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Atomic Three-Electron Integrals for Correlated Slater-Type s Orbitals

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A compact series expansion method is described for evaluation atomic three-electron integrals which involve odd powers of the three interelectronic distances and Slater-type s orbitals. Only one-dimensional integrals appear in the final expression, and these are readily amenable to machine computation. Convergence of the series is discussed.

Introduction

Great interest has arisen in recent years over the extension of energy calculations with the inclusion of electronic correlation to many-electron atoms, as a natural follow-on to the original Hylleraas technique for two-electron systems. These calculations depend upon the use of variational electronic wave functions which explicitly contain the interelectronic separations, since it is known that trial functions of this type converge more quickly towards the exact wavefunction than the conventional configuration-interaction functions. So long as only single-pair correlations are considered between the electrons, each term in the trial wavefunction will depend only upon one interelectronic distance r_{ik}. When this is the case the calculation of the electronic potential energy for an atom with three or more electrons will involve the evaluation of both two- and three-electron integrals, of which the most difficult will be that three-electron integral whose integrand involves three different r_{ik}'s forming a triangle. Following Hylleraas, it is usual to construct the trial functions from a basis set of Slater-type orbitals, together with correlation factors containing low positive integral powers of the r_{ik}'s. Certain calculations with Be have indicated that it may be necessary to go beyond single-pair correlations to double-pair correlations in the trial functions, in order to achieve the necessary precision in the calculation of the correlation energy. With such computations even more difficult four-electron integrals arise, but in this note we shall consider only the most difficult type of three-electron integral arising for a Slater-type s-orbital basis. This integral has been broken down into its component radial integrals in several publications [1–8], both for special cases and the general case, but it is felt that the new treatment outlined here is neater and will give rise to simpler (and therefore faster) computer programmes for such integrals.

General Formulae

Denoting the volume element for integration over the whole of configuration space for electrons 1, 2, 3 by $d\tau$, we consider

$$I = \int d\tau\, r_1^{n_1-1}\, r_2^{n_2-1}\, r_3^{n_3-1}\, r_{12}^{n_{12}}\, r_{23}^{n_{23}}\, r_{13}^{n_{13}} \exp(-a_1 r_1 - a_2 r_2 - a_3 r_3)\,, \qquad (1)$$

with the usual nomenclature, where n_{12}, n_{23}, n_{13}, are odd integers $\geqq -1$, and n_1, n_2, n_3 are positive integers.

To integrate over the electronic angular coordinates we expand each r_{ik}^n in spherical harmonics [9]:

$$r_{12}^n = \sum_{p=0}^{\frac{1}{2}(n+1)} \sum_{l=0}^{\infty} d(n,l,p)\, r_>^n \left(\frac{r_<}{r_>}\right)^{l+2p} P_l(\cos\theta_{12}), \quad n \text{ odd}; \tag{2}$$

where

$$d(n,l,p) = \frac{(-\tfrac{1}{2}n)_l}{(\tfrac{1}{2})_l} \frac{(l-\tfrac{1}{2}n)_p}{(l+\tfrac{3}{2})_p} \frac{(-\tfrac{1}{2}-\tfrac{1}{2}n)_p}{p!}, \tag{3}$$

and

$$(a)_l = \frac{\Gamma(a+l)}{\Gamma(a)}.$$

Here $r_<$ and $r_>$ are the least and greatest in magnitude, respectively, of r_1 and r_2, while θ_{12} is the angle between them.

For the radial integrations we subdivide the integration region into six regions specified by the six possible permutations

$$r_i < r_j < r_k, \tag{4}$$

where it is understood that (i,j,k) stands for any one of the six permutations of the numbers (1, 2, 3) amongst themselves. In subsequent formulae it will be understood that a sum over i,j,k means a sum over these six permutations.

Substituting (2) and (3) into (1), and remembering (4), we integrate over all angles to obtain:

$$I = (4\pi)^3 \sum_{i,j,k} \sum_{p=0}^{\frac{1}{2}(n_{ij}+1)} \sum_{q=0}^{\frac{1}{2}(n_{jk}+1)} \sum_{s=0}^{\frac{1}{2}(n_{ik}+1)} \int_0^{\infty} dr_k \int_0^{r_k} dr_i \int_{r_i}^{r_k} dr_j\, r_i^L\, r_j^M\, r_k^N \, f(r_i/r_k) \exp(-a_i r_i - a_j r_j - a_k r_k), \tag{5}$$

where

$$L = n_i + 1 + 2p,$$
$$M = n_j + 1 + n_{ij} - 2p + 2q,$$
$$N = n_k + 1 + n_{ik} + n_{jk} - 2q,$$

and

$$f(u) \equiv f_{pqs}^{n_{ij}, n_{jk}, n_{ik}}(u) = \sum_{l=0}^{\infty} \frac{d(n_{ij}, l, p)\, d(n_{jk}^{ri}, l, q)\, d(n_{ik}, l, s)}{(2l+1)^2} u^{2l+2s}. \tag{6}$$

Integrating over r_j, r_k, in that order, after setting $r_i = ur_k$, this reduces to

$$I = (4\pi)^3 \sum_{i,j,k} \sum_{p,q,s} \sum_{m=0}^{M} \frac{M!(N+L+m+1)!}{m!\, b^{M+1-m}} \int_0^1 du\, u^L f(u) \left[\frac{u^m}{\{(a+b)u+c\}^g} - \frac{1}{\{au+b+c\}^g}\right] \tag{7}$$

where

$$a = a_i,$$
$$b = a_j,$$
$$c = a_k$$
$$g = N + L + m + 2,$$

and the summation limits for p, q, s are as before.

