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Fourier transform of the product of N one-center hydrogenic orbitals

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Integrating the radial part of the Fourier transform of the product of N hydrogenic orbitals results in an associated Legendre function that can be reduced to a finite series of elementary functions. This transform is found to depend on a polynomial in the wave vector k divided by a binomial in k^2 raised to a power that is the sum of principle quantum numbers. This form facilitates the analytical reduction of integrals arising from orthogonalization corrections in atomic processes. Transforms for the product of orbital pairs $(1s,1s)$ through $(1s,3d)$ are given explicitly.

I. INTRODUCTION

Matrix elements in atomic physics are sometimes more easily integrated by Fourier transforming parts of the integrand and then using a technique such as Feynman parametrization.[1] The general formula for the Fourier transform of a hydrogenic orbital in an arbitrary state, found by Podolski and Pauling,[2] is sufficient to calculate the first-order scattering amplitude for three-body charge transfer,[3,4] but knowledge of the Fourier transform of a product of two hydrogenic orbitals,

$$I_{\nu\tau}(\mathbf{k})=\int d^3r\, e^{-i\mathbf{k}\cdot\mathbf{r}}u_\nu^*(\mathbf{r})u_\tau(\mathbf{r}) , \tag{1}$$

is required for matrix elements involving bound-state projection operators such as orthogonalization corrections in charge transfer.[5,6]

Fourier transforms of pairs of orbitals (in arbitrary states) centered on different coordinates, used for evaluating Coulomb integrals in molecular physics, have been given in various forms containing one-dimensional integrals.[7] For principle quantum numbers of ν and τ equal, Alper[8] has found an analytic solution in terms of four-dimensional spherical harmonics.

Because of the simplification of one-center orbitals, an analytic result for (1) can be found for specific pairs using straightforward, but tedious, integration term by term. In Sec. II of this paper a finite-series solution is found for general ν and τ that is in an elementary form conducive to Feynman parametrization. The equations for the special cases $\nu=ns$ and $\nu=1s$, which contain fewer sums than the equations for the general case, are also given. Explicit transforms for $\nu=1s$ and $\tau=\{1s$ through $3d\}$ are listed. In Sec. III it is shown that the present approach is easily extended to include the Fourier transform of the product of any number of hydrogenic orbitals.

II. THE FOURIER TRANSFORM OF THE PRODUCT OF TWO HYDROGENIC ORBITALS

First expand the exponential and the orbitals as series,

$$e^{-i\mathbf{k}\cdot\mathbf{r}}=4\pi\sum_{\mathsf{L}=0}^{\infty}\sum_{\mathsf{M}=-\mathsf{L}}^{\mathsf{L}}(-i)^{\mathsf{L}}j_{\mathsf{L}}(kr)Y_{\mathsf{LM}}(\hat{\mathbf{k}})Y^*_{\mathsf{LM}}(\hat{\mathbf{r}}) , \tag{2}$$

and

$$u_{ulm}(\mathbf{r})=(P_0)^{3/2}N_{nl}F_{nl}(2P_0r/n)Y_{lm}(\hat{\mathbf{r}}) , \tag{3}$$

where

$$P_0=Z/a_0 , \tag{4}$$

and

$$N_{nl}F_{nl}(x)=\frac{2}{n^2}\sqrt{(n-l-1)!(n+l)!}\times\sum_{s=0}^{n-l-1}\frac{(-1)^s x^{s+l}e^{-x/2}}{(n-l-1-s)!(2l+1+s)!s!} , \tag{5}$$

and similarly for the primed orbital.

Using the product formula[9] and completeness for spherical harmonics, the angular part of (1) is integrated to give

$$\int d\Omega\, Y^*_{\mathsf{LM}}(\Omega)Y^*_{l'm'}(\Omega)Y_{lm}(\Omega)=(-1)^{m'}\sum_{L=|l-l'|}^{l+l'}\sum_{M=-L}^{L}(-1)^M\left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}\right]^{1/2}\times\begin{pmatrix} l & l' & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l' & L\\ m & -m' & M\end{pmatrix}\delta_{\mathsf{L}L}\delta_{\mathsf{M},-M} . \tag{6}$$

