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A Method for Achieving Analytic Formulas for Three Body Integrals Consisting of Powers and Exponentials in All Three Interparticle Hyllerass Coordinates

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A Method for Achieving Analytic Formulas for Three Body Integrals Consisting of Powers and Exponentials in All Three Interparticle Hylleraas Coordinates

by

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Abstract

After an introduction to the variational principle of three body systems via the Helium atom, we present general analytical formulas for the radial parts of integrals that occur when three body systems are described using wave functions that consist of powers and exponentials in all three interparticle Hylleraas coordinates [1]. This work is an extension of integrals given by Harris, Frolov and Smith, Jr. [2]. Specifically included are radial integrals encountered in calculations involving the dipole moment matrix element in Hylleraas coordinates that contain a function $f(kr_1)$ (such as a spherical Bessel function) in addition to a plane wave, a hydrogenic orbital and exponentials in all three interparticle coordinates.

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Introduction

This paper consists of two main sections. The first section is an introduction to the variational principle for three body systems, which is an approximation technique that provides accurate ground state energies and wavefunctions. Once the accurate ground state wavefunctions are found by the variational principle, the second section is a novel way of obtaining closed form analytical formulas for the matrix elements of a dipole transition, $\mu_z = \int \psi_d^*(z_1 + z_2)\psi_c d\tau$. This leads directly to the atomic absorption coefficient, $\sigma = (6.812 \times 10^{-20} cm^2) k(k^2 + 2I) \left|\mu_z\right|^2$, an important quantity of interest for photodetachment.

Section 1

The Ground State of Helium

The Helium atom consists of two electrons in orbit around a nucleus that contains two protons. The non-relativistic Hamiltonian, neglecting the motion of the nucleus and given in atomic units, is

$$H = -\frac{1}{2}\left(\nabla_{r_1}^2 + \nabla_{r_2}^2\right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1}$$

where r_1 and r_2 denote the electron distances from the nucleus [3].

In this study, we would like to determine the ground state energy (the amount of energy it would take to strip off the two electrons) and ground state wavefunction for this system. The ground state energy has been measured with great precision in the laboratory. The experimental value for the ground state energy of helium is $E = -79.005151042\ eV$ [4]. This is the number we would like to reproduce theoretically. In many other three-body problems with non-Coulombic potentials there have been found exact solutions. For an example of "heliumlike" potentials that have exact solutions see Crandall, Whitnell and Betteha [5]. Straton has demonstarated the usefulness of integral transforms for determining analytically reduced forms for a general class of integrals containing multicenter products of 1s hydrogenic orbitals, Yukawa or Coulomb potentials, and plane waves [6][7][8][9]. Yet, it is an unfortunate fact that no exactly solvable solutions (in terms of algebraic expressions) exist for the helium atom.

The feature that makes solving this system difficult is the electron/electron repulsion term. Therefore, we will start by ignoring the electron/electron repulsion term. Thus, the approximated Hamiltonian is,

$$H = -\frac{1}{2}\left(\nabla^2_{r_1} + \nabla^2_{r_2}\right) - \frac{2}{r_1} - \frac{2}{r_2} \tag{2}$$

With the electron/electron repulsion term ignored, the Hamiltonian is just two independent hydrogen Hamiltonians with twice the Coulomb potential. Let us assume two 1s hydrogen electrons have the radial wavefunction:

$$\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \psi_{He}(\mathbf{r}_1,\mathbf{r}_2) = Ae^{-\lambda(r_1+r_2)} \tag{3}$$

where λ equals Z/a_0. We write the 1s hydrogen electron ground state in the form,

$$\psi_{100}(\mathbf{r}) = \frac{\lambda^{3/2}}{\sqrt{\pi}}e^{-\lambda r}. \tag{4}$$

Thus the normalization constant for the total system is,

$$A = \frac{\lambda^3}{\pi}. \tag{5}$$

Using the eigensystem equation,

$$H\psi = E\psi, \tag{6}$$

the ground state wavefunction is spherically symmetric. Thus, the angular part is constant and we find

$$\begin{aligned} H\psi = -\tfrac{1}{2}\left(\tfrac{1}{r_1^2}\tfrac{\partial}{\partial r_1}\left(r_1^2\tfrac{\partial}{\partial r_1}\right)Ae^{-\lambda(r_1+r_2)} + \tfrac{1}{r_2^2}\tfrac{\partial}{\partial r_2}\left(r_2^2\tfrac{\partial}{\partial r_2}\right)Ae^{-\lambda(r_1+r_2)}\right) \\ -\tfrac{2}{r_1}Ae^{-\lambda(r_1+r_2)} - \tfrac{2}{r_2}Ae^{-\lambda(r_1+r_2)} \end{aligned} \tag{7}$$

or

$$H\psi = \left[-\frac{1}{2}\left(\lambda^2 - \frac{2\lambda}{r_1} + \lambda^2 - \frac{2\lambda}{r_2}\right) - \frac{2}{r_1} - \frac{2}{r_2}\right]Ae^{-\lambda(r_1+r_2)}. \tag{8}$$

The equality must hold for any r_1 and r_2,

$$\begin{aligned} -\tfrac{1}{2}\lambda^2 + \tfrac{\lambda}{r_1} - \tfrac{1}{2}\lambda^2 + \tfrac{\lambda}{r_2} - \tfrac{2}{r_1} - \tfrac{2}{r_2} &= E \\ -\lambda^2 + \tfrac{\lambda-2}{r_1} + \tfrac{\lambda-2}{r_2} &= E. \end{aligned} \tag{9}$$

Therefore, $\lambda = 2$, and $E = -4\ a.u.$ Using $1\ a.u. = 27.211\ eV$, we find $E = -108.8\ eV$.