Since $f(u)$ can be written as in (6), then the u integration in (7) may be expressed in terms of basic integrals of the type

$$I_{fg} = \int_0^1 \frac{du\, u^f}{(\alpha u + \beta)^g}, \tag{8}$$

which obey the recurrence relations

$$\begin{aligned} \alpha I_{f+1,g} &= I_{f,g-1} - \beta I_{fg}, \\ \alpha(g-1) I_{fg} &= f I_{f-1,g-1} - (\alpha+\beta)^{1-g}, \end{aligned} \tag{9}$$

for $f \neq 0$, $g \neq 1$; and

$$\alpha(1-g) I_{0g} = (\alpha+\beta)^{1-g} - \beta^{1-g}, \quad g \neq 1, \tag{10}$$

$$\alpha \cdot I_{01} = \log_e\left(1 + \frac{\alpha}{\beta}\right). \tag{11}$$

In closed form

$$I_{fg} = \alpha^{-f-1} \sum_{h=0}^{f} \frac{\binom{f}{h}(-\beta)^{f-h}}{(h-g+1)} [(\alpha+\beta)^{h-g+1} - \beta^{h-g+1}], \tag{12}$$

but for computation (9) is preferable when it is numerically stable.

Example

As an example, we note that if $n_{12} = n_{23} = n_{13} = -1$, then $p = q = s = 0$, and

$$\begin{aligned} f_{000}^{1\,-1\,-1}(u) \equiv S(u) &= \sum_{l=0}^{\infty} u^{2l}/(2l+1)^2 \\ &= \frac{1}{2u} \int_0^1 \frac{dx}{x} \log_e\left(\frac{1+xu}{1-xu}\right). \end{aligned} \tag{13}$$

Similarly, if $n_{12} = n_{32} = -n_{13} = 1$, as considered by Burke [2], then we need only calculate

$$f_{000}^{11\,-1},\ f_{110}^{11\,-1},\ f_{010}^{11\,-1} = f_{100}^{11\,-1}.$$

By rearranging the series for $f(u)$ somewhat we find

$$f_{000}^{11\,-1} = \frac{1}{2} + \frac{1}{4}(1+u^2) S(u) + \frac{1}{8}\left(\frac{1}{u} - u\right) \log_e\left(\frac{1+u}{1-u}\right), \tag{14}$$

$$f_{110}^{11\,-1} = -\frac{1}{2u^2} + \frac{1}{4}\left(1 + \frac{1}{u^2}\right) S(u) + \frac{1}{8}\left(\frac{1}{u^3} - \frac{1}{u}\right) \log_e\left(\frac{1+u}{1-u}\right), \tag{15}$$

$$f_{010}^{11\,-1} = \frac{1}{4} S(u) + \frac{1}{16}\left(1 - \frac{1}{u^2}\right) + \frac{1}{32}\left(\frac{1}{u^3} - u\right) \log_e\left(\frac{1+u}{1-u}\right). \tag{16}$$

Convergence

By inspection of the u integration in (7), and by comparing (6) with (13), it is obvious that the infinite series resulting from term-by-term integration of $f(u)$

will converge at least as quickly as the series resulting from term-by-term integration of $S(u)$. To examine the convergence of the latter we consider

$$J = \int_0^1 \frac{du\, u^n\, S(u)}{(\alpha u + \beta)^g},$$

where n is a positive integer. Expanding $S(u)$ as in (13), we find

$$J = \sum_{l=0}^{\infty} J_l/(2l+1)^2,$$

where

$$J_l = \int_0^1 \frac{du\, u^{n+2l}}{(\alpha u + \beta)^g} < \frac{\beta^{-g}}{(2l+1)},$$

so that the series for J converges more quickly than the series

$$\sum_{l=0}^{\infty} \frac{1}{(2l+1)^3}.$$

Hence the series for the u integration in (7) converges at least as quickly as the latter series.

References

1. James, H. M., and A. S. Coolidge: Physic. Rev. **49**, 688 (1936).
2. Burke, E. A.: Physic. Rev. **130**, 1871 (1963); J. math. Physics **6**, 1691 (1965).
3. Öhrn, Y., and J. Nordling: J. chem. Physics **39**, 1864 (1963).
4. McKoy, V.: J. chem. Physics **42**, 2959 (1965).
5. Roberts, P. J.: Proc. physic. Soc. (London) **89**, 789 (1966).
6. Seung, S., and E. B. Wilson: J. chem. Physics **47**, 5343 (1967).
7. Larsson, S.: Physic. Rev. **169**, 49 (1968).
8. Perkins, J. F.: J. chem. Physics **48**, 1985 (1968).
9. Sack, R. A.: J. math. Physics **5**, 245 (1964).

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