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NOTES

The Analytical and Recursive Evaluation of Two-Center Integrals

In calculating the interaction energy (to first order) between two atoms, supposed fixed at internuclear distance R, there arise the two integrals:

$$I(i, i') = \int (r_{1A})^i \exp(-ar_{1A})\, Y_{lM}(\hat{r}_{1A}) \frac{1}{r_{12}} (r_{2B})^{i'} \exp(-br_{2B})\, Y_{l'M'}(\hat{r}_{2B})\, d\mathbf{r}_{1A}\, d\mathbf{r}_{2B} \tag{1}$$

$$\text{and} \qquad J(i) = \int \frac{(r_{1A})^i}{r_{1B}} \exp(-ar_{1A})\, Y_{lM}(\hat{r}_{1A})\, dr_{1A}, \tag{2}$$

where $M' = -M$.

Here, the subscripts 1 and 2 refer to electrons 1 and 2 associated with nuclei A and B, respectively. The vector $\mathbf{R}$ is taken to be $\mathbf{r}_B - \mathbf{r}_A$.

When the atoms are in the ground state or low excited states, these integrals may be evaluated fairly easily. One method would be to expand $1/r_{12}$ in terms of r_{1A}, r_{2B}, R, and spherical harmonics which would then allow integration over the separate variables. If one or both of the atoms are in high excited states, however, so that i, i', l, and l' may be large, it is necessary either to employ numerical integration or to find a set of recurrence relationships in terms of which each integral can be expressed.

The purpose of this article is to describe one set of recurrence relationships which will allow the integrals (1) and (2) to be evaluated exactly. Since they may both be evaluated in the same fashion, we will restrict the discussion to the more complicated integral (1).

When $i = l$ and $i' = l'$, (1) may be reduced to a one-dimensional integral by using the Fourier transform of $1/r$ and by noting that [1]

$$\int_0^\infty \exp(-ar) r^{l+2} j_l(kr)\, dr = 2^{l+1}(l+1)!\, \frac{ak^l}{(k^2 + a^2)^{l+2}}. \tag{3}$$

The result obtained is then differentiated $(i - l)$ times with respect to a and $(i' - l')$ times with respect to b, to give

$$I(i, i') = \sum_{L=0}^{l+l'} Y_{L0}(\hat{R})\, D_L \left(\frac{\partial}{\partial a}\right)^p \left(\frac{\partial}{\partial b}\right)^q \left[ab \int_0^\infty \frac{k^{l+l'} j_L(kR)\, dk}{(k^2 + a^2)^{l+2}(k^2 + b^2)^{l'+2}}\right], \tag{4}$$

where $p = i - l$ and $q = i' - l'$. The coefficient D_L is given as

$$D_L = 2^{l+l'+7}(l+1)!\,(l'+1)!\,[2l+1)(2l'+1)/(4\pi(2L+1))]^{1/2} \times (-1)^{(i-i'+L+2M)/2} C(l, l', L; M)\, C(l, l', L; 0) \tag{5}$$

The Clebsch-Gordon coefficients $C(l, l', L; M)$ may be found in reference [2]. Note that $D_L = 0$ unless $(l + l' + L)$ is even, so that only the integrals with odd integrands appearing in the sum (4) need be considered.

Now $j_L(\rho)$ can be written as

$$j_L(\rho) = \sum_{s=0}^{L} C_{L,s} H_{L,s}(\rho)/\rho^{s+1}, \tag{6}$$

where

$$H_{L,s}(\rho) = \begin{cases} \sin\rho & \text{if } L+s \text{ is even,} \\ \cos\rho & \text{if } L+s \text{ is odd,} \end{cases}$$

and $C_{L,s}$ is defined by the recurrence relationships

$$\begin{aligned} C_{0,0} &= 1; \\ C_{L,L} &= (2L-1)\, C_{L-1,L-1}; \\ C_{L,0} &= (-1)^L\, C_{L-1,0}; \\ C_{L,s} &= (L+s-1)\, C_{L-1,s-1} + (-1)^{L-s} C_{L-1,s}, \qquad s \neq 0, L. \end{aligned}$$

Therefore, we need only evaluate the expression

$$\left(\frac{\partial}{\partial a}\right)^p \left(\frac{\partial}{\partial b}\right)^q \left[ab \int_0^\infty \frac{k^j H_{L,s}(kR)\, dk}{(k^2+a^2)^m (k^2+b^2)^n}\right] = \left(\frac{\partial}{\partial a}\right)^p \left(\frac{\partial}{\partial b}\right)^q [abT(j, m, n)] \tag{7}$$

for the values L and s implied in the expressions (4) and (6). Here, $j = l + l' - (s+1)$ and has opposite parity to $L + s$ if we only consider those values of L having the same parity as $l + l'$ [so that the integrand in (7) is odd]. We do not put $m = l + 2$ and $n = l' + 2$ for a reason which will become apparent when we carry out the differentiation.