However, the above solution ignored the electron/electron repulsion. The electron/electron repulsion term is [10]

$$V_{12} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{4\pi}{2l+1} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{r_<^l}{r_>^{l+1}} Y_{lm}(\theta_1, \phi_1) Y_{lm}^*(\theta_2, \phi_2) \tag{10}$$

with expectation value

$$< V_{12} >= A^2 \iint \frac{e^{-2\lambda(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \tag{11}$$

or

$$\begin{aligned} < V_{12} > &= A^2 \textstyle\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \iint e^{-2\lambda(r_1+r_2)} \frac{r_<^l}{r_>^{l+1}} r_1^2 r_2^2 dr_1 dr_2 \\ & \quad \times \textstyle\iint Y_{lm}(\theta_1, \phi_1) sin\theta_1 d\theta_1 d\phi_1 \\ & \quad \times \textstyle\iint Y_{lm}^*(\theta_2, \phi_2) sin\theta_2 d\theta_2 d\phi_2. \end{aligned} \tag{12}$$

Looking at the first spherical part and knowing that $Y_{00} = Y_{00}^* = \frac{1}{\sqrt{4\pi}}$, we have

$$\iint Y_{lm}(\theta_1, \phi_1) sin\theta_1 d\theta_1 d\phi_1 = \sqrt{4\pi} \iint Y_{lm}(\theta_1, \phi_1) Y_{00}^*(\theta_1, \phi_1) sin\theta_1 d\theta_1 d\phi_1 = \sqrt{4\pi}\delta_{0l}\delta_{0m}. \tag{13}$$

Therefore Eq. (12) simplifies to

$$< V_{12} >= A^2 \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \iint e^{-2\lambda(r_1+r_2)} \frac{r_<^l}{r_>^{l+1}} r_1^2 r_2^2 dr_1 dr_2 \sqrt{4\pi}\delta_{0l}\delta_{0m}\sqrt{4\pi}\delta_{0l}\delta_{0m}$$
$$= 16\pi^2 A^2 \iint e^{-2\lambda(r_1+r_2)} \frac{1}{r_>} r_1^2 r_2^2 dr_1 dr_2. \tag{14}$$

In order to integrate this expression, we pick the limits of integration carefully,

$$< V_{12} >= 16\pi^2 A^2 \int e^{-2\lambda r_2} \left[\int_0^{r_2} e^{-2\lambda r_1} r_1^2 r_2 dr_1 + \int_{r_2}^{\infty} e^{-2\lambda r_1} r_1 r_2^2 dr_1 \right] dr_2, \tag{15}$$

which can also be shown to be

$$\begin{aligned} < V_{12} > &= 16\pi^2 A^2 \int e^{-2\lambda r_2} \left[\frac{r_2 - e^{-2\lambda r_2} r_2 - \lambda e^{-2\lambda r_2} r_2^2}{4\lambda^3} \right] dr_2 \\ &= 16\pi^2 A^2 \frac{5}{128\lambda^5} \\ &= 16\pi^2 \left(\frac{\lambda^3}{\pi} \right)^2 \frac{5}{128\lambda^5} \\ &= \frac{5}{8}\lambda \\ &= \frac{5}{4} \end{aligned} \tag{16}$$

in atomic units. Thus, $E = -4\ a.u. + \frac{5}{4}\ a.u. = -\frac{11}{4}\ a.u.$ or $E = -74.8\ eV$. This is an improvement on the first approximation, which ignores the electron/electron interaction.

Using the Variational Principle

In most cases, it is best to use the variational technique to improve the wavefunction. Let λ be our variational parameter that will need to be minimized at the end of our calculation. Starting with the trial wavefuction,

$$\psi_{He}(\mathbf{r}_1,\mathbf{r}_2) = \frac{\lambda^3}{\pi} e^{-\lambda(r_1+r_2)}. \tag{17}$$

The expectation value is

$$
\begin{aligned}
< H > &= \iint \left[-\lambda^2 + \tfrac{\lambda-2}{r_1} + \tfrac{\lambda-2}{r_2}\right] \tfrac{\lambda^6}{\pi^2} e^{-2\lambda(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + \tfrac{5}{8}\lambda \\
&= -\tfrac{\lambda^8}{\pi^2} \iint e^{-2\lambda(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&\quad + (\lambda-2)\tfrac{\lambda^6}{\pi^2} \iint \tfrac{1}{r_1} e^{-2\lambda(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&\quad + (\lambda-2)\tfrac{\lambda^6}{\pi^2} \iint \tfrac{1}{r_2} e^{-2\lambda(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 + \tfrac{5}{8}\lambda
\end{aligned}
\tag{18}
$$

