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Calculation of Integrals over ab initio Pseudopotentials

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Abstract

An approach is presented for the evaluation of the two distinct types of one-electron integrals arising from the ab initio pseudopotentials introduced by Kahn and Goddard. The integrals are shown to reduce to a sum over products of angular and radial integrals, the latter being approximated by power and asymptotic series combined with appropriate recursion relations. The method is valid for arbitrary angular momenta of both the pseudopotential and the Cartesian Gaussian basis functions.

I. Introduction

A number of approaches have been made to the problem of defining potentials that mimic the effects of core electrons in a many-electron atom. One such approach which has met with considerable success is the ab initio pseudopotential originally formulated by Kahn and Goddard[1,2] and modified by others.[3,4,5] In this approach the procedure for finding a pseudopotential for the core of an atom is to define a transformation from the atomic Hartree-Fock valence orbitals to nodeless, well-behaved pseudoorbitals. A numerical pseudopotential is then obtained by requiring that the pseudoorbitals reproduce the HF valence orbital energies. The numerical pseudopotential is then fit to a linear combination of Gaussians of the general form $r^{n-2} \exp(-\xi r^2)$. The only task in employing such a pseudopotential in a molecular calculation using Cartesian Gaussian basis functions is the evaluation of the corresponding one-electron integrals. Several computer programs have been written to evaluate these integrals over s,p,d (and recently f) type pseudopotentials. In this paper we present a method of evaluation which has no inherent limitations on the angular momenta of either basis functions or pseudopotential.

II. Reduction to Angular and Radial Integrals

The form of the ab initio pseudopotential is

$$U(r) = U_{L+1}(r) + \sum_{\ell=0}^{L} \sum_{m-\ell}^{\ell} |\ell m> \left[U_\ell(r) - U_{L+1}(r)\right] < \ell m| \qquad (1)$$

where L is the largest angular momentum orbital appearing in the core. The U_ℓ's are expressed analytically by a fit of the numerical potential to a linear combination of Gaussians:

$$r^2\left[U_\ell(r) - \frac{N_c}{r}\right] = \sum_j d_{j\ell}\left[r^{n_j} \exp(-\xi_j r^2)\right] \qquad (2)$$

where N_c is the number of core electrons. Alternatively, the difference potential $[U_\ell(r) - U_{L+1}(r)]$ may be fit with the same expansion, allowing employment of different sets of n_j and ξ_j for different ℓ. In all implementations of this pseudopotential to date, n_j has been restricted to the values [0,1,2], though this work assumes no such restriction. In the development to follow, we will consider a single term in the expansion, abbreviating n_j and ξ_j as n' and ξ.

The general form of a Cartesian Gaussian function on center A is

$$\phi_A(n_A,\ell_A,m_A,\alpha_A) = N(n_A,\ell_A,m_A,\alpha_A)\, x_A^{n_A}\, y_A^{\ell_A}\, z_A^{m_A} \exp(-\alpha_A r_A^2) \qquad (3)$$

where the normalization constant is

$$N(n_A,\ell_A,m_A,\alpha_A) = (2\alpha_A/\pi)^{\frac{3}{4}}(4\alpha_A)^{(n_A+\ell_A+m_A)/2}\left[(2n_A-1)!!(2\ell_A-1)!!(2m_A-1)!!\right]^{-\frac{1}{2}} \qquad (4)$$

The calculation of integrals between ϕ_A and ϕ_B and the operator $U(r_C)$ results in two distinct types of integrals (which we also refer to as type 1 and type 2).

$$\chi_{AB} = \int d\tau\, \phi_A\, r_C^{n'-2} \exp(-\xi r_C^2)\, \phi_B \tag{5}$$

and

$$\mathcal{Y}_{AB} = \sum_{m=-\ell}^{\ell} \int_0^{\infty} dr_C \left[\int d\Omega_C \phi_A Y_{\ell m}(\Omega_C)\right] r_C^{n'} \exp(-\xi r_C^2) \left[\int d\Omega_C Y_{\ell m}(\Omega_C)\phi_B\right] \tag{6}$$

where the $Y_{\ell m}$ are real, orthonormal spherical polynomials; χ_{AB} refers to the U_{L+1} term in the potential and $\mathcal{Y}_{AB}$ to the U_ℓ or $U_\ell - U_{L+1}$ terms.

