j_1\,Y_{1\,0}(\hat{\omega})u^2(1-u)^2\{\kappa_2\,R_{AB}^5/\lambda^2\,Y_{1\,0}(\hat{R}_{AB})Y_{1\,0}(\hat{R}_{AB}) - 3\kappa_3\,R_{AB}^4/\lambda^3\,/4\pi\}\}$$

$$-\kappa_2'\,R_{CD}^4/\lambda'^2\,u'^2(1-u')Y_{1\,0}(\hat{R}_{CD})\{\kappa_4\,R_{AB}^5/\lambda^3\,u^3(1-u)^2\,q\,\{j_0\,/4\pi - j_2\,Y_{2\,0}(\hat{\omega})$$

$$(1/5\pi)^{1/2}\} - \kappa_3\,R_{AB}^5/\lambda^3\,q\,u^2(1-u)^2(2u-1)j_1\,Y_{1\,0}(\hat{R}_{AB})Y_{1\,0}(\hat{\omega}) + \{\kappa_2\,R_{AB}^5/\lambda^2\,Y_{1\,0}(\hat{R}_{AB})$$

$$Y_{1\,0}(\hat{R}_{AB}) - 3\kappa_3\,R_{AB}^4/\lambda^3\,/4\pi\}u^2(1-u)^2\,j_0\,\}] \tag{B16}$$

$$M_{1\,7} = \langle 2p_{\pm1}\,A\,2p_{\pm1}\,B\,\frac{1}{r_{12}}\,2p_{\pm1}\,C\,1sD\rangle = 4\xi_A\xi_B\xi_C\xi_D C_2(\xi_A)C_2(\xi_B)C_2(\xi_C)C_1(\xi_D)\sqrt{\pi}$$

$$[\kappa_2'\,R_{CD}^4/\lambda'^3\,u'^2(1-u')\,\{-\kappa_4\,R_{AB}^5/\lambda^4\,u^3(1-u)^3\,q^3\,\{-(3/20\pi)(2/7)^{1/2}\,j_3$$

$$Y_{3\,\pm1}^*(\hat{\omega}) - 3/10\pi\,j_1\,Y_{1\,\pm1}^*(\hat{\omega})\} + \kappa_3\,R_{AB}^5/\lambda^3\,q^2u^2(1-u)^2\{uY_{1\,\pm1}^*(\hat{R}_{AB})$$

$$(j_2\,Y_{2\,0}(\hat{\omega})(1/20\pi)^{1/2} + j_0\,/4\pi) + (1-u)j_2\,(3/20\pi)^{1/2}\,Y_{2\,\pm2}^*(\hat{\omega})Y_{1\,\pm1}(\hat{R}_{AB})\}$$

$$-q\,j_1\,Y_{1\,\pm1}^*(\hat{\omega})u^2(1-u)^2\{\kappa_2\,R_{AB}^5/\lambda^2\,Y_{1\,\pm1}(\hat{R}_{AB})Y_{1\,\pm1}^*(\hat{R}_{AB}) - 3\kappa_3\,R_{AB}^4/\lambda^3\,/4\pi\}$$

$$-\kappa_2'\,R_{CD}^4/\lambda'^2\,u'^2(1-u')Y_{1\,\pm1}^*(\hat{R}_{CD})\{\kappa_4\,R_{AB}^5/\lambda^3\,u^3(1-u)^2\,q\,\{j_0\,/4\pi + j_2\,Y_{2\,0}(\hat{\omega})$$

$$(1/20\pi)^{1/2}\} - \kappa_3\,R_{AB}^5/\lambda^3\,q\,u^2(1-u)^2\,(uY_{1\,\pm1}^*(\hat{R}_{AB})Y_{1\,\pm1}(\hat{\omega}) + (1-u)Y_{1\,\pm1}^*(\hat{\omega})Y_{1\,\pm1}(\hat{R}_{AB})$$