Let us do this piece by piece. The first integral is

$$
\begin{aligned}
&\iint e^{-2\lambda(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&= 16\pi^2 \int e^{-2\lambda r_1} r_1^2 dr_1 \int e^{-2\lambda r_2} r_2^2 dr_2 \\
&= 16\pi^2 \tfrac{1}{4\lambda^3} \tfrac{1}{4\lambda^3} \\
&= \tfrac{\pi^2}{\lambda^6}.
\end{aligned}
\tag{19}
$$

Now, the second integral is

$$
\begin{aligned}
&\iint \tfrac{1}{r_1} e^{-2\lambda(r_1+r_2)} d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&= 16\pi^2 \int e^{-2\lambda r_1} r_1 dr_1 \int e^{-2\lambda r_2} r_2^2 dr_2 \\
&= 16\pi^2 \tfrac{1}{4\lambda^2} \tfrac{1}{4\lambda^3} \\
&= \tfrac{\pi^2}{\lambda^5}.
\end{aligned}
\tag{20}
$$

Therefore,

$$
\begin{aligned}
< H > &= -\tfrac{\lambda^8}{\pi^2}\tfrac{\pi^2}{\lambda^6} + (\lambda-2)\tfrac{\lambda^6}{\pi^2}\tfrac{\pi^2}{\lambda^5} + (\lambda-2)\tfrac{\lambda^6}{\pi^2}\tfrac{\pi^2}{\lambda^5} + \tfrac{5}{8}\lambda \\
&= -\lambda^2 + (\lambda-2)\lambda + (\lambda-2)\lambda + \tfrac{5}{8}\lambda \\
&= \lambda^2 - \tfrac{27}{8}\lambda.
\end{aligned}
\tag{21}
$$

We find the minimum of this function to be:

$$
\frac{d}{d\lambda} < H >= 2\lambda - \frac{27}{8} = 0 \tag{22}
$$

or

$$\lambda = \frac{27}{16} = 1.6875. \tag{23}$$

Thus, the ground state energy is

$$E = -\frac{729}{256}\ a.u. = -2.848\ a.u. = -77.5\ eV \tag{24}$$

which is within 2% of the experimental value.

Hylleraas coordinates

The most common coordinates in which to compute the variational integrals are the Hylleraas coordinates [1]. In this coordinate system, one uses wavefunctions of the type

$$\psi(r_1, r_2, r_{12}) = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \sum_{l,m,n} c_{lmn} s^l t^{2m} u^n, \tag{25}$$

where $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|$ and $\hat{P}_{12}$ is the permutation operator for two identical electrons. The Hylleraas approach explicitly accounts for the interactional motions of the two electrons through the variable $u = r_{12}$. In fact the Hylleraas coordinate system is not a formal solution for the helium atom [11] [12], yet it has had great success in yielding accurate values for the ground state energies of three body systems. For example, a basis set of six wavefunctions could look like [13],

$$\begin{aligned}\psi_1 &= e^{-\alpha r_1-\beta r_2-\gamma r_{12}}\\ \psi_2 &= e^{-\alpha r_1-\beta r_2-\gamma r_{12}}u\\ \psi_3 &= e^{-\alpha r_1-\beta r_2-\gamma r_{12}}t^2\\ \psi_4 &= e^{-\alpha r_1-\beta r_2-\gamma r_{12}}s\\ \psi_5 &= e^{-\alpha r_1-\beta r_2-\gamma r_{12}}s^2\\ \psi_6 &= e^{-\alpha r_1-\beta r_2-\gamma r_{12}}u^2,\end{aligned} \tag{26}$$

where

$$\psi = \sum_i c_i \psi_i \tag{27}$$

From this, one can obtain $E = -2.90324$ $a.u.$, which differs from the "exact" value by only 0.00048 $a.u.$ In fact, the ground state of Helium is one of the most accurate theoretical numbers that has been calculated by quantum mechanical approximation methods. In particular, K. Frankowski and C.L. Pekeris obtained in 1966 the value $E = -2.9037243770326$ $a.u.$ [14]. It should be noted that in this discussion we have ignored the the mass polarisation term $(-\frac{1}{M}\nabla_{r_1}\cdot\nabla_{r_2})$ and relativistic correction term $(-\frac{\hat{p}^4}{8c^2})$ that are given in Pekeris' earlier work [15][16].

The usual volume element $d^3r_1d^3r_2 = r_1^2r_2^2 sin\theta_1 sin\theta_1 dr_1dr_2d\theta_1d\theta_2d\phi_1d\phi_2$, can be modified by referring to Euler angles. The Euler angles are defined as:

$$\begin{gathered}\theta_1 = \Theta; \phi_1 = \Phi\\ cos\theta_2 = cos\Theta cos\Theta_2 + sin\Theta sin\Theta_2 cos\Psi\\ sin\theta_2 sin(\phi_2 - \Phi) = sin\Theta_2 sin\Psi\\ cos\theta_n = cos\Theta cos\Theta_n + sin\Theta sin\Theta_n cos(\Psi + \phi_n)\\ sin\theta_n sin(\phi_n - \Phi) = sin\Theta sin(\Psi + \phi_n); n > 2,\end{gathered} \tag{28}$$

where n allows one to generalize to more particles if needed. The motivation for using the Euler angles Θ, Φ, Ψ, is the important fact that the angles can be separated from one another and can be solved for more readily [17]. Using these angles transforms the volume element into

$$dV = d^3r_1d^3r_2 = r_1^2r_2^2dr_1dr_2sin\theta_1sin\theta_{12}d\theta_1d\theta_{12}d\phi_1d\Psi. \tag{29}$$