The reduction of χ_{AB} proceeds by transforming the exponential parts of ϕ_A and ϕ_B to center C in the following manner:

$$\exp(-\alpha_A r_A^2) = \exp(-\alpha_A r_C^2 - 2\alpha_A \underset{\sim}{CA}\cdot \underset{\sim}{r}_C - \alpha_A |\underset{\sim}{CA}|^2) \tag{7}$$

where

$$\underset{\sim}{CA} = \underset{\sim}{C} - \underset{\sim}{A} \tag{8}$$

If we now define

$$D_{ABC} = 4\pi N(n_A,\ell_A,m_A,\alpha_A)N(n_B,\ell_B,m_B,\alpha_B) \quad \exp(-\alpha_A|\underset{\sim}{CA}|^2 - \alpha_B|\underset{\sim}{CB}|^2), \tag{9}$$

$$\underset{\sim}{k} = -2(\alpha_A \underset{\sim}{CA} + \alpha_B \underset{\sim}{CB}), \tag{10}$$

and

$$\alpha = \alpha_A + \alpha_B + \xi, \tag{11}$$

χ_{AB} is simplified to

$$\chi_{AB} = \frac{D_{ABC}}{4\pi} \int dr\, r_C^{n'-2} \exp(-\alpha r_C^2) \exp(\underset{\sim}{k}\cdot\underset{\sim}{r}_C) x_A^{n_A} y_A^{\ell_A} z_A^{m_A} x_B^{n_B} y_B^{\ell_B} z_B^{m_B} \tag{12}$$

The next step is to expand $\exp(\underset{\sim}{k}\cdot\underset{\sim}{r}_C)$ in spherical coordinates:

$$\exp(\underset{\sim}{k}\cdot\underset{\sim}{r}_C) = 4\pi \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} M_\lambda(kr_C) Y_{\lambda\mu}(\theta_k,\phi_k) Y_{\lambda\mu}(\theta_C,\phi_C) \tag{13}$$

where M_λ is a modified spherical Bessel function of the first kind:

$$M_\lambda(x) = x^\lambda \left(\frac{1}{x}\frac{d}{dx}\right)^\lambda \frac{\sinh x}{x} \quad (14)$$

$$= i^\lambda\, j_\lambda\, (-ix) \quad (15)$$

Transforming x_A, y_A, z_A, x_B, y_B, z_B to point C and separating variables of integration we obtain

$$X_{AB} = D_{ABC} \sum_{a=o}^{n_A} \sum_{b=o}^{\ell_A} \sum_{c=o}^{m_A} \sum_{d=o}^{n_B} \sum_{e=o}^{\ell_B} \sum_{f=o}^{m_B} \binom{n_A}{a}\binom{\ell_A}{b}\binom{m_A}{c}\binom{n_B}{d}\binom{\ell_B}{e}\binom{m_B}{f}$$

$$CA_x^{\,n_A-a}\; CA_y^{\,\ell_A-b}\; CA_z^{\,m_A-c}\; CB_x^{\,n_B-d}\; CB_y^{\,\ell_B-e}\; CB_z^{\,m_B-f}$$

$$\sum_{\lambda=o}^{\infty} \Omega_\lambda^{a+d,b+e,c+f}\; Q_\lambda^{a+b+c+d+e+f+n'}(k,\alpha) \quad (16)$$

where

$$\hat{x}_c = x_c/r_c \text{ etc.} \quad (17)$$

and where the angular integral is defined as

$$\Omega_\lambda^{IJK} = \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\Omega_k) \int d\Omega\; \hat{x}^I\; \hat{y}^J\; \hat{z}^K\; Y_{\lambda\mu}(\Omega) \quad (18)$$

and the radial integral as

$$Q_\lambda^N(k,\alpha) = \int_0^\infty dr\; r^N \exp(-\alpha r^2) M_\lambda(kr) \quad (19)$$

The product of powers of $\hat{x}_c$, $\hat{y}_c$ and $\hat{z}_c$ in the angular integral may be expanded in a sum of spherical polynomials of orders up to I + J + K and differing from I + J + K by a multiple of 2. By orthogonality, then, the sum over λ may be truncated at a+b+c+d+e+f, and (a+b+c+d+e+f)-λ must be even.

