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Note

Integrals of the Resolvent of the Hydrogenic Hamiltonian Over STO Basis Functions

Recent work on the calculation of lower bounds for energy levels of atoms necessitated the evaluation of integrals of the type $\langle \varphi_1 |(\mathscr{H} + \mathscr{E})^{-1} | \varphi_2 \rangle$, where φ_1 and φ_2 are Slater-type orbitals and $\mathscr{H}$ is the hamiltonian for the hydrogen atom or an ion isoelectronic with it. The usefulness of these integrals in lower bounds work has not yet been fully investigated, but the method of evaluating the integrals, which may be useful in other problems also, is presented here.

The resolvent $(\mathscr{H} + \mathscr{E})^{-1}$ is well known as an integral operator whose kernel is the Green's function for $\mathscr{H}$. This has been derived in a variety of forms by several authors [1–4], and a few special cases of integrals over it have been evaluated [5]. The form used here is essentially that given by Mapleton [6] and later by Hameka [7], but since minor differences in conventions can cause confusion in application, a brief description of the derivation of the resolvent as used here is given.

The hamiltonian is written in Hartree units,

$$\mathscr{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}.$$

As is well known, $\mathscr{H} + \mathscr{E}$ can be written as

$$\mathscr{H} + \mathscr{E} = \sum_{l=0}^{\infty} (\mathscr{H}_l + \mathscr{E})\,\mathscr{O}_l$$

where $\mathscr{O}_l$ is the projector onto the subspace of a specific value of l, and

$$\mathscr{H}_l = -\frac{1}{2}\nabla_r{}^2 - \frac{Z}{r} + \frac{l(l+1)}{2r^2}.$$

Since the subspaces corresponding to different l values are orthogonal, the inverse can be written

$$(\mathscr{H} + \mathscr{E})^{-1} = \sum_{l=0}^{\infty} (\mathscr{H}_l + \mathscr{E})^{-1}\,\mathscr{O}_l$$

and this will be valid whenever $\mathscr{E}$ is a positive constant other than $\frac{1}{2}(Z/n)^2$, where n is a natural number.

Now if φ_1 and φ_2 are written as

$$\varphi_1 = r^{\mu} e^{-\alpha r} Y_{lm}(\theta, \varphi)$$

and

$$\varphi_2 = r^\nu e^{-\beta r} Y_{l'm'}(\theta, \varphi),$$

we find

$$\langle \varphi_1 | (\mathscr{H} + \mathscr{E})^{-1} | \varphi_2 \rangle = \delta_{ll'} \delta_{mm'} \langle r^\mu e^{-\alpha r} | (\mathscr{H}_l + \mathscr{E})^{-1} | r^\nu e^{-\beta r} \rangle.$$

To determine the functions $(\mathscr{H}_l + \mathscr{E})\, r^\nu e^{-\beta r}$ we need the solutions of the equation

$$(\mathscr{H}_l + \mathscr{E})\, f(r) = 0. \tag{1}$$

The substitutions

$$\tau = (2\mathscr{E})^{1/2},$$
$$\rho = 2\tau r,$$

and

$$f(r) = \rho^l e^{-\rho/2} P(\rho)$$

show that P must satisfy Kummer's equation

$$\rho P'' + (2l + 2 - \rho)\, P' - \left(l + 1 - \frac{Z}{\tau}\right) P = 0,$$

the solutions of which may be taken as ${}_1F_1(a; 2l + 2; \rho)$ and $U(a; 2l + 2; \rho)$, where $a = l + 1 - Z/\tau$. It is easily shown that the Wronskian $w(r) = W(\rho)$ of any two independent solutions of Eq. (1) is $c\rho^{-2}$, and the constant c, as evaluated by using the asymptotic forms of Kummer's functions, is $-(2l + 1)!\,(2\tau)/\Gamma(a)$. Then, following standard procedure [8, 9], we find