$$+\{\kappa_2\,R_{AB}^5/\lambda^2\,Y_{1\,\pm1}^*(\hat{R}_{AB})Y_{1\,\pm1}(\hat{R}_{AB}) - 3\kappa_3\,R_{AB}^4/\lambda^3\,/4\pi\}j_0\,u^2(1-u)^2\}] \tag{B17}$$

$$M_{1\,8} = \langle 2p_0\,A\,2p_0\,B\,\frac{1}{r_{12}}\,2p_0\,C\,2p_0\,D\rangle = 8\xi_A\xi_B\xi_C\xi_D C_2(\xi_A)C_2(\xi_B)C_2(\xi_C)C_2(\xi_D)\pi$$

$$\{\kappa_4'\,R_{CD}^5/\lambda'^4\,u'^3(1-u')^3\,[\kappa_4\,R_{AB}^5/\lambda^4\,u^3(1-u)^3\,q^4\,\{(3/35\pi)(1/\pi)^{1/2}\,Y_{4\,0}(\hat{\omega})j_4$$

$$-(9/14\pi)(1/5\pi)^{1/2}\,j_2\,Y_{2\,0}(\hat{\omega}) + (9/80\pi^2)j_0\,\} + \kappa_3\,R_{AB}^5/\lambda^3\,u^3(1-u)^3$$

$$q^3\,Y_{1\,0}(\hat{R}_{AB})(2u-1)\{(1/5\pi)(27/28)^{1/2}\,j_3\,Y_{3\,0}(\hat{\omega}) - (9/20\pi)j_1\,Y_{1\,0}(\hat{\omega})\} +$$

$$q^2\,\{\kappa_2\,R_{AB}^5/\lambda^2\,Y_{1\,0}(\hat{R}_{AB})Y_{1\,0}(\hat{R}_{AB}) - 3\kappa_3\,R_{AB}^4/\lambda^3\,/4\pi\}u^2(1-u)^2$$

$$\{j_0\,/4\pi - (1/5\pi)^{1/2}\,j_2\,Y_{2\,0}(\hat{\omega})\}\,]$$

$$-\kappa_3' R_{CD}^5/\lambda'^3 u'^2 (1-u')^2 [\kappa_4 R_{AB}^5/\lambda^4 u^3 (1-u)^3 \{(2u'-1)Y_{1\,0}(\hat{R}_{AB})\{(1/5\pi)$$

$$(27/28)^{1/2} Y_{3\,0}(\hat{\omega})j_3 -(9/20\pi)Y_{1\,0}(\hat{\omega})j_1 \}\}+\kappa_3 R_{AB}^5/\lambda^3 u^2 (1-u)^2 q\; Y_{1\,0}(\hat{R}_{AB})$$

$$Y_{1\,0}(\hat{R}_{CD})(2u-1)(2u'-1)(j_0/4\pi -(1/5\pi)^{1/2} Y_{2\,0} j_0)+(\kappa_2 R_{AB}^5/\lambda^2 Y_{1\,0}(\hat{R}_{AB})$$

$$Y_{1\,0}(\hat{R}_{AB})-3\kappa_3 R_{AB}^4/\lambda^3 /4\pi)u^2 (1-u)^2 q(2u'-1)j_1 Y_{1\,0}(\hat{\omega})Y_{1\,0}(\hat{R}_{CD})]$$

$$+u'^2 (1-u')^2 \{\kappa_2' R_{CD}^5/\lambda'^2 Y_{1\,0}(\hat{R}_{CD})Y_{1\,0}(\hat{R}_{CD})-3\kappa_3' R_{CD}^4/\lambda'^3 /4\pi\}[\kappa_4 R_{AB}^4/\lambda^4$$

$$u^3 (1-u)^3 q^2 \{j_0/4\pi -(1/5\pi)^{1/2} j_2 Y_{2\,0}(\hat{\omega})\} - \kappa_3 R_{AB}^5/\lambda^3 u^2 (1-u)^2 q(2u-1)$$

$$Y_{1\,0}(\hat{R}_{AB})Y_{1\,0}(\hat{\omega})j_1 +\{\kappa_2 R_{AB}^5/\lambda^2 Y_{1\,0}(\hat{R}_{AB})Y_{1\,0}(\hat{R}_{AB})-3\kappa_3 R_{AB}^4/\lambda^3 /4\pi\}\}\} \qquad \text{(B18)}$$