The δ functions remove the infinite summations in (2) and the second 3-j symbol is zero[10] unless $-M=m-m'$ so that (1) can be written

$$I_{n'l'n',nlm}(\mathbf{k})=\sum_{L=|l-l'|}^{l+l'}(-1)^{-m}[(2l+1)(2l'+1)(2L+1)]^{1/2}\times\begin{bmatrix} l & l' & L \\ 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} l & l' & L \\ m & -m' & m'-m \end{bmatrix} I^L_{n'l'm',nlm}(k)Y_{L,m-m'}(\hat{\mathbf{k}}) \;, \tag{7}$$

where

$$I^L_{n'l'm',nlm}(k)=(-i)^L 8\sqrt{\pi}\frac{(P_0P_0')^{3/2}}{n^2n'^2}\sqrt{(n'-l'-1)!(n'+l')!(n-l-1)!(n+l)!}\times\sum_{s=0}^{n-l-1}\sum_{s'=0}^{n'-l'-1}\frac{(-1)^{s+s'}(2P_0/n)^{l+s}(2P_0'/n')^{l'+s'}I_{Lw}(\gamma,k)}{(n-l-1-s)!(2l+1+s)!s!(n'-l'-1-s')!(2l'+1+s')!s'!} \;, \tag{8}$$

$$\begin{aligned} I_{Lw}(\gamma,k)&=\sqrt{\pi/2k}\int_0^\infty dr\, r^{w+5/2-1}e^{-\gamma r}J_{L+1/2}(kr) \\ &=\frac{\sqrt{\pi/2k}\,\Gamma(L+w+3)}{(\gamma^2+k^2)^{(w+5/2)/2}}P_{w+3/2}^{-(L+1/2)}[\gamma(\gamma^2+k^2)^{-1/2}] \;, \end{aligned} \tag{9}$$

$$\gamma=P_0/n+P_0'/n' \;,$$

and

$$w=l+s+l'+s'>L \;, \tag{10}$$

Ref. 11.

The form of the solution in (9) is compact but is not conducive to subsequent analytic momentum integration. Using recursion relations[12] repeatedly it can be shown that

$$P^{-\omega}_{\omega+1+y}(\cos\phi)=\sum_{g=1}^{t}\frac{C_{yg}(\cos\phi)^{y-2g+3}(\sin\phi)^{1+2g-2}}{\Gamma(g+\omega)2^{\omega+g-1}} \;, \tag{11}$$

where

$$t=\begin{cases}(y+2)/2 & \text{for } y \text{ even} \\ (y+3)/2 & \text{for } y \text{ odd} \;,\end{cases} \tag{12}$$

$$C_{y1}=1, \quad C_{12}=-1, \quad \text{and} \quad C_{yg}=C_{y-1,g}-yC_{y-2,g-1} \;. \tag{13}$$

Then the final form for (9) is

$$I_{Lw}(\gamma,k)=\frac{(L+w+2)!}{(\gamma^2+k^2)^{w+2}}\sum_{g=1}^{t}D_{Lyg}\gamma^{y-2g+3}k^{L+2g-2} \tag{14}$$

$$=\frac{(L+w+2)!}{(\gamma^2+k^2)^{n+n'}}\sum_{g=1}^{t}\sum_{u=0}^{c}D_{Lyg}\gamma^{2(c-g-u)+y+3}\times k^{2(g+u-1)+L} \;, \tag{15}$$

where

$$D_{Lyg}=C_{yg}/\{[2(g+L)-1]!!\} \;,$$

$$y=w-L \;,$$

and

$$c=n+n'-w-2 \;. \tag{16}$$

For the special case of $l'=m'=0$, the summation in (7) collapses to one term $L\equiv l$ giving[13]

$$I_{n'00,nlm}(\mathbf{k})=I^l_{n'00,nlm}(k)Y_{lm}(\hat{\mathbf{k}}) \;, \tag{17}$$

$$w=l+s+s' \;,$$

and

$$y=s+s' \;. \tag{18}$$

If $n'=1$, the s' sum also collapses to one term $s'\equiv 0$ and

$$w=l+s \;,$$

and

$$y=s \;. \tag{19}$$

Finally, if $n-l-1=0$ (a nodeless wave function), the remaining three sums collapse to the valuer $s\equiv 0$, $g\equiv 1$, and $u\equiv 0$.

The Fourier transforms (1) for the common case, $n'=1$ and $P_0=P_0'$, are given below for $\tau=\{1s \text{ through } 3d\}$:

$$I_{1s,1s}(k)=\frac{32\sqrt{\pi}}{[4+(k/P_0)^2]^2} \;, \tag{20}$$

$$I_{1s,2s}(k)=\frac{512\sqrt{2\pi}(k/P_0)^2}{[9+4(k/P_0)^2]^3} \;, \tag{21}$$

$$I_{1s,2p}(k)=\frac{-i256\sqrt{6\pi}(k/P_0)}{[9+4(k/P_0)^2]^3} \;, \tag{22}$$

$$I_{1s,3s}(k)=\frac{864\sqrt{3\pi}[16(k/P_0)^2+27(k/P_0)^4]}{[16+9(k/P_0)^2]^4}\ , \tag{23}$$

$$I_{1s,3p}(k)=\frac{-i\,576\sqrt{6\pi}(k/P_0)[16+27(k/P_0)^2]}{[16+9(k/P_0)^2]^4}\ , \tag{24}$$

and

$$I_{1s,3d}(k)=\frac{-13824\sqrt{30\pi}(k/P_0)^2}{5[16+9(k/P_0)^2]^4}\ . \tag{25}$$