Since the functions involved depend only on r_1, r_2 and r_{12}, the angles ϕ_1, θ_1 and ψ can be integrated, producing a factor of $8\pi^2$, leaving

$$dV = 8\pi^2r_1^2r_2^2dr_1dr_2sin\theta_{12}d\theta_{12}. \tag{30}$$

Using, $r_{12}^2 = r_1^2+r_2^2-2r_1r_2cos\theta_{12}$, we have that $r_1r_2sin\theta_{12}d\theta_{12} = r_{12}dr_{12}$; consequently,

$$dV = 8\pi^2r_1r_2r_{12}dr_1dr_2dr_{12}. \tag{31}$$

Note that the volume element is only a function of r_1, r_2, r_{12}. This allows integration over three coordinates rather than the usual six.

Let P be the probability density such that,

$$P = 8\pi^2\int_0^\infty\int_0^\infty\int_{|r_1-r_2|}^{r_1+r_2}\psi^*\psi r_1r_2r_{12}dr_1dr_2dr_{12}. \tag{32}$$

Note, the absolute values can be handled by

$$|r_1-r_2| = \begin{cases} r_1-r_2 & r_1 \geq r_2 \\ -(r_1-r_2) & r_1 < r_2 \end{cases} \tag{33}$$

Thus,

$$P = 8\pi^2\int_0^\infty\left[\int_0^{r_2}\int_{-(r_1-r_2)}^{r_1+r_2}\psi^*\psi r_1r_2r_{12}dr_{12}dr_1 + \int_{r_2}^\infty\int_{r_1-r_2}^{r_1+r_2}\psi^*\psi r_1r_2r_{12}dr_{12}dr_1\right]dr_2 \tag{34}$$

The Hamiltonian in the basis (r_1, r_2, r_{12}) is

$$
\begin{aligned}
H \;=\; & -\tfrac{1}{2}\tfrac{\partial^2}{\partial r_1^2} - \tfrac{1}{2}\tfrac{\partial^2}{\partial r_2^2} - \tfrac{\partial^2}{\partial r_{12}^2} - \tfrac{1}{r_1}\tfrac{\partial}{\partial r_1} - \tfrac{1}{r_2}\tfrac{\partial}{\partial r_2} - \tfrac{2}{r_{12}}\tfrac{\partial}{\partial r_{12}} \\
& -\tfrac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}}\tfrac{\partial^2}{\partial r_1 \partial r_{12}} - \tfrac{r_2^2 - r_1^2 + r_{12}^2}{2r_2 r_{12}}\tfrac{\partial^2}{\partial r_2 \partial r_{12}} \\
& -(\tfrac{Z}{r_1} + \tfrac{Z}{r_2} - \tfrac{1}{r_{12}}).
\end{aligned}
\tag{35}
$$

(See Appendix for derivation.)

The overlap integral matrix elements is defined as $\Delta_{ij} = \langle \psi_i \mid \psi_j \rangle$ or

$$
\Delta_{ij} = \begin{bmatrix}
\langle \psi_1 \mid \psi_1 \rangle & \langle \psi_1 \mid \psi_2 \rangle & \langle \psi_1 \mid \psi_1 \rangle & \cdots \\
\langle \psi_2 \mid \psi_1 \rangle & \langle \psi_2 \mid \psi_2 \rangle & \langle \psi_2 \mid \psi_3 \rangle & \cdots \\
\langle \psi_3 \mid \psi_1 \rangle & \langle \psi_3 \mid \psi_2 \rangle & \langle \psi_3 \mid \psi_3 \rangle & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}. \tag{36}
$$

This is sometimes referred to as the metric because it shares many similar properties to those of g_{uv}, the gravitational tensor. Projecting the overlap integral onto the coordinate basis,

$$
\begin{aligned}
\langle \psi_i \mid \psi_j \rangle &= \left\langle \psi_i \left| \int |r\rangle \langle r| \, dV \right| \psi_j \right\rangle \\
&= \int \langle \psi_i \,|\, r \rangle \langle r \mid \psi_j \rangle \, dV \\
&= \int \psi_i^* \psi_j dV,
\end{aligned}
\tag{37}
$$

it can be seen that

$$
\langle \psi_i \mid \psi_j \rangle = 8\pi^2 \int_0^\infty \int_0^\infty \int_{|r_1 - r_2|}^{r_1 + r_2} \psi_i^* \psi_j r_1 r_2 r_{12} dr_1 dr_2 dr_{12}. \tag{38}
$$

Likewise, for the Hamiltonian matrix elements, we have

$$
\langle \psi_i \,| H |\, \psi_j \rangle = 8\pi^2 \int_0^\infty \int_0^\infty \int_{|r_1 - r_2|}^{r_1 + r_2} \psi_i^* (H \psi_j) r_1 r_2 r_{12} dr_1 dr_2 dr_{12}, \tag{39}
$$

where

$$H_{ij} = \begin{bmatrix} \langle\psi_1 |H| \psi_1\rangle & \langle\psi_1 |H| \psi_2\rangle & \langle\psi_1 |H| \psi_3\rangle & \dots \\ \langle\psi_2 |H| \psi_1\rangle & \langle\psi_2 |H| \psi_2\rangle & \langle\psi_2 |H| \psi_3\rangle & \cdots \\ \langle\psi_3 |H| \psi_1\rangle & \langle\psi_3 |H| \psi_2\rangle & \langle\psi_3 |H| \psi_3\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}. \tag{40}$$