The reduction of the type 2 integral, y_{AB} , proceeds in a manner similar to that of χ_{AB} . When the exponential parts of ϕ_A and ϕ_B are transformed to point C we obtain

$$y_{AB} = \frac{D_{ABC}}{4\pi} \sum_{m=-\ell}^{\ell} \int_0^\infty dr_C \left[\int d\Omega_C x_A^{n_A} y_A^{\ell_A} z_A^{m_A} \exp(\underset{\sim}{k}_A \cdot \underset{\sim}{r}_C) Y_{\ell m}(\Omega_C)\right]$$

$$r_C^{n'} \exp(-\alpha r_C^2) \left[\int d\Omega_C\, x_B^{n_B} y_B^{\ell_B} z_B^{m_B} \exp(\underset{\sim}{k}_B \cdot \underset{\sim}{r}_C) Y_{\ell m}(\Omega_C)\right] \tag{20}$$

where D_{ABC} and α are defined as before, and

$$\underset{\sim}{k}_A = -2\alpha \underset{\sim\sim}{CA} \tag{21}$$

$$\underset{\sim}{k}_B = -2\alpha \underset{\sim\sim}{CB} \tag{22}$$

Transforming x_A, y_A, z_A, x_B, y_B, z_B to center C, and reexpressing $\exp(\underset{\sim}{k}_A \cdot \underset{\sim}{r}_C)$ and $\exp(\underset{\sim}{k}_B \cdot \underset{\sim}{r}_C)$, y_{AB} becomes

$$y_{AB} = 4\pi D_{ABC} \sum_{a=0}^{n_A} \sum_{b=0}^{\ell_A} \sum_{c=0}^{m_A} \sum_{d=0}^{n_B} \sum_{e=0}^{\ell_B} \sum_{f=0}^{m_B} \binom{n_A}{a}\binom{\ell_A}{b}\binom{m_A}{c}\binom{n_B}{d}\binom{\ell_B}{e}\binom{m_B}{f}$$

$$CA_x^{n_A-a}\ CA_y^{\ell_A-b}\ CA_z^{m_A-c}\ CB_x^{n_B-d}\ CB_y^{\ell_B-e}\ CB_z^{m_B-f}$$

$$\sum_{\lambda=0}^{\infty} \sum_{\bar{\lambda}=0}^{\infty} Q_{\lambda\bar{\lambda}}^{a+b+c+d+e+f+n'} (k_A, k_B, \alpha) \sum_{m=-\ell}^{\ell} \Omega_{\lambda\ell m}^{abc}\, \Omega_{\bar{\lambda}\ell m}^{def} \tag{23}$$

where the angular integral $\Omega_{\lambda\ell m}^{abc}$ is given by

$$\Omega_{\lambda\ell m}^{abc} = \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\Omega_k) \int \frac{d\Omega}{4\pi}\, \hat{x}^a\, \hat{y}^b\, \hat{z}^c\, Y_{\lambda\mu}(\Omega) Y_{\ell m}(\Omega) \tag{24}$$

and the radial integral $Q_{\lambda\bar{\lambda}}^{N}$ is given by

$$Q_{\lambda\bar{\lambda}}^{N} (k_A, k_B, \alpha) = \int_0^\infty dr\, r^N \exp(-\alpha r^2) M_\lambda(k_A r) M_{\bar{\lambda}}(k_B r) \tag{25}$$

As with the type 1 angular integral, $\Omega^{abc}_{\lambda \ell m}$ may be reexpressed by expanding $x^a y^b z^c$ as a sum of spherical polynomials of order up to a+b+c and differing from a+b+c by a multiple of 2. Therefore, using the vector sum rule for spherical polynomials, the only nonzero terms in the sum over λ are

$$\max(\ell - a - b - c, o) \le \lambda \le \ell + a + b + c \qquad (26)$$

and likewise for $\bar{\lambda}$. Also consistent with the first type of angular integral, $\ell + a + b + c - \lambda$ must be even.