$$M_{1\,9} = <2p_{\pm 1} A\; 2p_{\pm 1} B\; \frac{1}{r_{1\,2}}\; 2p_{\pm 1} C\; 2p_{\pm 1} D> =8\xi_A\xi_B\xi_C\xi_D C_2(\xi_A)C_2(\xi_B)C_2(\xi_C)C_2(\xi_D)\pi$$

$$\{\kappa_4' R_{CD}^5/\lambda'^4 u'^3 (1-u')^3 [\kappa_4 R_{AB}^5/\lambda^4 u^3 (1-u)^3 q^4 \{(3/140\pi)(1/\pi)^{1/2} Y_{4\,0}(\hat{\omega})j_4$$

$$+(3/14\pi)(1/5\pi)^{1/2} j_2 Y_{2\,0}(\hat{\omega})+3j_0/(40\pi^2)\} -\kappa_3 R_{AB}^5/\lambda^3 u^2 (1-u)^2$$

$$q^3 \{(1-u)Y_{1\,\pm 1}(\hat{R}_{AB})\{-(3/20\pi)(2/7)^{1/2} j_3 Y^*_{3\,\pm 1}(\hat{\omega})-(3/10\pi)j_1 Y^*_{1\,\pm 1}(\hat{\omega})\} -$$

$$uY^*_{1\,\pm 1}(\hat{R}_{AB})\{-(3/20\pi)(2/7)^{1/2} j_3 Y_{3\,\pm 1}(\hat{\omega})-(3/10\pi)j_1 Y_{1\,\pm 1}(\hat{\omega})\} +$$

$$q^2 \{(1/20\pi)^{1/2} j_2 Y_{2\,0}(\hat{\omega})+j_0/4\pi\}\{\kappa_2 R_{AB}^5/\lambda^2 Y^*_{1\,\pm 1}(\hat{R}_{AB})Y_{1\,\pm 1}(\hat{R}_{AB})-3\kappa_3 R_{AB}^4/\lambda^3 /4\pi\}]$$

$$+\kappa_3' R_{CD}^5/\lambda'^3 u'^2 (1-u')^2 [\kappa_4 R_{AB}^5/\lambda^4 u^3 (1-u)^3 q^2 (-(1-u')Y_{1\,\pm 1}(\hat{R}_{CD})$$

$$\{(3/20\pi)(2/7)^{1/2} Y^*_{3\,\pm 1}(\hat{\omega})j_3 +(3/10\pi)Y^*_{1\,\pm 1}(\hat{\omega})j_1 \}+u'Y^*_{1\,\pm 1}(\hat{R}_{CD})$$

$$\{(3/10\pi)Y_{1\,\pm 1}(\hat{\omega})j_1 +(3/20\pi)(2/7)^{1/2} Y_{3\,\pm 1}(\hat{\omega})j_3 \})-\{\kappa_2 R_{AB}^5/\lambda^2$$

$$Y^*_{1\,\pm 1}(\hat{R}_{AB})Y_{1\,\pm 1}(\hat{R}_{AB})-3\kappa_3 R_{AB}^4/\lambda^3 /(4\pi)\}u^2 (1-u)^2 j_1 \{Y_{1\,\pm 1}(\hat{R}_{CD})Y^*_{1\,\pm 1}(\hat{\omega})$$

$$(1-u')-Y_{1\,\pm 1}(\hat{\omega})Y^*_{1\,\pm 1}(\hat{R}_{CD})u'\}+\kappa_3 R^5/\lambda^3 q^2 \{-(1-u)(1-u')Y_{1\,\pm 1}(\hat{R}_{AB})Y_{1\,\pm 1}(\hat{R}_{CD})$$

$$(3/10\pi)^{1/2} j_2 Y^*_{2\,\pm 2}(\hat{\omega})-\{u'(1-u)Y_{1\,\pm 1}(\hat{R}_{AB})Y^*_{1\,\pm 1}(\hat{R}_{CD})$$