$$\begin{aligned}
&(\mathscr{H}_l + \mathscr{E})^{-1} \chi(r) \\
&\quad = -2\rho^l e^{-\rho/2} \Big\{ U(a; 2l + 2; \rho) \int_0^\rho \sigma^l e^{-\sigma/2} {}_1F_1(a; 2l + 2; \sigma) \frac{\chi(\sigma/2\tau)}{W(\sigma)} \frac{d\sigma}{2\tau} \\
&\qquad + {}_1F_1(a; 2l + 2; \rho) \int_\rho^\infty e^{-\sigma/2} \sigma^l U(a; 2l + 2; \rho) \frac{\chi(\sigma/2\tau)}{W(\sigma)} \frac{d\sigma}{2\tau} \\
&\quad = -2 \frac{\Gamma(a)\, \rho^l e^{-\rho/2}}{(2l + 1)!\,(2\tau)^{\nu+2}} \Big\{ U(a; 2l + 2; \rho) \int_0^\rho e^{-\sigma/2} {}_1F_1(a; 2l + 2; \sigma)\, \sigma^{l+\nu+2} e^{-\beta\sigma/2\tau}\, d\sigma \\
&\qquad + {}_1F_1(a; 2l + 2; \rho) \int_\rho^\infty e^{-\sigma/2} \sigma^{l+\nu+2} U(a; 2l + 2; \sigma)\, e^{-\beta\sigma/2\tau}\, d\sigma \Big\}.
\end{aligned}$$

Then

$$\begin{aligned}
I = \int_0^\infty & r^{\mu+2} e^{-\alpha r} [(\mathscr{H}_l + \mathscr{E})^{-1} r^\nu e^{-\beta r}]\, dr = \\
& - \frac{2\Gamma(a)}{(2l + 1)!\,(2\tau)^{\mu+\nu+5}} \Big\{ \int_0^\infty \rho^{\mu+l+2} e^{-(\alpha/2\tau+1/2)\rho} U(a; 2l + 2; \rho) \int_0^\rho \sigma^{\nu+l+2} e^{-(\beta/2\tau+1/2)\sigma} \\
& \times {}_1F_1(a; 2l + 2; \sigma)\, d\sigma\, d\rho + \int_0^\infty \rho^{\mu+l+2} e^{-(\alpha/2\tau+1/2)\rho} {}_1F_1(a; 2l + 2; \rho) \\
& \times \int_\rho^\infty \sigma^{\nu+l+2} U(a; 2l + 2; \rho)\, e^{-(\beta/2\tau+1/2)\sigma}\, d\sigma\, d\rho \Big\}.
\end{aligned}$$

The second integral is transformed into the same form as the first by Dirichlet's theorem, yielding

$$I = -\frac{2\Gamma(a)}{(2l+1)!\,(2\tau)^{\mu+\nu+5}}\left[V\left(a, l; \mu, \frac{\alpha+\tau}{2\tau}; \nu, \frac{\beta+\tau}{2\tau}\right)\right.$$
$$\left. + V\left(a, l; \nu, \frac{\beta+\tau}{2\tau}; \mu, \frac{\beta+\tau}{2\tau}\right)\right], \tag{2}$$

where

$$V(a, l; \mu, x; \nu, y) \equiv \int_0^\infty \rho^{\mu+l+2} e^{-x\rho} U(a; 2l+2; \rho) \int_0^\rho \sigma^{\nu+l+2} e^{-y\sigma} {}_1F_1(a; 2l+2; \sigma)\, d\sigma\, d\rho.$$

The first step in evaluating this integral is to substitute for ${}_1F_1$ its power series representation; each term then becomes an elementary integral of the type

$$\int_0^\rho \sigma^n e^{-y\sigma}\, d\sigma = \frac{n!}{y^{n+1}}\left\{1 - e^{-y\rho}\sum_{k=0}^{n}\frac{(y\rho)^k}{k!}\right\}.$$