III. Evaluation of the Angular Integrals

To evaluate the angular integrals we first expand the real orthonormal spherical polynomials $Y_{\lambda\mu}$ in terms of $\hat{x}$, $\hat{y}$ and $\hat{z}$:

$$Y_{\lambda\mu} = \sum_{r,s,t}^{\lambda} y_{rst}^{\lambda\mu} \, \hat{x}^r \, \hat{y}^s \, \hat{z}^t , \qquad r+s+t=\lambda \tag{27}$$

The complete angular integrals are then

$$\Omega_{\lambda}^{IJK} = \sum_{\mu=-\lambda}^{\lambda} \left[\sum_{r,s,t}^{\lambda} y_{rst}^{\lambda\mu} \, \hat{k}_x^{\,r} \, \hat{k}_y^{\,s} \, \hat{k}_z^{\,t} \right]$$

$$\sum_{r,s,t}^{\lambda} y_{rst}^{\lambda\mu} \int d\Omega \; \hat{x}^{I+r} \, \hat{y}^{J+s} \, \hat{z}^{K+t} \tag{28}$$

$$\Omega_{\lambda\ell m}^{abc} = \sum_{\mu=-\lambda}^{\lambda} \left[\sum_{r,s,t}^{\lambda} y_{rst}^{\lambda\mu} \, \hat{k}_x^{\,r} \, \hat{k}_y^{\,s} \, \hat{k}_z^{\,t} \right]$$

$$\sum_{r,s,t}^{\lambda} \sum_{u,v,w}^{\ell} y_{rst}^{\lambda\mu} \, y_{uvw}^{\ell m} \int d\Omega \; \hat{x}^{a+r+u} \, \hat{y}^{b+s+v} \, \hat{z}^{c+t+w} \tag{29}$$

The evaluation of the integral is straightforward:

$$(4\pi)^{-1} \int d\Omega \, \hat{x}^i \, \hat{y}^j \, \hat{z}^k = \begin{cases} 0 & i,\ j \text{ or } k \text{ odd} \\ \dfrac{(i-1)!!(j-1)!!(k-1)!!}{(i+j+k)!!} & i,\ j \text{ and } k \text{ even} \end{cases} \tag{30}$$

IV. Type 1 Radial integral, $Q_\ell^n(k,\alpha)$.

Gradshteyn and Ryzhik reexpress the type 1 radial integral as[6]

$$Q_\ell^n(k,\alpha) = \sqrt{\pi}\, k^\ell 2^{-\ell-2} \alpha^{-(\ell+n+1)/2}\, R\, \phi\left((\ell+n+1)/2;\ \ell+3/2;\ k^2/4\alpha\right) \qquad (31)$$

where R is the ratio of gamma functions,

$$R = \Gamma\left((\ell+n+1)/2\right)/\Gamma(\ell+3/2) = \begin{cases} \dfrac{\sqrt{\pi}\,(\ell+n-1)!!}{2(2\ell+1)!!} & n+\ell \text{ even} \\[2ex] \dfrac{(\ell+n-1)!!}{(2\ell+1)!!} & n+\ell \text{ odd} \end{cases} \qquad (32)$$

and ϕ is the degenerate hypergeometric function.

The confluent hypergeometric series for ϕ is[7]

$$\phi(a,b,z) = 1 + \frac{a}{b}\frac{z}{1!} + \frac{a(a+1)}{b(b+1)}\frac{z^2}{2!} + \cdots \qquad (33)$$

The resulting expression for $Q_\ell^n(k,\alpha)$ is equivalently obtained by substitution of a power series for the modified spherical Bessel function $M_\ell(kr)$ in Eq. 19. An asymptotic series for ϕ is given by[7]

$$\phi(a;b;z) = R^{-1} z^{a-b} \exp(z) \left[1 + \frac{(b-a)(1-a)}{1!} z^{-1} + \frac{(b-a)(b-a+1)(1-a)(2-a)}{2!} z^{-2} + \cdots\right] \qquad (34)$$

Although this series diverges, the magnitudes of the terms decrease until a minimum is reached, at which point the partial sum represents a best approximation to ϕ . Summing to this minimum gives 12 figure accuracy for the following n and z:

n	0	1	2	3	4	5	6	7	>7
$Z \geq$	31.	28.	25.	23.	22.	20.	19.	18.	15.

Note that the asymptotic form truncates for $n+\ell$ even and $n \geq \ell + 2$ providing an exact analytical expression for ϕ . An exactly equivalent form for these n and ℓ is found by noting[7]

$$\phi\,(a;b;z) = \exp(z)\,\phi\,(b-a;b;-z) \tag{35}$$

Substitution of the confluent hypergeometric series yields

$$\phi\,(a;b;z) = \exp(z)\left[1 - \frac{(b-a)z}{b\;1!} + \frac{(b-a)(b-a+1)}{b(b+1)2!}\;z^2 + \cdots\right] \tag{36}$$

In contrast to the asymptotic series, evaluation of this form for $n+\ell$ even and $n \geq \ell + 2$ presents no problems for small z. For other n and ℓ, however, when it doesn't terminate, Eq. 36 is not useful, owing to differencing.