$$+u(1-u')Y^*_{1\pm1}(\hat{R}_{AB})Y_{1\pm1}(\hat{R}_{CD})\}(j_0/4\pi +(1/20\pi)^{1/2}Y_{20}(\hat{\omega})j_2)$$

$$-uu'Y^*_{1\pm1}(\hat{R}_{AB})Y^*_{1\pm1}(\hat{R}_{CD})(3/10\pi)^{1/2}Y_{2\pm2}(\hat{\omega})j_2\ ] +\{\kappa_2 R^5_{CD}/\lambda^2$$

$$Y^*_{1\pm1}(\hat{R}_{CD})Y_{1\pm1}(\hat{R}_{CD})-3\kappa'_3 R^4_{CD}/\lambda'^3/(4\pi)\}u'^2(1-u')^2\ [\kappa_4 R^5_{AB}/\lambda^4\ u^3(1-u)^3$$

$$q^2(j_0/4\pi +(1/20\pi)^{1/2}Y_{20}(\hat{\omega})j_2)-\kappa_3 R^4_{AB}/\lambda^3\ q^2u^2(1-u)^2\ j_1$$

$$\{(1-u)Y_{1\pm1}(\hat{R}_{AB})Y^*_{1\pm1}(\hat{\omega})+uY_{1\pm1}(\hat{\omega})Y^*_{1\pm1}(\hat{R}_{AB})\}+j_0$$

$$\{\kappa_2 R^5_{AB}/\lambda^2\ Y^*_{1\pm1}(\hat{R}_{AB})Y_{1\pm1}(\hat{R}_{AB})-3\kappa_3 R^4_{AB}/\lambda^3/(4\pi)\}]\} \tag{B19}$$

$$M_{20}=<2p_{\pm1}A\ 2p_0 B\frac{1}{r_{12}}2sC\ 2sD>=2C_2(\xi_A)C_2(\xi_B)C_2(\xi_C)C_2(\xi_D)\xi_A\xi_B$$

$$\{q^2 j_2 (3/20\pi)^{1/2}Y^*_{2\pm1}(\hat{\omega})\kappa_4 R^5_{AB}/\lambda^4\ u^3(1-u)^3 -qj_1\ [Y^*_{1\pm1}(\hat{\omega})Y_{10}(\hat{R}_{AB})(1-u)$$

$$-uY^*_{1\pm1}(\hat{R}_{AB})Y_{10}(\hat{\omega})]u^2(1-u)^2\ \kappa_3 R^5_{AB}/\lambda^3 -\kappa_2 R^5_{AB}j_0\ u^2(1-u)^2/\lambda^2\ Y^*_{1\pm1}(\hat{R}_{AB})Y_{10}(\hat{R}_{AB})\}$$

$$[R^5_{CD}\kappa'_4 u'^2(1-u')^2\ \xi_C\xi_D/\lambda'^4 -R^4_{CD}\kappa'_3(u'\xi_C+(1-u')\xi_D)$$

$$u'(1-u')/\lambda'^3 +R^3_{CD}u'(1-u')\kappa'^2_2/\lambda'^2\ ] \tag{B20}$$

$$M_{21}=<2p_{\pm1}A\ 1sB\frac{1}{r_{12}}2p_{\pm1}C\ 1sD>=2C_2(\xi_A)C_1(\xi_B)C_2(\xi_C)C_1(\xi_D)\xi_A\xi_B\xi_C\xi_D$$

$$[\kappa'_3 R^4_{CD}u'^2(1-u')^2\ /\lambda'^3\ \{\kappa_3 R^4_{AB}/\lambda^3\ q^2u^2(1-u)^2\ (3/10\pi)^{1/2}Y^*_{2\pm2}(\hat{\omega})j_2$$

$$-qj_1\ \kappa_2 R^4_{AB}u^2(1-u)^2/\lambda^2\ Y^*_{1\pm1}(\hat{R}_{AB})Y_{1\pm1}(\hat{\omega})\}+\kappa'^2_2 R'^4_{CD}/\lambda'^3\ u'^2(1-u')\{qj_1\ \kappa_3 R^4_{AB}/\lambda^3$$