The eigensystem is

$$H\psi = E\psi. \tag{41}$$

Muliplying by both sides by ψ^* and integrating over all space the energy eigenvalue can be expressed as

$$E = \frac{\int \psi^*(H\psi)dV}{\int \psi^*\psi dV} = \frac{\sum c_i^* c_j H_{ij}}{\sum c_i^* c_j \Delta_{ij}}. \tag{42}$$

where $\psi = \sum c_i\psi_i$ and the sigma means we sum over any repeated index ([18] p.187). Thus,

$$E \sum c_i^* c_j \Delta_{ij} = \sum c_i^* c_j H_{ij}. \tag{43}$$

To find the values of c_i that make E a minimum, we differentiate with respect to each c_k:

$$\frac{\partial E}{\partial c_k} \sum c_i^* c_j \Delta_{ij} + E \frac{\partial}{\partial c_k} \sum c_i^* c_j \Delta_{ij} = \frac{\partial}{\partial c_k} \sum c_i^* c_j H_{ij}. \tag{44}$$

The condition for a minimum is that $\frac{\partial E}{\partial c_k} = 0$ for all $k = 1, 2, 3...$, which leads to the set of equations to diagonalize,

$$\sum_i c_i(H_{ij} - \Delta_{ij}E) = 0. \tag{45}$$

For smaller basis sets, we may also use the fact that for a non-trivial solution it is necessary the determinant of the coefficients to vanish,

$$det[H_{ij} - \Delta_{ij} E] = 0. \tag{46}$$

This equation leads to a large polynomial in E, where the lowest value energy, E_{min}, corresponds to the ground-state energy. Plugging E_{min} back into $\sum_i c_i(H_{ij} - \Delta_{ij} E) = 0$, one can determine the coefficients c_i.

Section 2

Photodetachment

Starting in the 1940's, Chandrasekhar expanded on the study of the continuous absorption coefficient of the negative hydrogen ion initiated by Jen [19]. The key problem is to evaluate the (length gauge) dipole transition matrix element $\mu_z = \int \psi_d^*(z_1 + z_2)\psi_c d\tau$ [20], where ψ_d denotes the wave function of the ground state of the ion and ψ_c is a continuum state wave function correspond to the outgoing electron. Once the dipole transition matrix elements are evaluated, the standard length formula for the atomic absorption coefficient is

$$\sigma = (6.812 \times 10^{-20} cm^2) k(k^2 + 2I) \left|\mu_z\right|^2, \tag{47}$$

where I denotes the electron affinity and k is the momentum of the ejected electron, with all quantities in atomic units [21][22][13]. Evaluating μ_z for wave functions ψ_d of the Hylleraas form [1] has historically been done via numerical integration. We present an analytical integration method for such wave functions herein. Although this formalism was developed for the specific problem of photodetachment, it is likely to find utility in other problems that calculate dipole transitions involving single photons or laser fields. In order to evaluate μ_z, we shall assume ψ_d to be a wave function of the Hylleraas form, and ψ_c a plane wave representation of the outgoing electron and a 1s state for the remaining electron:

$$\psi_c = \frac{1}{\sqrt{2\pi}}(e^{ikz_1 - r_2} + e^{ikz_2 - r_1}), \tag{48}$$

where we have chosen the z-axis of the coordinate system to correspond to the propagation direction of the outgoing electron.

Definitions

The Hylleraas coordinate system [1] utilizes coordinates $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|$, and one builds wavefunction of the type

$$\psi_d(r_1, r_2, r_{12}) = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12})e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \sum_{l,m,n} c_{lmn} s^l t^{2m} u^n. \tag{49}$$

The action of the Hamiltonian on Hylleraas wavefunctions leads to generic radial integrals of the type found by Calais and Lowdin [23], Sack, Roothaan and Kolos [24], and more recently Bhatia [25][26]

$$\Gamma_{lmn}(\alpha, \beta, \gamma) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_{12} r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}, \tag{50}$$

where α, β, γ are non-negative real numbers. We also assume that l, m, n are non-negative integers. A compact analytical formula for Eqn. (50) has been provided by Harris, Frolov and Smith [2],

$$\Gamma_{lmn}(\alpha, \beta, \gamma) = 2l!m!n! \sum_{l'=0}^{l} \sum_{m'=0}^{m} \sum_{n'=0}^{n} \frac{\begin{pmatrix} m - m' + l' \\ l' \end{pmatrix} \begin{pmatrix} l - l' + n' \\ n' \end{pmatrix} \begin{pmatrix} n - n' + m' \\ m' \end{pmatrix}}{(\alpha + \beta)^{m - m' + l' + 1} (\alpha + \gamma)^{l - l' + n' + 1} (\beta + \gamma)^{n - n' + m' + 1}}. \tag{51}$$