Recursion relations were derived and implemented to allow most Q_ℓ^n's to be calculated from just a few starting values. Referring back to Eq. 18 and discussion, we first note that only $Q_\lambda^{a+b+c+d+e+f+n'}$ for which $a+b+c+d+e+f-\lambda$ is even are required, as all others are paired with vanishing angular integrals. Secondly, we note a recursion relation on $M_\ell(x)$:

$$M_\ell(x) = M_{\ell-2}(x) - \frac{(2\ell-1)}{x}\;M_{\ell-1}\,(x) \tag{37}$$

Using this relation and integration by parts, a number of recursion relations on the Q_ℓ^n may be derived:

$$Q_\ell^{\ell+2} = \frac{k}{2\alpha} Q_{\ell-1}^{\ell+1} \tag{38A}$$

$$Q_\ell^{n} = \frac{1}{k}\left[2\alpha Q_{\ell-1}^{n+1} - (n + \ell - 1)\, Q_{\ell-1}^{n-1}\right] \tag{38B}$$

$$Q_\ell^{n} = \frac{1}{(n+\ell+1)}\left[2\alpha Q_\ell^{n+2} - k\, Q_{\ell+1}^{n+1}\right] \tag{38C}$$

$$Q_\ell^{n} = \frac{1}{2\alpha}\left[(n+\ell-1)\, Q_\ell^{n-2} + k\, Q_{\ell-1}^{n-1}\right] \tag{38D}$$

$$Q_\ell^{n} = \frac{1}{2\alpha}\left\{(n+\ell-3)\, Q_{\ell-2}^{n-2} + \left[k-(2\ell-1)\,\frac{2\alpha}{k}\right] Q_{\ell-1}^{n-1}\right\} \tag{38E}$$

$$Q_\ell^{n} = \frac{1}{(n+\ell+1)}\left\{2\alpha Q_{\ell+2}^{n+2} - \left[k - (2\ell+3)\,\frac{2\alpha}{k}\right] Q_{\ell+1}^{n+1}\right\} \tag{38F}$$

Upon examination of the asymptotic form of $Q_\ell^{\,n}$, eqs. 38C and 38F are found to give serious differencing errors for $\frac{k^2}{4\alpha}$ large. Likewise, the alternating series reveals that eqs. 38B and 38E have a differencing problem for $\frac{k^2}{4\alpha}$ small. Figure 1 gives separate stable recurrence schemes for small and large $k^2/4\alpha$. Switching from one to the other at $k^2/4\alpha = 3.0$ yields a relative accuracy of 10^{-13} in the $Q_\ell^{\,n}$.

V. Type 2 Radial Integral

A. Double Power Series

A double power series for the type 2 radial integral, $Q^N_{\lambda\bar{\lambda}}(k_A,k_B,\alpha)$, is suggested by substitution of power series for both modified spherical Bessel functions appearing in Eq. 25. From Abramowitz and Stegun[8]

$$M_\lambda(z) = z^\lambda \sum_{j=0}^{\infty} \frac{(z/\sqrt{2})^{2j}}{j\,!(2\lambda+1+2j)!!} \tag{39}$$

Therefore

$$Q^N_{\lambda\bar{\lambda}}(k_A,k_B,\alpha) = k_A{}^\lambda k_B{}^{\bar{\lambda}} \sum_{j=0}^{\infty} \frac{(k_A/\sqrt{2})^{2j}}{j\,!(2\lambda+1+2j)!!} \sum_{i=0}^{\infty} \frac{(k_B/\sqrt{2})^{2i}}{i\,!(2\bar{\lambda}+1+2i)!!} \int_0^\infty dr\, r^{N+\lambda+\bar{\lambda}+2j+2i} \exp(-\alpha r^2) \tag{40}$$

The integral is evaluated as

$$\int_0^\infty dr\, r^M \exp(-\alpha r^2) = \begin{cases} \dfrac{(M-1)!!}{(2\alpha)^{(M+1)/2}} \sqrt{\dfrac{\pi}{2}} , & M \text{ even} \\[2ex] \dfrac{(M-1)!!}{(2\alpha)^{(M+1)/2}} , & M \text{ odd} \end{cases} \tag{41}$$

