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Analytic Evaluation of Integrals in Variational Calculations of Scattering Theory*

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Analytic procedures are presented for the evaluation of the free–free exchange integrals which occur in the variational approach to scattering theory. Expressions are obtained which are suitable for numerical calculation on a computer. The method is based on a (known) analytic formula for the complex Laplace transform of the exponential integral function.

Interest in the application of variational methods in the scattering of electrons and positrons by atoms has increased substantially in recent years [1–5]. Such calculations involve integrals of a type not encountered in bound state problems. These incorporate both bound state and continuum type functions. The evaluation of such integrals has been discussed by Lyons and Nesbet [6] and by Harris and Michels [7]. In our work on the scattering problem, we have somewhat different continuum functions than employed by these authors and we have developed procedures for the required integrals. These procedures enable analytic expressions to be obtained for all integrals, including the troublesome free-free exchange integrals. The expressions are easily adopted for numerical evaluation on a computer.

The continuum wavefunctions should behave asymptotically as appropriate combinations of the linearly independent solutions for a free particle. The radial parts of the linearly independent solution are the spherical Bessel and Neumann functions $j_l(kr)$ and $n_l(kr)$. In the literature cited, the component of the external solution which behaves asymptotically as $j_l(kr)$ has been referred to as the "S" function, while the other has been called a "C" function. The singularity of the Neumann function at the origin is troublesome in such calculations, and a choice

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suggested by Armstead [8] has frequently been employed. Neglecting angular factors, this is

$$C_a = [j_{l_a+1}(k_a r) + \frac{l+1}{k_a r} j_{l_a+2}(k_a r)]. \tag{1a}$$

The subscript a refers to a particular channel

$$S_a = j_{l_a}(k_a r) \tag{1b}$$

The function C_a given above has the potentially undesirable property that it differs from the correct function n_l by terms of order r^{-3} at large r. It is, of course, not singular at the origin. Since inaccuracies in the asymptotic functions must be compensated by the "short-range functions," we believe that it is more desirable to use functions which are correct for values of r for which terms of order r^{-3} are not negligible. The following choice for the function C_a is nonsingular and differs from the free particle solution by terms which are exponentially small at large r:

$$C_a = (1 - e^{-\beta r})^{2l_a+1}\, n_{l_a}(k_a r). \tag{2a}$$

We also find it convenient to introduce a similar exponential factor into S_l, although this is not required in order to prevent a singularity

$$S_l = (1 - e^{-\gamma r})^{2l+1}\, j_l(kr). \tag{2b}$$

The "cut-off" factors involving the exponentials actually make the integrals easier to compute and at the same time are useful in testing the quality of the results obtained. The calculated cross sections (or R matrix elements) should be independent of the values chosen for β and γ, since these quantities do not affect the asymptotic values of S_a and C_a. The results can be tested for stability with respect to variation of β and γ. Stability must be obtained if the calculations are to have physical significance.

We are interested in matrix elements of the type

$$\langle \eta_a(1)\, S_d(2)\, Y^M_{Ll_al_d}(\Omega_1\Omega_2) \left| \frac{1}{r_{12}} \right| S_b(1)\, \eta_c(2)\, Y^M_{Ll_bl_c}(\Omega_1\Omega_2)\rangle, \tag{3}$$

in which the η are Slater type orbitals

$$\eta_a = N_a r^{n_a} e^{-\zeta_a r} Y_{l_a m_a}(\theta, \phi), \tag{4}$$

N_a is a normalization constant, and $n_a \geqslant l_a$. The function $Y^M_{Ll_al_d}(\Omega_1\Omega_2)$ is an angular function for two particles for a state specified by total angular momentum

L, azimuthal component M, and individual particle angular momenta l_a and l_d. Specifically,

$$Y^M_{L,l_al_d}(\Omega_1\Omega_2) = \sum_{m_am_d} (l_am_al_dm_d \mid l_al_dLM)\, Y^{m_a}_{l_a}(\Omega_1)\, Y^{m_d}_{l_d}(\Omega_2). \tag{5}$$