Integrals $\Lambda_{lmn}(\alpha,\beta,\gamma;k)$

In the calculations of electric dipole moments elements using Hylleraas wavefunctions, one encounters integrals of the form

$$\Lambda_{lmn}(\alpha,\beta,\gamma;k)=\frac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}}r_1^l r_2^m r_{12}^n(z_1+z_2)(e^{ikz_1-r_2}+e^{ikz_2-r_1})d^3x_1d^3x_2, \tag{52}$$

where we have dropped the normalization constant $1/\sqrt{2\pi}$ from ψ_c. This is the integral we must evaluate. The approach we adopt, however, may well be generalizable to a wider set of single photoionization and laser problems where one can find integrals that take on similar forms to Eqn. (52) [27][28] [29][30]. Eqn. (52) can be written in the form

$$\begin{aligned}\Lambda_{lmn}(\alpha,\beta,\gamma;k) &= \tfrac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}}r_1^l r_2^m r_{12}^n z_1 e^{ikz_1-r_2}d^3x_1d^3x_2\\ &+ \tfrac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}}r_1^l r_2^m r_{12}^n z_1 e^{ikz_2-r_1}d^3x_1d^3x_2\\ &+ \tfrac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}}r_1^l r_2^m r_{12}^n z_2 e^{ikz_1-r_2}d^3x_1d^3x_2\\ &+ \tfrac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}}r_1^l r_2^m r_{12}^n z_2 e^{ikz_2-r_1}d^3x_1d^3x_2.\end{aligned} \tag{53}$$

We will break this into smaller pieces by defining each term in the previous equation as

$$\begin{aligned}\Lambda_{lmn}(\alpha,\beta,\gamma;k) &= \Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k)\\ &+ \Lambda^{12}_{lmn}(\alpha,\beta,\gamma;k)\\ &+ \Lambda^{21}_{lmn}(\alpha,\beta,\gamma;k)\\ &+ \Lambda^{22}_{lmn}(\alpha,\beta,\gamma;k).\end{aligned} \tag{54}$$

Integrals $\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k)$

We first focus our attention on the term,

$$\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) = \frac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^l r_2^m r_{12}^n z_1 e^{ikz_1-r_2} d^3x_1 d^3x_2. \tag{55}$$

Using spherical harmonic expansions [31];

$$z = r\sqrt{\frac{4\pi}{3}}Y_{10}(\theta,\phi)\;, \tag{56}$$

and

$$e^{ikrcos\theta} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(kr)Y_{lm}(\theta_r,\phi_r)Y^*_{lm}(\theta_k,\phi_k)\;, \tag{57}$$

it can be shown that

$$\begin{aligned}\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi}\sqrt{\tfrac{4\pi}{3}}\textstyle\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^l r_2^m r_{12}^n r_1 Y_{10}(\theta_1,\phi_1) \\ & \times e^{-r_2}\textstyle\sum_{L=0}^{\infty}\sum_{m=-L}^{L} i^L j_L(kr_1)Y_{LM}(\theta_1,\phi_1)Y^*_{LM}(\theta_k,\phi_k)d^3x_1d^3x_2.\end{aligned} \tag{58}$$

By expressing the volume element in terms of the solid angle $d\Omega_{12}$ (See Calais [23])

$$\begin{aligned} d^3x_1d^3x_2 &= r_1^2 sin\theta_1 dr_1 d\theta_1 d\phi_1 r_2^2 sin\theta_2 dr_2 d\theta_2 d\phi_2 \\ &= r_1^2 sin\theta_1 dr_1 d\theta_1 d\phi_1 r_2^2 sin\theta_{12} dr_2 d\theta_{12} d\phi_{12} \\ &= r_1^2 dr_1 d\Omega_1 r_2^2 dr_2 d\Omega_{12}, \end{aligned} \tag{59}$$

we may more readily evaluate the integral. With this transformation, one finds

$$\begin{aligned}\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi}\sqrt{\tfrac{4\pi}{3}}\textstyle\sum_{L=0}^{\infty}\sum_{m=-L}^{L} i^L Y^*_{LM}(\theta_k,\phi_k) \\ & \times \textstyle\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^n e^{-r_2} j_L(kr_1)dr_1dr_2 \\ & \times \textstyle\int Y_{10}(\theta_1,\phi_1)Y_{LM}(\theta_1,\phi_1)d\Omega_1\int d\Omega_{12}.\end{aligned} \tag{60}$$

Using orthogonality,

$$\begin{aligned}\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) &= \frac{1}{2\pi}\sqrt{\frac{4\pi}{3}}\sum_{L=0}^{\infty}\sum_{m=-L}^{L} i^L Y^*_{LM}(\theta_k,\phi_k) \\ &\times\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^n e^{-r_2} j_L(kr_1)dr_1 dr_2 \\ &\times\delta_{L1}\delta_{M0}\int d\Omega_{12}\end{aligned} \tag{61}$$

or

$$\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) = \frac{1}{2\pi}i\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^n e^{-r_2} j_1(kr_1)dr_1 dr_2\int d\Omega_{12}. \tag{62}$$

The last integral can be written out in terms of spherical angles,

$$\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) = \frac{1}{2\pi}i\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^n e^{-r_2} j_1(kr_1)dr_1 dr_2\int sin\theta_{12}d\theta_{12}d\phi_{12}. \tag{63}$$