$$u^2(1-u)^2\ Y^*_{1\pm1}(\hat{R}_{AB})Y^*_{1\pm1}(\hat{\omega})+j_0\ \kappa_2 R^4_{AB}u^2(1-u)/\lambda^2\ Y^*_{1\pm1}(\hat{R}_{AB})Y^*_{1\pm1}(\hat{R}_{CD})\}] \tag{B21}$$

$$M_{22}=<2p_0A\ 1sB\frac{1}{r_{12}}2p_0C\ 1sD>=2C_2(\xi_A)C_1(\xi_B)C_2(\xi_C)C_1(\xi_D)\xi_A\xi_B\xi_C\xi_D$$

$$[\kappa'_3 R^4_{CD}u'^2(1-u')^2\ /\lambda'^3\ \{\kappa_3 R^4_{AB}/\lambda^3\ q^2u^2(1-u)^2\ (j_0/4\pi-j_2\ (1/5\pi)^{1/2}Y_{20}(\hat{\omega}))$$

$$-qj_1\ \kappa_2 R^4_{AB}u^2(1-u)/\lambda^2\ Y_{10}(\hat{R}_{AB})Y_{10}(\hat{\omega})\}+\kappa'^2_2 R'^4_{CD}/\lambda'^3\ u'^2(1-u')\{qj_1\ \kappa_3 R^4_{AB}/\lambda^3$$

$$u^2 (1-u)^2 Y_{1,0}(\hat{R}_{CD})Y_{1,0}(\hat{\omega})+j_0 \, \kappa_2 \, R_{AB} u^2 (1-u)/\lambda^2 \, Y_{1,0}(\hat{R}_{AB})Y_{1,0}(\hat{R}_{CD})\}] \tag{B22}$$

$$M_{2,3} = \langle 2p_{\pm'} A \, 2p_0 \, B \frac{1}{r_{12}} 2p_{\pm'} C \, 1sD \rangle = 8C_2(\xi_A)C_2(\xi_B)C_2(\xi_C)C_1(\xi_D)\pi$$

$$\{-\kappa_2' R_{CD}^4/\lambda'^3 \, u'^2 (1-u')^2 \, [q^3 (1/4\pi)(18/35)^{1/2} \, Y_{3,\pm2}(\hat{\omega})Y_{0,0} \, \kappa_4 \, R_{AB}^5/\lambda^4 \, u^3 (1-u)^3 \, j_3$$

$$-q^2 j_2 \, \kappa_3 \, R_{AB}^5/\lambda^3 \, u^3 (1-u)^2 \, \{(6/20\pi)^{1/2} \, Y_{2,\pm1}^*(\hat{\omega})Y_{1,0}(\hat{R}_{AB})(1-u)-u(3/20\pi)^{1/2}$$

$$Y_{1,\pm1}^*(\hat{R}_{AB})Y_{2,\pm1}^*(\hat{\omega})\} -qY_{1,\pm1}^*(\hat{\omega})Y_{0,0} \, j_1 \, \kappa_2 \, R_{AB}^5/\lambda^2 \, u^2 (1-u)^2 \, Y_{1,\pm1}^*(\hat{R}_{AB})Y_{1,0}(\hat{R}_{AB})]$$

$$-\kappa_2' R_{CD}^4/\lambda'^2 \, u'^2 (1-u')Y_{1,\pm1}^*(\hat{R}_{CD})Y_{0,0} \, [-q^2 j_2 \, \kappa_4 \, R_{AB}^5/\lambda^4 \, u^3 (1-u)^3 \, (3/20\pi)^{1/2}$$

$$Y_{2,\pm1}^*(\hat{\omega})+qj_1 \, \kappa_3 \, R_{AB}^5/\lambda^3 \, u^3 (1-u)^2 \, \{Y_{1,\pm1}^*(\hat{\omega})Y_{1,0}(\hat{R}_{AB})(1-u)-uY_{1,\pm1}^*(\hat{R}_{AB})Y_{1,0}(\hat{\omega})\}$$