Here $(l_am_al_dm_d \mid l_al_dLM)$ is a vector coupling coefficient as defined by Edmonds [9]. Integrals in which one or both S's are replaced by a C are also required. Integrals of this class are free-free exchange integrals. Although our free–free direct integrals and bound–free integrals differ in some respects from those considered in Refs. [6, 7], their evaluation does not pose serious problems and many of the procedures described in those references are applicable. Our detailed considerations here will be limited to the troublesome integrals of type (3).

We proceed by expressing the functions j_l and n_l as finite trigonometric series. Thus,

$$n_l(kr) = \sum_{m=1}^{l+1} a_m^{(l)} \frac{\sin(kr + \theta_m)}{r^m}, \tag{6}$$

in which θ_m is either 0 or $\pi/2$ and $a_m^{(l)}$ is a number. A similiar series exists for j_l. The usefulness of the cut-off factors is that when the series expansions (6) are substituted in the matrix element, no singularities exist at the origin. Each term in S_l or C_l is proportional to r^l or a higher power of r near the origin.

After the angular integrations have been performed, the matrix element (3) can be expressed as a sum of integrals of the form

$$\begin{aligned} &U(l_1, n_1, l_2, n_2, l \mid \beta, p, k_b, \theta_b, \gamma, q, k_d, \theta_d) \\ &\quad = \int_0^\infty dr \int_0^\infty dx (1 - e^{-\beta x})^{l_1}\, x^{n_1} e^{-px} \sin(k_b x + \theta_b) \\ &\quad\quad \times \frac{r_<^l}{r_>^{l+1}} (1 - e^{-\gamma r})^{l_2}\, r^{n_2} e^{-qr} \sin(k_d r + \theta_d). \end{aligned} \tag{7}$$

The specific relation between the matrix element and the U integrals is

$$\begin{aligned} &\left\langle \eta_a(1)\, S_d(2)\, Y^M_{Ll_al_d}(\Omega_1\Omega_2) \left| \frac{1}{r_{12}} \right| S_b(1)\, \eta_c(2)\, Y^M_{Ll_bl_c}(\Omega_1\Omega_2) \right\rangle \\ &\quad = N_aN_c \sum_{m_bm_d} a_{m'}^{(d)} a_{m'}^{(b)} C(L, l_a, l_d; l; l_bl_c) \\ &\quad\quad \times U(l_1, n_1, l_2, n_2, l \mid \beta_b, p, k_b, \theta_b, \beta_d, q, k_d, \theta_d), \end{aligned} \tag{8}$$

in which C is a numerical coefficient depending on the angular momenta involved

$$C(L, l_a, l_d; l, l_b, l_c) = (-1)^{l_a+l_b-L}[(2l_a+1)(2l_b+1)(2l_c+1)(2l_d+1)]^{1/2} \times \begin{Bmatrix} L & l_d & l_a \\ l & l_b & l_c \end{Bmatrix} \begin{pmatrix} l_b & l & l_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_c & l & l_d \\ 0 & 0 & 0 \end{pmatrix}. \tag{9}$$

Here $\{\cdots\}$ represents a $6-j$ symbol, while $(\cdots)$ stands for a $3-j$ symbol and

$$l_1 = 2l_b + 1, \qquad l_2 = 2l_d + 1,$$
$$n_1 = n_a + 2 - m_b \geqslant n_a + 1 - l_b; \qquad n_2 = n_c + 2 - m_d \geqslant n_c + 1 - l_d, \tag{10}$$

while $r_<(r_>)$ is the lesser (greater) of r and x. The index l lies in the range

$$\max\{|l_a - l_b|, |l_c - l_d|\} \leqslant l \leqslant \min\{l_a + l_b, l_c + l_d\}. \tag{11}$$

We see that both $n_1 + l$ and $n_2 + l \geqslant 1$. Further, it is easily verified that

$$l_1 - (l+1) \geqslant 0, \qquad \text{and} \quad l_2 - (l+1) \geqslant 0,$$

so that there are no singularities at either $x = 0$ or $r = 0$.