This leads to

$$V(a, l; \mu, x; \nu, y) = \sum_{k=0}^{\infty}\frac{(a)_k\,(\nu+l+k+2)!}{(2l+2)_k\,k!\,y^{\nu+l+k+3}}\left\{\int_0^\infty \rho^{\mu+l+2} e^{-x\rho} U(a; 2l+2; \rho)\, d\rho\right.$$
$$\left. \times -\sum_{j=0}^{\nu+l+k+2}\frac{y^j}{j!}\int_0^\infty \rho^{\mu+l+j+2} e^{-(x+y)\rho} U(a; 2l+2; \rho)\, d\rho\right\},$$

where $(a)_k$ is Pochhammer's symbol, defined by

$$(a)_0 = 1,$$
$$(a)_{k+1} = (a)_k\,(a+k).$$

The integrals in this expression are given in Slater's book [10] in terms of hypergeometric functions; the integral in the first term can be factored out of the summation, which then also yields a hypergeometric function. We thus finally arrive at

$$V(a, l; \mu, x; \nu, y) = \frac{(\mu+l+2)!\,(\mu-l+1)!\,(\nu+l+2)!}{\Gamma(a+\mu-l+2)\,x^{\mu+l+3} y^{\nu+l+3}}$$
$$\times {}_2F_1\left(a, \mu+l+3; a+\mu-l+2; 1-\frac{1}{x}\right)$$
$$\times {}_2F_1\left(a, \nu+l+3; 2l+2; \frac{1}{y}\right)$$

$$- \frac{1}{y^{\nu+l+3}(x+y)^{\mu+l+3}} \sum_{k=0}^{\infty} \frac{(a)_k (\nu+l+k+2)!}{(2l+2)_k\, k!\, y^k}$$

$$\times \sum_{j=0}^{\nu+l+k+2} \frac{(\mu+l+j+2)!\,(\mu-l+j+1)!}{j!\,\Gamma(a+\mu-l+j+2)} \left(\frac{y}{x+y}\right)^j$$

$$\times {}_2F_1\left(a, \mu+l+j+3; a+\mu-l+j+2; 1-\frac{1}{x+y}\right). \tag{3}$$

Before discussing the application of this formula, we need to determine what limitation it imposes on the parameters. The first, already mentioned, is that $-\mathscr{E}$ must not lie in the spectrum of $\mathscr{H}_l$. Next, in the inner sum in Eq. (3) the upper limit is replaced temporarily by infinity, and the ratio test can be applied to the resulting series by noting that

$$0 < y/(x+y) < 1$$

and

$$\lim_{j\to\infty} {}_2F_1\left(a; \mu+l+j+3; a+\mu-l+j+1; 1-\frac{1}{x+y}\right)$$

$$= {}_1F_0\left(a;; 1-\frac{1}{x+y}\right) = (x+y)^a \quad [|x+y| > 1.$$

The series is seen to be convergent, and so its partial sums, which occur in Eq. (3), approach a constant value as $k \to \infty$. With the help of this fact it is easy to show that to assure convergence of the series in Eq. (3), we must have $y > 1$. From Eq. (2) we then see that this applies to x also. This means that

$$\alpha > \tau; \qquad \beta > \tau.$$

It can be seen that with these restrictions the arguments of the hypergeometric functions in Eq. (3) are within the circle of convergence of the series definition of these functions, and analytical continuation is not necessary.

In application only one evaluation of the function ${}_2F_1$ by series summation is needed. If we write

$$f_k \equiv {}_2F_1(a, k; n; \xi),$$

then

$$f_n = (1-\xi)^{-a}$$

$$f_{n+1} = \left[1 + \frac{a\xi}{n(1-\xi)}\right] f_n$$

and, for $j > n$,

$$f_{j+1} = \{(n-j) f_{j-1} + [2j - n + (a-j)\,\xi] f_j\}/[j(1-\xi)].$$

Since STO's are usually chosen so that μ and $\nu \geqslant l$, this suffices for the evaluation of the function with two integral parameters in Eq. (3). For the others define

$$g_j \equiv {}_2F_1(a, n + j; a + j; \xi).$$

Then

$$g_0 = (1 - \xi)^{-n} \tag{4}$$

$$g_1 = a \sum_{k=0}^{\infty} \binom{n+k}{k} \frac{\xi^k}{a+k} = a \int_0^1 t^{a-1}(1 - t\xi)^{-n-1}\, dt \tag{5}$$

and, for $j \geqslant 1$

$$g_{j+1} = \{[a + j - 1 - (a - j - n)\,\xi]\, g_j - (a + j - 1)\, g_{j-1}\}(a + j)/[(n + j)\, j\xi]. \tag{6}$$

These recursion relations are easily derived from the Gauss formulas connecting contiguous hypergeometric functions.