$$+j_0 \, \kappa_2 \, R_{AB}^5/\lambda^2 \, u^2 (1-u)^2 \, Y_{1,\pm1}^*(\hat{R}_{AB})Y_{1,0}(\hat{R}_{AB})\} \tag{B23}$$

$$M_{2,4} = \langle 2p_{\pm'} A \, 2p_0 \, B \frac{1}{r_{12}} 2p_{\pm'} C \, 2p_0 D \rangle = 8C_2(\xi_A)C_2(\xi_B)C_2(\xi_C)C_2(\xi_D)\pi$$

$$\{\kappa_4' R_{CD}^5/\lambda'^4 \, u'^3 (1-u')^3 \, \{q^3 \kappa_4 \, R_{AB}^5/\lambda^4 \, u^3 (1-u)^3 \, [(1/7)(15/4\pi)^{1/2} \, j_4 \, Y_{4,\pm2}^*(\hat{\omega})$$

$$+(2/7)(5/4\pi)^{1/2} \, Y_{2,\pm2}^*(\hat{\omega})j_2 \,]-q^2 \kappa_3 \, R_{AB}^5 u^3 (1-u)^2 /\lambda^3 \, [Y_{1,0}(\hat{R}_{AB})(1-u)(3/28\pi)^{1/2}$$

$$-uY_{1,\pm1}^*(\hat{R}_{AB})(j_3 (1/5\pi)(6/5)^{1/2} \, Y_{3,\pm1}^*(\hat{\omega})-(3/20\pi)Y_{1,\pm1}^*(\hat{\omega})j_1 \,]-q^2 \kappa_2 \, R_{AB}^5/\lambda^2$$

$$u^2 (1-u)^2 \, Y_{1,\pm1}^*(\hat{R}_{AB})Y_{1,0}(\hat{R}_{AB})(3/20\pi)^{1/2} \, Y_{2,\pm1}^*(\hat{\omega})j_2 \, \} +\kappa_3' R_{CD}^5/\lambda'^3 \, u'^3 (1-u')^2$$

$$\{q^3 \kappa_4 \, R_{AB}^5/\lambda^4 \, u^3 (1-u)^3 \, [(3/28\pi)^{1/2} \, j_3 (1-u')Y_{3,\pm2}^*(\hat{\omega})Y_{1,0}(\hat{R}_{CD})-u'Y^*(\hat{R}_{CD})$$

$$(j_3 (1/5\pi)(6/5)^{1/2} \, Y_{3,\pm1}^*(\hat{\omega})-(3/20\pi)j_1 \, Y_{1,\pm1}^*(\hat{\omega})]+q^2 \kappa_3 \, R_{AB}^5/\lambda^3 \, u^3 (1-u)^2$$

$$[-(1-u)(1-u')(6/20\pi)^{1/2} \, Y_{1,0}(\hat{R}_{AB})Y_{1,0}(\hat{R}_{CD})Y_{2,\pm2}^*(\hat{\omega})j_2 \, +u(1-u')(3/20\pi)^{1/2}$$

$$Y_{1,\pm1}^*(\hat{R}_{AB})Y_{1,0}(\hat{R}_{CD})Y_{2,\pm1}^*(\hat{\omega})j_2 \, +u'(1-u)(3/20\pi)^{1/2} \, Y_{1,\pm1}^*(\hat{R}_{CD})Y_{1,0}(\hat{R}_{AB})$$

$$Y_{2,\pm1}^*(\hat{\omega})j_2 \, +uu'Y_{1,\pm1}^*(\hat{R}_{AB})Y_{1,0}(\hat{R}_{CD})(-(1/5\pi)^{1/2} \, Y_{2,0}(\hat{\omega})j_2 \, +j_0 \, /4\pi)]-\kappa_2 \, R_{AB}^5/\lambda$$