Let us consider the integral on x first. Thus

$$U = A + B$$

with

$$A = \int_0^\infty dr(1 - e^{-\gamma r})^{l_2} r^{n_2-l-1} e^{-qr} \sin(k_d r + \theta_d) I_1(r),$$
$$B = \int_0^\infty dr(1 - e^{-\gamma r})^{l_2} r^{n_2+l} e^{-qr} \sin(k_d r + \theta_d) I_2(r), \tag{12}$$

and

$$I_1(r) = \int_0^r dx(1 - e^{-\beta x})^{l_1} x^{n_1+l} e^{-px} \sin(k_b x + \theta_b),$$
$$I_2(r) = \int_r^\infty dx(1 - e^{-\beta x})^{l_1} x^{n_1-l-1} e^{-px} \sin(k_b x + \theta_b). \tag{13}$$

In order to evaluate these expressions, it is convenient to introduce the auxiliary integral

$$F(\mu, l, m, a, k_1, \theta_1, k_2, \theta_2) = \int_0^\infty e^{-\mu x}(1 - e^{-ax})^l x^m \sin(k_1 x + \theta_1) \sin(k_2 x + \theta_2)\, dx. \tag{14}$$

This integral is defined for $m \geqslant -l$ ($l > 0$) and can be evaluated by elementary techniques. A computer program was written to evaluate F using a recurrence relation based on integration by parts. The procedure is described briefly in the appendix. We also need the indefinite integral ($m \geqslant 0$)

$$\int x^m e^{-\mu x} \sin(kx + \theta)\, dx$$

$$= m! e^{-\mu x} \sum_{\nu=1}^{m+1} \frac{1}{(m+1-\nu)!} \frac{x^{m+1-\nu}}{(\mu^2 + k^2)^{\nu/2}} \sin(kx + \theta + \nu\alpha), \tag{15}$$

in which $\alpha = \tan^{-1} k/\mu$.

We also require an integral similar to (13) but with the parameter m negative. This integral can be given in terms of functions related to the exponential integral

$$\int_r^\infty \frac{e^{-\mu x}}{x^n} \sin(kx + \phi)\, dx = \operatorname{Im} \left\{ \frac{e^{i\phi}}{r^{n-1}} E_n[(\mu - ik)r] \right\}, \tag{16}$$

in which E_n is [10]

$$E_n(z) = \int_1^\infty \frac{e^{-zt}}{t^n}\, dt.$$

This function is defined for z such that $\operatorname{Re}(z) > 0$.

The double integral A [Eq. (12)] can be evaluated using Eqs. (14) and (15), since the exponent $n_1 + l$ in I_1 is never negative. In this case, it is convenient to expand the factor $(1 - e^{-\beta x})^{l_1}$ in binomial series:

$$A = (n_1 + l)! \sum_{t=0}^{l_1} (-1)^t \binom{l_1}{t} \left\{ \frac{1}{[(p + t\beta)^2 + k_b{}^2]^{(n_1 + l_1 + 1)/2}} \right.$$

$$\times F(q, l_2, n_2 - l - 1, \gamma, k_a, \theta_a, 0, \theta_b + \alpha(n_1 + l + 1))$$

$$- \sum_{\nu=1}^{n_1+l+1} \frac{1}{(n_1 + l + 1 - \nu)!} \frac{1}{[(p + t\beta)^2 + k_b{}^2]^{\nu/2}}$$

$$\left. \times F(p + q + t\beta, l_2, n_2 + n_1 - \nu, \gamma, k_a, \theta_a, k_b, \theta_b + \nu\alpha) \right\}. \tag{17}$$

The parameter α is defined by

$$\alpha = \tan^{-1} [k_b/(p + t\beta)]. \tag{18}$$

The complications of the exchange problem are contained in B. There are two cases:

(I) $n_1 - l - 1 \geqslant 0$

(II) $n_1 - l - 1 < 0$.