Now we can convert angles into magnitudes by law of cosines

$$cos\theta_{12} = \frac{r_1^2+r_2^2-r_{12}^2}{2r_1r_2}. \tag{64}$$

This gets one into a function of the basis (r_1, r_2, r_{12}) by noting that

$$r_{12}dr_{12} = r_1r_2sin\theta_{12}d\theta_{12}. \tag{65}$$

In order to determine the limits, we note that when $\theta_{12} = 0$ then $cos\theta_{12} = 1$. Therefore we have $r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2$ and we find $r_{12} = |r_1 - r_2|$. Also, when $\theta_{12} = \pi$ then $cos\theta_{12} = -1$. Therefore we have $r_{12}^2 = r_1^2 + r_2^2 + 2r_1r_2$ and $r_{12} = r_1 + r_2$. Using Eqn. (65) with the correct limits of integration and after evaluating the ϕ_{12} integral, we find the result,

$$\Lambda^{11}_{lmn}(\alpha,\beta,\gamma;k) = i\int\int\int_{|r_1-r_2|}^{r_1+r_2} e^{-\alpha r_1-(\beta+1)r_2-\gamma r_{12}} r_1^{l+2} r_2^{m+1} r_{12}^{n+1} j_1(kr_1) dr_1 dr_2 dr_{12}. \tag{66}$$

Integrals $\Lambda^{12}_{lmn}(\alpha,\beta,\gamma;k)$

The second term is

$$\Lambda^{12}_{lmn}(\alpha,\beta,\gamma;k) = \frac{1}{8\pi^2}\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^l r_2^m r_{12}^n z_1 e^{ikz_2-r_1} d^3x_1 d^3x_2 \tag{67}$$

or

$$\begin{aligned}\Lambda^{12}_{lmn}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi}\sqrt{\tfrac{4\pi}{3}}\textstyle\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^l r_2^m r_{12}^n r_1 Y_{10}(\theta_1,\phi_1) \\ & e^{-r_1}\textstyle\sum_{L=0}^{\infty}\sum_{m=-L}^{L} i^L j_L(kr_2) Y_{LM}(\theta_2,\phi_2) Y^*_{LM}(\theta_k,\phi_k) d^3x_1 d^3x_2.\end{aligned} \tag{68}$$

Using the expansion [32],

$$\begin{aligned}Y_{10}(\theta_1,\phi_1) &= \textstyle\sum_{M'=-1}^{1}[D^{(1)}_{0M'}(0,\theta_2,\phi_2)]^* Y_{1M'}(\theta_{12},\phi_{12}) \\ &= \textstyle\sum_{M'=-1}^{1}[\sqrt{\tfrac{4\pi}{3}} Y_{1M'}(,\theta_2,\phi_2)]^* Y_{1M'}(\theta_{12},\phi_{12})\end{aligned} \tag{69}$$

one finds

$$\begin{aligned}\Lambda^{12}_{lmn}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi}\tfrac{4\pi}{3}\textstyle\sum_{L=0}^{\infty}\sum_{M=-L}^{L}\sum_{M'=-1}^{1} i^L Y^*_{LM}(\theta_k,\phi_k) \\ & \times\textstyle\int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^n e^{-r_1} j_L(kr_2) dr_1 dr_2 \\ & \times\textstyle\int Y^*_{1M'}(\theta_2,\phi_2) Y_{LM}(\theta_2,\phi_2) d\Omega_2 \int Y_{1M'}(\theta_{12},\phi_{12}) d\Omega_{12}\end{aligned}$$

$$
\begin{aligned}
= \quad & \tfrac{1}{2\pi}\tfrac{4\pi}{3}\sum_{L=0}^{\infty}\sum_{M=-L}^{L}\sum_{M'=-1}^{1} i^L Y_{LM}^*(\theta_k,\phi_k)r_2 \\
& \times \int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^{n} e^{-r_1} j_L(kr_2)dr_1 d \\
& \times \delta_{L1}\delta_{M'M}\int Y_{1M'}(\theta_{12},\phi_{12})d\Omega_{12}
\end{aligned}
$$

$$
\begin{aligned}
= \quad & \tfrac{1}{2\pi}\tfrac{4\pi}{3}\sum_{M=-1}^{1} iY_{1M}^*(\theta_k,\phi_k) \\
& \times \int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^{n} e^{-r_1} j_1(kr_2)dr_1 dr_2 \\
& \times \int Y_{1M}(\theta_{12},\phi_{12})d\Omega_{12}.
\end{aligned} \tag{70}
$$

Here we note that $\int e^{i\phi}d\phi = 0$, which means only $M = 0$ will be the non-zero term in the summation. Thus, we have

$$
\begin{aligned}
\Lambda_{lmn}^{12}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi}\tfrac{4\pi}{3} iY_{10}^*(\theta_k,\phi_k) \\
& \times \int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^{n} e^{-r_1} j_1(kr_2)dr_1 dr_2 \\
& \times \int Y_{10}(\theta_{12},\phi_{12})d\Omega_{12}.
\end{aligned} \tag{71}
$$