After some rearrangement $Q^N_{\lambda\bar{\lambda}}$ becomes

$$Q^N_{\lambda\bar{\lambda}}(k_A,k_B,\alpha) = \frac{k_A{}^\lambda k_B{}^{\bar{\lambda}}}{(2\alpha)^{(n+\lambda+\bar{\lambda}+1)/2}} \sum_{I=0}^{\infty} \left(\frac{k_A{}^2}{4\alpha}\right)^I (n+\lambda+\bar{\lambda}+2I-1)!!\; T_I \tag{42}$$

where

$$T_I = \sum_{i=0}^{I} \frac{(k_B{}^2/k_A{}^2)^i}{(I-i)!\,i!\,(2\lambda+1+2I-2i)!!\,(2\bar{\lambda}+1+2i)!!} \tag{43}$$

T_I is now simply related to the hypergeometric function $F(a,b;\, c;\, z)$:

$$T_I = \left[(2\lambda+1+2I)!!\; I!\; (2\bar{\lambda}+1)!!\right]^{-1} F(-I,-\lambda-1/2-I;\, \bar{\lambda}+3/2\,;\, k_B{}^2/k_A{}^2) \tag{44}$$

where we have used

$$F(a,b;c;z) = \sum_{i=0}^{\infty} \frac{a!!b!!}{c!!} \frac{z^i}{i!} \tag{45}$$

Recursion relations on the F's (ref 8, p. 558, Eqs. 15.2.10 and 15.2.11) allow a recursion relation to be derived for T_I:

$$T_{I+1} = (\beta + \gamma_z)\, T_I + \delta\, (1-z^2)\, T_{I-1} \tag{46}$$

where

$$\delta = - \frac{(\lambda+\bar{\lambda} + 2I+3)}{(I+1)(2\lambda+3+2I)(2\bar{\lambda}+3+2I)(\lambda+\bar{\lambda}+2I+1)(\lambda+\bar{\lambda}+I+2)} \tag{47}$$

$$\beta = \frac{1}{(I+1)(2\lambda+3+2I)} - I(2\lambda+1+2I)\delta\ , \tag{48}$$

$$\gamma = \frac{1}{(I+1)(2\bar{\lambda}+3+2I)} - I(2\bar{\lambda}+1+2I)\delta\ , \tag{49}$$

$$z = k_B{}^2/k_A{}^2 \tag{50}$$

B. Single Power Series

A single power series for the radial integral is found by substituting a power series for just one of the modified spherical Bessel functions:

$$Q^N_{\lambda\bar{\lambda}}\ (k_A,k_B,\alpha) = \frac{k_A{}^\lambda}{\alpha^{(N+\lambda+1)/2}} \sum_{j=0}^{\infty} \frac{(k_A{}^2/2\alpha)^j}{j\ !(2\lambda+1+2j)!!}\, Q_\lambda^{N+\lambda+2j}\ (k_B/\sqrt{\alpha}\,,1) \tag{51}$$

Evaluation of the type 1 radial integral $Q_\ell{}^n$ for arbitrary n has already been discussed; however, the scheme is only practical when these quantities are obtained with a minimum of effort. An upwards recursion relation on n is found in a manner similar to the other recursion relations presented in Section IV:

$$Q_\ell^{\,n}(k,\gamma) = \frac{1}{\gamma}\left[\left(\frac{k^2}{4\alpha} + \frac{2n-5}{2}\right)Q_\ell^{n-2} + \frac{(\ell-n+4)(\ell+n-3)}{4}\,Q_\ell^{n-4}\right] \qquad (52)$$

Thus, only $Q_{\bar{\lambda}}^{N+\lambda}$ and $Q_{\bar{\lambda}}^{N+\lambda+2}$ are required initially to compute an arbitrary number of terms in the series.