Case I can be treated by the procedure used for A.

$$B = (n_1 - l - 1)! \sum_{t=0}^{l_1} (-1)^t \binom{l_1}{t} \sum_{\nu=1}^{n_1-l} \frac{1}{(n_1 - l - \nu)!} \frac{1}{[(p + t\beta)^2 + k_b{}^2]^{\nu/2}}$$

$$\times F(p + q + t\beta, l_2, n_2 + n_1 - \nu, \gamma, k_d, \theta_d, k_b, \theta_b + \nu\alpha). \tag{19}$$

The quantity α remains as defined in Eq. [15].

In Case II, (13) is used to calculate I_2. We then encounter integrals of the form

$$J_{m,n}(z) = \int_0^\infty e^{-zt} t^m E_n(t)\, dt, \tag{20}$$

in which m and n are positive integers and z is complex. These integrals can be obtained by differentiation of a tabulated integral, the Laplace transform of E_n [10]. The result is

$$J_{m,n}(z) = (-1)^{n-1} \Bigg\{ \frac{(n + m - 1)!}{(n - 1)!} z^{-(n+m)} \ln(1 + z)$$

$$- \sum_{k=1}^{m} \frac{(n + m - k - 1)!m!}{k(n - 1)!(m - k)!} \frac{z^{-(n+m-k)}}{(1 + z)^k}$$

$$+ \sum_{k=1}^{n-1} \frac{(-1)^k}{k} \frac{(n + m - k - 1)!}{(n - 1 - k)!} z^{-(n+m-k)} \Bigg\}. \tag{21}$$

The computation of $J_{m,n}$ can be delicate. Equation (18) would appear to indicate that $J_{m,n}(z)$ is highly singular at $z = 0$. However, this is not the case, and there is a considerable amount of cancellation between the terms of (18). An alternative expression for $J_{m,n}(z)$ exists which can be used conveniently to generate a power series expansion for small z.

$$J_{m,n}(z) = m! \int_1^\infty \frac{du}{u^n(u + z)^{m+1}} = \sum_{k=0}^\infty \frac{(-1)^k(m + k)!}{k!(m + n + k)} z^k. \tag{22}$$

After some straightforward algebra, we obtain

$$B = -\tfrac{1}{2} \sum_{t=0}^{l_1} (-1)^t \binom{l_1}{t} \sum_{s=0}^{l_2} (-1)^s \binom{l_2}{s} \operatorname{Re}\{z_2^{-(m+1)}$$

$$\times [e^{i(\theta_a+\theta_b)} J_{m,\mu}(z_1/z_2) - e^{-i(\theta_a-\theta_b)} J_{m,\mu}(z_1{}^*/z_2)]\}, \tag{23}$$

in which $m = n_1 + n_2$, $z_1 = q + s\gamma - ik_a$,

$$\mu = l + 1 - n_1, \qquad z_2 = p + t\beta - ik. \tag{24}$$

These expressions can be readily evaluated on a computer using complex arithmetic.

The combination of [17] and either [19] or [23] according to the value of the parameters, completes the determination of the free–free exchange integral U, as specified by Eq. (6).

We conclude with a numerical example, which arises in the electron–hydrogen scattering problem. This involves the free–free exchange integral with hydrogenic $2p$ wavefunctions and continuum functions. We will present results for the combination

$$U(1, 2, 1, 2, 0, \mid \beta, p, k, \theta_b, \beta, p, k, \theta_a)$$
$$+ \tfrac{2}{5} U(1, 2, 1, 2, 2 \mid \beta, p, k, \theta_b, \beta, p, k, \theta_a). \tag{25}$$

The factor of (2/5) connecting the U functions with $l = 0$ and $l = 2$ arises from the angular factors in (8). We have compared the results obtained through the procedure described here with that obtained by numerical integration in which the infinite integrals are terminated at R_m (Table I).