III. THE FOURIER TRANSFORM OF THE PRODUCT OF N HYDROGENIC ORBITALS

The Fourier transform of a product of N hydrogenic orbitals occurring in higher-order orthogonalization correction terms, can be found using the same function, (14) or (15). However, for each additional orbital two series must be introduced; one to account for the product of spherical harmonics, and another for the expansion of the Laguerre polynomials as in (5). The general result is

$$I_{\sigma_1\sigma_2\cdots\sigma_N}(\mathbf{k})=\int d^3r\, e^{-i\mathbf{k}\cdot\mathbf{r}}u_{\sigma_1}(\mathbf{r})u_{\sigma_2}(\mathbf{r})\cdots u_{\sigma_N}(\mathbf{r}) \tag{26}$$

$$=\prod_{j=2}^{N}\left[\sum_{L_j=|L_{j-1}-l_j|}^{L_{j-1}+l_j}(-1)^{-\mu_j}[(2L_{j-1}+1)(2l_j+1)(2L_j+1)/4\pi]^{1/2}\times\begin{bmatrix}L_{j-1} & l_j & L_j\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}L_{j-1} & l_j & L_j\\ \mu_{j-1} & m_j & -\mu_j\end{bmatrix}\right] I^{L_N}_{\sigma_1\sigma_2\cdots\sigma_N}(k)Y_{L_Nm_N}(\hat{\mathbf{k}})\ , \tag{27}$$

where

$$I^{L_N}_{\sigma_1\sigma_2\cdots\sigma_N}(k)=\frac{(-i)L_N2^{N+2}\pi}{(\gamma^2+k^2)^{n_1+n_2+\cdots+n_N}}\prod_{i=1}^{N}\left[\frac{P_{0i}^{3/2}}{n_i^2}\sqrt{(n_i-l_i-1)!(n_i+l_i)!}\times\sum_{s_i=0}^{n_i-l_i-1}\frac{(-1)^{s_i}(2P_{0i}/n_i)^{l_i+s_i}}{(n_i-l_i-1-s_i)!(2l_i+1+s_i)!s_i!}(L_N+w_{ls}+2)!\times\sum_{g=1}^{t}\sum_{u=0}^{c}D_{L_Nyg}\gamma^{2(c-g-u)+y+3}k^{2(g+u-1)+L_N}\right]\ , \tag{28}$$

$$y=w_{ls}-L_N,\quad c=n_1+n_2+\cdots+n_N-w_{ls}-2,\quad L_1\equiv l_1\ , \tag{29}$$

$$\mu_j=\sum_{i=1}^{j}m_i,\quad w_{ls}=\sum_{h=1}^{N}l_h+s_h,\quad \gamma_N=\sum_{h=1}^{N}P_{0h}/n_h\ , \tag{30}$$

and where every L_j depends on all preceding L_j's. If the complex conjugate of any u_j in (26) is taken, then one must multiply (27) by $(-1)^{m_j}$ and change m_j to $-m_j$ throughout.

IV. DISCUSSION

The evaluation of matrix elements of atomic scattering theories that include orthogonalization corrections requires knowledge of the Fourier transform of products of one-centered hydrogenic orbitals. It has been shown that the Fourier transform of the product of N hydrogenic orbitals in arbitrary quantum states can be written as $1/(\gamma^2+k^2)^{n_1+n_2+\cdots+n_N}$ multiplied by a polynomial in k. Such a form allows any subsequent momentum expressions to be integrated by methods such as Feynman parametrization. One often considers cases where the σ_j represent low quantum numbers so that each series in (15), (27), and (28) involves only a few terms. Additionally, the form of (15) minimizes errors in combining terms with common powers of p. However, if it is possible to perform any subsequent momentum integration for a general term of (15), then a computer can sum the resulting terms even for large N or high quantum states. This approach was used as an independent check on the orthogonalization corrections for resonant charge transfer in proton-hydrogen scattering.[5]

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[1]Introducing the identity

$$\frac{1}{a^m b^n}=\frac{(m+n-1)!}{(m-1)!(n-1)!}\int_0^1 \frac{t^{m-1}(1-t)^{n-1}}{[at+b(1-t)]^{m+n}}dt$$

allows one to combine vector quantities from a and b so that a three-dimensional integral containing this product of denominators may be calculated by completing the square or by a convenient choice of axes, leaving a one-dimensional integral in the parameter t. See, R. P. Feynman, Phys. Rev. **76**, 769 (1949); and C. J. Joachain, *Quantum Collision Theory* (North-Holland, Amsterdam, 1983), p. 678.

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[10]See Ref. 9, p. 3.

[11]I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), Eq. 6.621 (1), last line, p. 711.

[12]See Ref. 11, Eq. 8.735 (4), p. 1006, and Eq. 8.755 (1), p. 1008.

[13]See Ref. 9, p. 12.