Owing to the power series expansion in $k_A^2/2\alpha$, one would expect the method to be inefficient when this quantity is large. When it is small, however, one might expect the method to be rapidly convergent, regardless of the size of $k_B^2/2\alpha$. Such is not the case for the following reasons. We may extract $\exp(k_B^2/4\alpha)$ from the $Q_\lambda^{N+\lambda+2j}$, hopefully leaving quantities that cannot become too large. We compare this with $\exp[(k_A+k_B)^2/4\alpha]$ that is extracted from the points and weights expression (eqs. 57 and 60) derived in the next section. It is apparent that the possibly large crossterm $\exp(k_Ak_B/2\alpha)$ is still hidden in eq. 51. Not only can this result in overflows, the number of terms in the series may be prohibitive. For these reasons, an effective upper limit to the utility of this method was found to be $(k_A + k_B)^2/2\alpha = 100$ when approximately 70 terms are required to give $Q_{\lambda\bar{\lambda}}^N$ (arbitrary $N,\lambda,\bar{\lambda}$) to an accuracy of 10^{-13}.

C. Gaussian Points and Weights Method

We can write the modified spherical Bessel function $M_\ell(z)$ in exponential form as

$$M_\ell(z) = \frac{1}{2z}\; R_\ell(-z)\exp(z) - (-1)^\ell R_\ell(z)\exp(-z) \qquad (53)$$

where

$$R_\ell(z) = \sum_{k=0}^{\ell} \frac{(\ell+k)!}{k!(\ell-k)!}\;(2z)^{-k} \qquad (54)$$

For large z, $M_\ell(z)$ becomes simply the first term in eq. 53. Thus, when

$k_A/\sqrt{\alpha}$ and $k_B/\sqrt{\alpha}$ are large, the type 2 radial integral is approximated by (after a change of variables $r \to r/\sqrt{\alpha}$

$$Q^N_{\lambda\bar{\lambda}}(k_A,k_B,\alpha) \approx \frac{1}{4k_Ak_B}\int_0^\infty dr\left(\frac{r}{\sqrt{\alpha}}\right)^{N-2}\exp\left(-r^2+\frac{k_A}{\sqrt{\alpha}}r+\frac{k_B}{\sqrt{\alpha}}r\right) \tag{55}$$

This form immediately suggests the use of a Gaussian points and weights scheme. We proceed by differentiating the integrand to find a maximum at

$$r_c = \frac{1}{4}(k_A+k_B)/\sqrt{\alpha} \pm \frac{1}{2}\left[\frac{1}{4}(k_A+k_B)^2/\alpha+2(N-2)\right]^{\frac{1}{2}} \tag{56}$$

For the range of $\frac{1}{2}(k_A+k_B)/\sqrt{\alpha}$ for which the method ultimately proved practical, the effect of the 2(N-2) term was very small. Therefore, in the interest of keeping r_c independent of N, we approximate the maximum as

$$r_c = \frac{1}{2}(k_A + k_B)/\sqrt{\alpha} \tag{57}$$

A change of variables $t = r-r_c$ should minimize the number of points in the numerical integration:

$$Q^N_{\lambda\bar{\lambda}} = \int_{-r_c}^{\infty} dt\ f(t, r_c, k_A, k_B, \alpha)\exp(-t^2) \tag{58}$$

where

$$f(t,r_c,k_A,k_B,\alpha) = \left(\frac{t+r_c}{\sqrt{\alpha}}\right)^N M_\lambda\left[\frac{k_A}{\sqrt{\alpha}}(t+r_c)\right] M_{\bar{\lambda}}\left[\frac{k_B}{\sqrt{\alpha}}(t+r_c)\right] \exp\left[-2r_c t - r_c^2\right] \tag{59}$$

We now extract

$$\exp\left[\frac{k_A}{\sqrt{\alpha}}(t+r_c)\right] \text{ and } \exp\left[\frac{k_B}{\sqrt{\alpha}}(t+r_c)\right]$$

from M_λ and $M_{\bar\lambda}$, respectively, (to give M_λ' and $M_{\bar\lambda}'$). Then f reduces to

$$f(t,r_c,k_A,k_B,\alpha) = \left(\frac{t+r_c}{\sqrt{\alpha}}\right)^N M_\lambda'\left[\frac{k_A}{\sqrt{\alpha}}(t+r_c)\right] M_{\bar\lambda}'\left[\frac{k_B}{\sqrt{\alpha}}(t+r_c)\right] \exp(r_c^2) \quad (60)$$

This maneuver forces M_λ' and $M_{\bar\lambda}'$ to be of reasonable magnitude and allows $\exp(r_c^2)$ to be extracted and combined directly with the exponential in D_{ABC}. $M_\ell'(z)$ is calculated using eqs. 53 and 54 for $z > 5.0$. For $z > 16.1$, only the first term is required. When $z \leq 5.0$, the power series in eq. 39 eliminates differencing problems.