TABLE I

Value of Combination (25)

θ_a	θ_b	Procedure as described	$R_m = 20$	$R_m = 50$
0	0	2.7714013	2.7714774	2.7714014
0	$\pi/2$	−1.1209391	−1.1175317	−1.1209391
$\pi/2$	0	−1.1209391	−1.1175484	−1.1209391
$\pi/2$	$\pi/2$	5.0165918	5.0136147	5.0165918

The fixed parameters employed have the values (atomic units)

$$\beta = 1.0,$$
$$p = 0.5,$$
$$k^2 = 0.46.$$

The program as constructed appears to yield accurate values to eight significant figures. We believe this to be sufficient accuracy for the problems of interest to us. Minor changes in the programs could be made which would lead to greater precision if this were necessary. Round-off and cancellation errors in the computation of J_{mn} are controlled by choosing Eq. (22) instead of Eq. (21) if

$$| z | < 1.0/m$$

or, if $m = 0{,}1$,

$$z < 0.5.$$

The series (22) is terminated when the last term added is less than 10^{-15}.

One point is obvious from inspection of Table I. If numerical integration is considered as a possible simple alternate to the procedure described here, it is necessary to continue to large values of r. As calculations are extended to more highly excited states than those of the $n = 2$ shell, the exponential factors in the wavefunctions decay less rapidly. We believe that for such states, numerical evaluation of the integrals would be a time-consuming alternative.

APPENDIX: Computation of Integrals of Type F

We consider here computation of integrals of the type F, as defined by Eq. (14). For positive values of m, the computation is entirely straightforward and need not be described here. Consider then the situation for negative values of m.

Suppose first that $m = -1$ and $l = 1$. We obtain elementary integrals of the form

$$\begin{aligned} &F(\mu, 1, -1, a, k_1, \theta_1, k_2\theta_2) \\ &\quad = \int_1^\infty \frac{[e^{-\mu x} - e^{-(\mu+a)x}]}{x} \sin(k_1 x + \theta_1)\sin(k_2 x + \theta_2)\, dx \\ &\quad = \tfrac{1}{2} \sum_{p=\pm 1} p \left\{ \tfrac{1}{2} \cos\phi \ln\left[\frac{(\mu + a)^2 + s^2}{\mu^2 + s^2}\right] - \sin\phi \left[\tan^{-1}\frac{s}{a} - \tan^{-1}\frac{s}{\mu + a}\right]\right\}, \end{aligned} \tag{A.1}$$

in which $\phi = \theta_1 - p\theta_2$, $s = k_1 - pk_2$.

We can then obtain values of F for any l (but $m = -1$), since

$$F(\mu, l+1, -1, a, k_1, \theta_1, k_2, \theta_2) = F(\mu, l, -1, a, k_1, \theta_1, k_2, \theta_2) - F(\mu + a, l, -1, a, k_1, \theta_1, k_2, \theta_2). \quad \text{(A.2)}$$

The values of F for $m < -1$ are now determined from those obtained for $m = -1$ through successive application recurrence of a relation obtained through intergration by parts. This relation is

$$\begin{aligned} &F(\mu, l, -m, a, k_1, \theta_1, k_2, \theta_2) \\ &\quad = (m-1)^{-1}\{laF(\mu + a, l-1, -m+1, a, k_1, \theta_1, k_2, \theta_2) \\ &\qquad - \mu F(\mu, l, -m+1, a, k_1, \theta_1, k_2, \theta_2) \\ &\qquad + k_1 F(\mu, l, -m+1, a, k_1, \theta_1 + \pi/2, k_2, \theta_2) \\ &\qquad + k_2 F(\mu, l, -m+1, a, k_1, \theta_1, k_2, \theta_2 + \pi/2)\}. \end{aligned}$$

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