The integral $T(j, m, n)$ may be written as

$$T(j, m, n) = \begin{cases} \mathrm{Re}(K) & \text{if } j \text{ is even,} \\ \mathrm{Im}(K) & \text{if } j \text{ is odd,} \end{cases}$$

where

$$K = \frac{1}{2}\int_{-\infty}^{\infty} \frac{x^j \exp(ixR)\, dx}{(x^2 + a^2)^m (x^2 + b^2)^n}. \tag{8}$$

K may be evaluated as a contour integral in the upper half plane by considering the integrand

$$A(z) = \frac{z^j \exp(izR)}{(z^2 + a^2)^m (z^2 + b^2)^n}. \tag{9}$$

The residue of $A(z)$ at the m pole $z = ia$ is

$$(-1)^m (i)^{j+1} \frac{1}{(m-1)!} \left(\frac{d}{dk}\right)^{m-1} (u), \tag{10}$$

where

$$u = \frac{\exp(-kR)\, k^j}{(k + a)^m (b^2 - k^2)^n},$$

evaluated at $k = a$.

To obtain a recurrence relationship for the derivatives of u, consider the relation

$$du/dk = uf, \qquad \text{where } f = R - \frac{m}{k + a} + \frac{2nk}{b^2 - k^2} + \frac{j}{k}. \tag{11}$$

Then $D^{t+1}u = C_0{}^t(D^t u) f + \cdots + C_r{}^t(D^{t-r}u)(D^r f) + \cdots + C_t{}^t u(D^t f)$,

$$\text{where} \quad D \equiv \frac{d}{dk} \quad \text{and} \quad C_r{}^t = \frac{t!}{r!(t - r)!}. \tag{12}$$

With f given in (11), we have

$$D^r f = \frac{(-1)^{r+1} m r!}{(k + a)^{r+1}} + 2n(D^r g) - (-1)^{r+1} \frac{j r!}{k^{r+1}}. \tag{13}$$

It is necessary to find $D^r g$, where

$$g = k/(b^2 - k^2). \tag{14}$$

To find a recurrence relationship for the derivatives of g we first observe that

$$(b^2 - k^2)(Dg) = 1 + 2kg$$

and

$$(b^2 - k^2)(D^2 g) = 2g + 4k(Dg). \tag{15}$$

Assume that, for $r \geqslant 2$,

$$(b^2 - k^2)(D^r g) = \alpha(D^{r-2} g) + \beta k(D^{r-1} g).$$

Then differentiating this expression once, we have

$$(b^2 - k^2)(D^{r+1} g) = (\alpha + \beta)(D^{r-1} g) + (\beta + 2)\, k(D^r g), \tag{16}$$

which is an expression of the same form. Making use of the method of induction we, therefore, have a recursion relationship for $D^r g$. This enables us to find $D^r f$ and so from (12) and (10) we can find the residue due to the pole at $z = ia$. The residue of the n pole at $z = ib$ is clearly obtained by interchanging m and n and a and b and, summing the residues, we can find $T(j, m, n)$. If $j = -1$ (otherwise, j is nonnegative), we must integrate around the origin and we then have the further contribution $\pi/2a^{2m}b^{2n}$ to the integral $T(j, m, n)$. This is the contribution which makes the interaction potential between two excited neutral atoms decay non-exponentially with internuclear distance.

Having found $T(j, m, n)$ for general j, m, and n, it only remains to differentiate this integral, as given by (7). Differentiating inside the integral sign with respect to a, in expression (8), we obtain the relations

$$\left(\frac{\partial}{\partial a}\right) T(j, m, n) = -2maT(j, m + 1, n),$$

$$\left(\frac{\partial}{\partial a}\right)^2 T(j, m, n) = -2mT(j, m + 1, n) + 4m(m + 1)\, a^2 T(j, m + 2, n). \tag{17}$$

The first of these relations leads to the recurrence relation

$$\left(\frac{\partial}{\partial a}\right)^{t+2} T(j, m, n) = -2ma \left(\frac{\partial}{\partial a}\right)^{t+1} T(j, m + 1, n) - 2m(t + 1) \left(\frac{\partial}{\partial a}\right)^{t} T(j, m + 1, n). \tag{18}$$

Therefore, it is necessary to find $T(j, m, n)$ for values of m and n other than $l + 2$ and $l' + 2$, respectively.

Similar relations exist for differentiation with respect to b, and we can, therefore, generate the expression (7) recursively. Consequently, the integral (1), as given by (4), may be evaluated exactly.

One disadvantage of the method is clearly the calculation of integrals T which, in a typical problem, will not be used. The user must then consider whether the accuracy is worth the large time involved in computation.

The program is simple to write and occupies little core space. The author has written and run the program, in its general form, on the IBM-360. The machine time used to calculate I in (1) is estimated as

$$\begin{aligned} &0.97 \text{ sec} \quad \text{for} \quad i = 3, \quad l = 0, \\ &0.88 \text{ sec} \quad \text{for} \quad i = 3, \quad l = 1, \\ &1.16 \text{ sec} \quad \text{for} \quad i = 4, \quad l = 2, \end{aligned}$$

and with $i' = 5$, $l' = 3$, $a = 2.5$, $b = 0.5$, $R = 10$. The time given is the C.P.U. time for execution. It is clear that $i - l$ is as important as l in determining the machine time and that the differentiation process in which the unused integrals T are generated is a serious drawback. However, if one were interested in the integrals I and J for many values of i, l, i', l', M but the same values a and b, the tabulation of the integrals T would undoubtedly reduce the time.

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References

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