$$u^2(1-u)^2 j_1 Y^*_{1\,\pm 1}(\hat{R}_{AB})Y_{1\,0}(\hat{R}_{AB})[Y^*_{1\,\pm 1}(\hat{\omega})Y_{1\,0}(\hat{R}_{CD})(1-u')-u'Y^*_{1\,\pm 1}(\hat{R}_{CD})Y_{1\,0}(\hat{\omega})$$

$$]\}+\kappa'_2 R^5_{CD}/\lambda' \, u'^2(1-u')^2 \, Y^*_{1\,\pm 1}(\hat{R}_{CD})Y_{1\,0}(\hat{R}_{CD})\{-q^2(3/20\pi)^{1/2} Y^*_{2\,\pm 1}(\hat{\omega})$$

$$j_2 \kappa_2 R^5_{AB}/\lambda^4 u^3(1-u)^3 +qj_1 u^2(1-u)^2 \kappa_3 R^5_{AB}/\lambda^3 (Y^*_{1\,\pm 1}(\hat{\omega})Y_{1\,0}(\hat{R}_{AB})(1-u)$$

$$-uY^*_{1\,\pm 1}(\hat{R}_{AB})Y_{1\,0}(\hat{\omega}))+\kappa_2 R^5_{AB}/\lambda^2 \, j_0 \, u^2(1-u)^2 \, Y^*_{1\,\pm 1}(\hat{R}_{AB})Y_{1\,0}(\hat{R}_{AB})\} \qquad \text{(B24)}$$
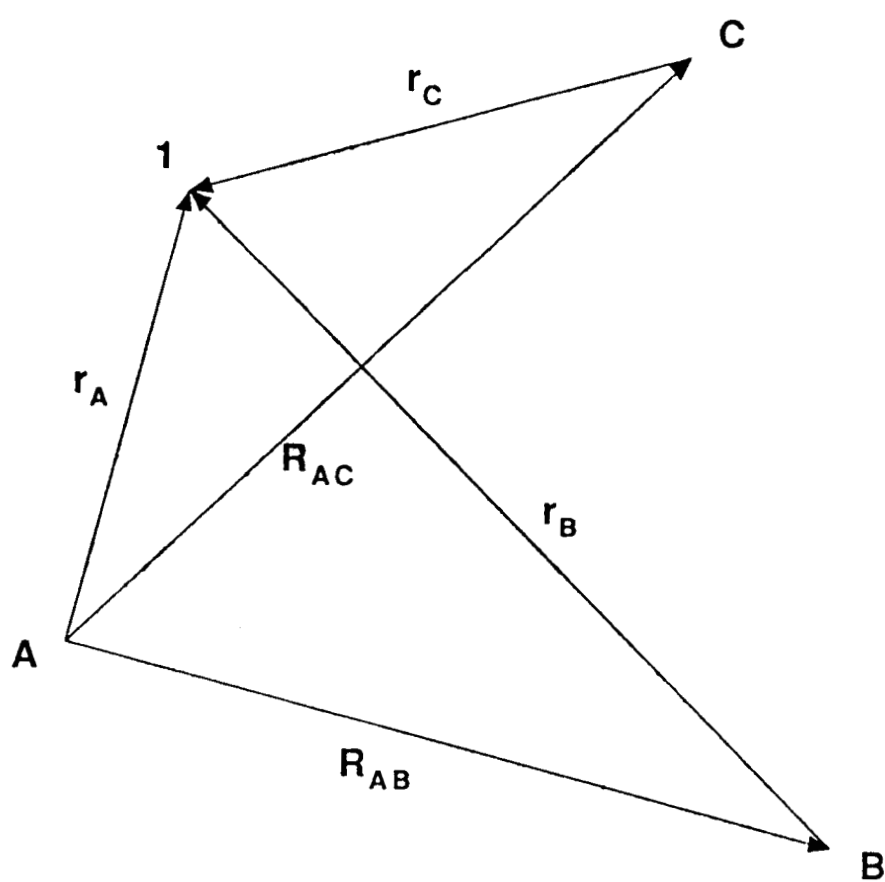
Fig. 1. The coordinate system for one-electron three-center integrals
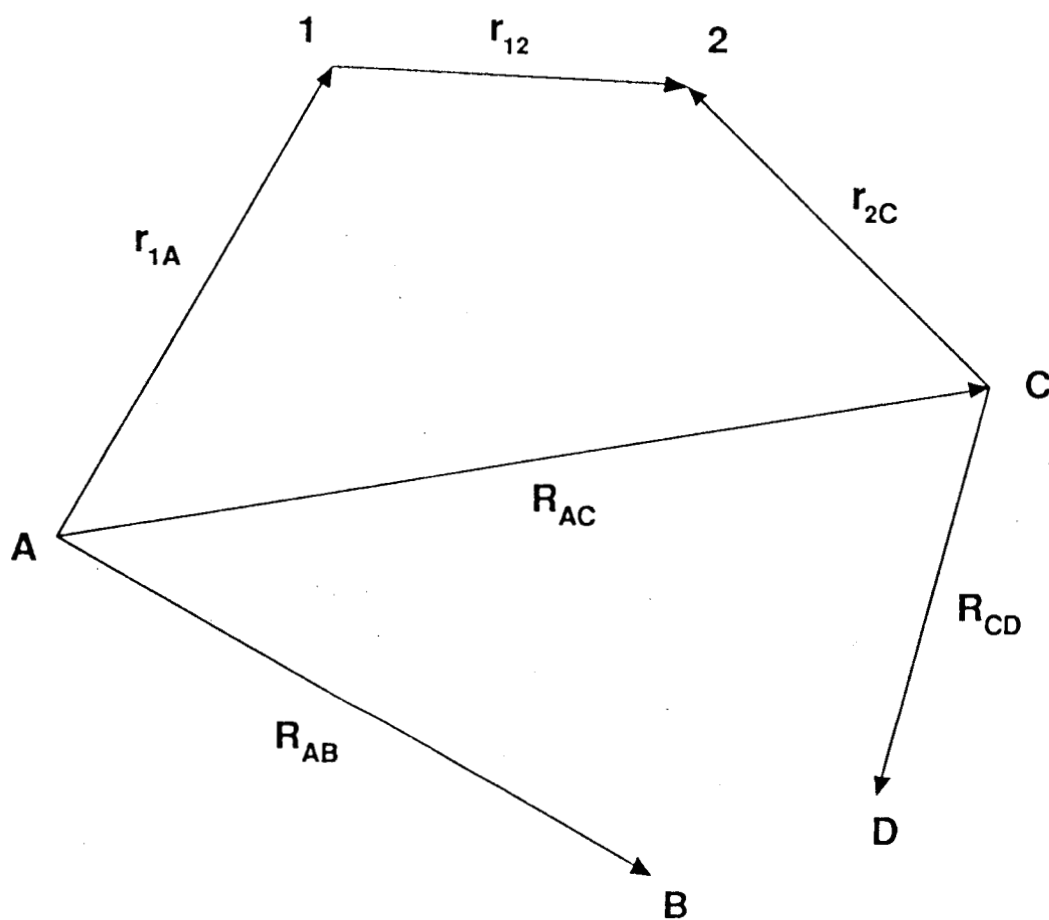
Fig. 2. The coordinate system for two-electron four-center integrals

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15. Supplementary Notes

16. Abstract

The troublesome multi-center molecular integrals of Slater-type orbitals (STO) in molecular physics calculations can be evaluated by using the Fourier transform and proper coupling of the two center exchange integrals. A numerical integration procedure is then readily rendered to the final expression in which the integrand consists of well known special functions of arguments containing the geometrical arrangement of the nuclear centers and the exponents of the atomic orbitals. A practical procedure has been devised for the calculation of a general multi-center molecular integrals coupling arbitrary Slater-type orbitals. Symmetry relations and asymptotic conditions are discussed. Explicit expressions of three-center one-electron nuclear-attraction integrals and four-center two-electron repulsion integrals for STO of principal quantum number n=2 are listed. A few numerical results are given for the purpose of comparison.

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