Equation 58 suggests calculating zeros of polynomials orthogonal with weight function $\exp(-r^2)$ over the integration range $[-r_c,\infty]$. It is inconvenient, however, to recalculate these zeros for each r_c. For sufficiently large r_c, $f(-r_c)$ is negligible compared with f(o) and we may employ the integration range $[-\infty,\infty]$. Thus, within this approximation the orthogonal polynomials are simply the Hermite polynomials. A table of the zeros and weights for up to 20 degree polynomials is found in Abramowitz and Stegun.[8]

The number of integration points required for a given accuracy decreases with increasing $(k_A + k_B)^2/2\alpha$, showing considerable dependence on $\lambda,\bar\lambda$ and N, also. The following conservative scheme produced $Q^N_{\lambda\bar\lambda}$ for all $\lambda,\bar\lambda$ and N to a relative accuracy of 10^{-13}.

Range of $(k_A+k_B)^2/2\alpha$	Number of points
$[10^2, 10^3]$	20
$[10^3, 10^5]$	10
$> 10^5$	5

Equations 58 and 60 may be used to calculate a crude approximation to $Q^N_{\lambda\bar\lambda}$. Using only the first term in $R_\ell(z)$ to calculate $M_\ell(z)$,

$$Q^{N}_{\lambda\bar{\lambda}} \approx \frac{\exp(r_c{}^2)}{4\alpha^{\frac{1}{2}(N-2)}k_A k_B} \int_{-r_c}^{\infty} dt\,(t+r_c)^{N-2}\exp(-t^2) \tag{61}$$

Approximating $t + r_c$ as r_c and the integration limits as $[-\infty, \infty]$, we arrive at

$$Q^{N}_{\lambda\bar{\lambda}} \simeq \exp(r_c{}^2)\left(\frac{r_c}{\sqrt{\alpha}}\right)^{N-2} \sqrt{\pi}/(4k_A k_B) \tag{62}$$

This expression may then be used to determine whether a particular term in eq. 2 is negligible, before any effort is spent calculating the possibly large number of radial integrals.

VI. The Computer Program

A computer program based on the method described herein was written for the CDC CYBER 170/750 computer at the University of Washington and tested on a CDC 7600 at Lawrence Livermore Laboratory (LLL). This program (which we have given the name MELDPS) has been implemented into the MELD system of programs here and into SCREEPER and POLYATOM at LLL. Testing was performed using a program from Los Alamos (LASLPS), that was developed from Luis Kahn's original pseudopotential program. Tests on several molecules yielded 10-place agreement between MELDPS and LASLPS integrals. It is noteworthy that MELDPS and LASLPS integrals both gave a GVB energy of -11.385102 hartrees for the iodine atom, a figure that differs appreciably from the number quoted by Kahn et al.,[1] -11.383535 hartrees. This inaccuracy and the need to compute integrals over f pseudopotentials were the motivation behind the modifications that produced LASLPS.

Timings showed MELDPS to be factors between 1.5 and 3 slower than LASLPS; however, for problems of reasonable size, the time spent computing pseudopotential integrals is small compared with that spent computing two-electron integrals. Alternative methods based on equations in reference 9 were also tried but proved to have numerical stability problems.

Figure 1. Recurrence algorithm for the type 1 radial integral Q_ℓ^n [a]

A. Large $k^2/4\alpha$, n even

n \ ℓ	0	1	2	3	4
0	S				
1		B			
2	S		B		
3		A		B	
4	D		A		B
5		D		A	
6	D		D		A

C. Small $k^2/4\alpha$, n even

n \ ℓ	0	1	2	3	4
0	C				
1		C			
2	S		C		
3		A		C	
4	D		A		S
5		D		A	
6	D		D		A

B. Large $k^2/4\alpha$, n odd

n \ ℓ	0	1	2	3	4
0					
1	S				
2		S			
3	D		E		
4		D		E	
5	D		D		E
6		D		D	

D. Small $k^2/4\alpha$, n odd

n \ ℓ	0	1	2	3	4
0					
1	F				
2		F			
3	D		F		
4		D		S	
5	D		D		S
6		D		D	

[a] S indicates the appropriate series given in Section IV.

A,B,C,D,E,F refer to recursion relations, eq. 38 A-F.

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