The two evaluations of the function V in Eq. (2) require in the inner summation the same sequence of values of ${}_2F_1$, and these can be saved from the first calculation for use in the second. Since the number needed is not known ahead, the following technique was used: an array of suitable size (200–300 words) was set to zero; on the first call to the subprogram for evaluating ${}_2F_1$, Eqs (4), (5), and (6) were used to build in this array a table of values up to the currently needed one. On subsequent calls the value was taken from the table unless the value thus found was zero, in which case Eq. (6) was used to extend the table. The inner sums in Eq. (3) depend on k only through its appearance in the upper limit, and so once the first of these is evaluated, subsequent ones require only the addition of a single term, not a complete summation. Finally, these inner sums usually reach a constant value (within machine precision) long before the outer summation can be stopped; time can be saved if the program recognizes this and discontinues calculating new values of the inner sum.

This procedure has several opportunities for loss of numerical accuracy, but analytical determination of the parameter values, if any, that will actually lead to serious loss appears very difficult. Printing of intermediate results indicates that the first term of the outer sum in Eq. (3) is typically positive, that all further contributions to it are negative, and that the final value is a negative number larger in magnitude than the initial value. So long as this pattern holds the evaluation of this sum is numerically satisfactory. The subtraction of the two terms in Eq. (3) causes no loss, since they are of opposite signs, and so the magnitudes are added.

The performance on typical data can be judged from Table 1. In each of the cases listed one of the STO's is an eigenfunction of $\mathscr{H}_l$, and this fact has been used in calculating the exact values for comparison. It can be seen that no serious loss

TABLE I

Examples of Calculations of $\langle \varphi_1 \mid (\mathscr{H} + \mathscr{E})^{-1} \mid \varphi_2 \rangle^a$

l	Z	$\mathscr{E}$	μ	α	ν	β	$\langle r^{\mu} e^{-\alpha r} \mid (\mathscr{H} + \mathscr{E})^{-1} \mid r^{\nu} e^{-\beta r} \rangle$, exact value	Error in Calculated Value	Relative Error	Time (msec)
0	2	1.0	0	2.0	1	3.0	$-6/625 = -0.0096$	7×10^{-17}	7×10^{-15}	17
0	2	0.250	0	2.0	0	1.0	$-8/189 = -0.042328042328042328$	3×10^{-16}	7×10^{-15}	13
1	2	0.25	1	1.0	2	3.0	$-15/128 = -0.1171875$	-3×10^{-16}	-3×10^{-15}	17
1	2	0.25	1	1.0	1	1.5	$-3072/3125 = -0.98304$	-2×10^{-15}	-2×10^{-15}	17
2	3	0.25	3	9.0	2	1.0	$-2016/10^7 = -0.0002016$	-1×10^{-18}	-5×10^{-15}	20
3	4	0.245	4	24.0	3	1.0	$-(25367150592/17) \times 10^{-17} = 0.149218532894 \times 10^{-7}$	-2×10^{-18}	-1×10^{-10}	40
0	10	0.405	0	10.0	2	30.0	$-(6/1269632) \times 10^{-3} = -0.4725778808347615 \times 10^{-8}$	-3×10^{-23}	-8×10^{-15}	30

[a] All calculations were done in REAL*8 format on an IBM 370/165 computer; the timer resolution is 1/60 second.

of accuracy occured except in one case, and even in that one about ten figures were correct.

The computer program, written in FORTRAN IV and assembler language for an IBM 370, has been submitted to the Quantum Chemistry Program Exchange. An all-FORTRAN version for adaptation to other machines is also available.

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