Expanding $Y_{10}(\theta_{12},\phi_{12})$ in terms of trigonometric functions leads to

$$
\begin{aligned}
\Lambda_{lmn}^{12}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi} i \int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^{n} e^{-r_1} j_1(kr_2)dr_1 dr_2 \\
& \times \int\int cos\theta_{12} sin\theta_{12} d\theta_{12} d\phi_{12}.
\end{aligned} \tag{72}
$$

Applying Eqn. (64) and Eqn. (65) to the angle integral, we find

$$
\begin{aligned}
\Lambda_{lmn}^{12}(\alpha,\beta,\gamma;k) \quad = \quad & \tfrac{1}{2\pi} i \int\int e^{-\alpha r_1-\beta r_2-\gamma r_{12}} r_1^{l+3} r_2^{m+2} r_{12}^{n} e^{-r_1} j_1(kr_2)dr_1 dr_2 \\
& \times \int \tfrac{r_1^2+r_2^2-r_{12}^2}{2r_1 r_2}\tfrac{r_{12}}{r_1 r_2} dr_{12} \int d\phi_{12}
\end{aligned} \tag{73}
$$

or

$$\Lambda^{12}_{lmn}(\alpha,\beta,\gamma;k) = \frac{1}{2}i\int\int\int e^{-(\alpha+1)r_1-\beta r_2-\gamma r_{12}}j_1(kr_2) \times(r_1^{l+3}r_2^{m}r_{12}^{n+1}+r_1^{l+1}r_2^{m+2}r_{12}^{n+1}-r_1^{l+1}r_2^{m}r_{12}^{n+3})dr_1dr_2dr_{12}. \quad (74)$$

The final two integrals $\Lambda^{21}_{lmn}(\alpha,\beta,\gamma;k)$ and $\Lambda^{22}_{lmn}(\alpha,\beta,\gamma;k)$ are essentially identical to the proceding integrals with r_1 and r_2 switched. Putting this all together leads to the result,

$$\begin{aligned}\Lambda_{lmn}(\alpha,\beta,\gamma;k) &= i\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2} dr_{12}j_1(kr_1)r_1^{l+2}r_2^{m+1}r_{12}^{n+1}e^{-\alpha r_1-(\beta+1)r_2-\gamma r_{12}}\\ &+\frac{i}{2}\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2} dr_{12}j_1(kr_1)(r_1^{l}r_2^{m+3}r_{12}^{n+1}+r_1^{l+2}r_2^{m+1}r_{12}^{n+1}-r_1^{l}r_2^{m+1}r_{12}^{n+3})\\ &\qquad\times e^{-\alpha r_1-(\beta+1)r_2-\gamma r_{12}}\\ &+\frac{i}{2}\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2} dr_{12}j_1(kr_2)(r_1^{l+3}r_2^{m}r_{12}^{n+1}+r_1^{l+1}r_2^{m+2}r_{12}^{n+1}-r_1^{l+1}r_2^{m}r_{12}^{n+3})\\ &\qquad\times e^{-(\alpha+1)r_1-\beta r_2-\gamma r_{12}}\\ &+i\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2} dr_{12}j_1(kr_2)r_1^{l+1}r_2^{m+2}r_{12}^{n+1}e^{-(\alpha+1)r_1-\beta r_2-\gamma r_{12}},\end{aligned} \quad (75)$$

where $j_1(x)=\frac{sinx}{x^2}-\frac{cosx}{x}$ is the spherical Bessel function of the first kind.

Integrals $J_{LMN}(a,b,c;k)$

The integrals that make up $\Lambda_{lmn}(\alpha,\beta,\gamma;k)$ share many similarities with $\Gamma_{lmn}(\alpha,\beta,\gamma)$, with one additional function $j_1(kr)$. We follow the definition given by Frolov and Wardlaw [33],

$$J_{LMN}(a,b,c;k)=\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2} dr_{12}j_1(kr_1)r_1^Lr_2^Mr_{12}^Ne^{-ar_1-br_2-cr_{12}}, \quad (76)$$

where a, b, c are non-negative real numbers. We also assume that L, M, N are non-negative integers.

Deriving an analytic formula for integrals of this type is the remaining goal in this study.

By switching the arguments in $J_{LMN}(a, b, c; k)$ to $J_{LMN}(b, a, c; k)$, Eq. (76) can be used in the cases where the spherical Bessel function has kr_2 as its argument. Using $J_{LMN}(a, b, c; k)$, Eqn. (75) becomes

$$\begin{gathered}\Lambda_{lmn}(\alpha,\beta,\gamma;k) = iJ_{l+2,m+1,n+1}(\alpha,\beta+1,\gamma;k) \\ +\tfrac{i}{2}\left[J_{l,m+3,n+1}(\alpha,\beta+1,\gamma;k) + J_{l+2,m+1,n+1}(\alpha,\beta+1,\gamma;k) - J_{l,m+1,n+3}(\alpha,\beta+1,\gamma;k)\right] \\ +\tfrac{i}{2}\left[J_{m,l+3,n+1}(\beta,\alpha+1,\gamma;k) + J_{m+2,l+1,n+1}(\beta,\alpha+1,\gamma;k) - J_{m,l+1,n+3}(\beta,\alpha+1,\gamma;k)\right] \\ +iJ_{m+2,l+1,n+1}(\beta,\alpha+1,\gamma;k),\end{gathered} \tag{77}$$

where we now assume that $l, m,$ are non-negative integers and n is an integer such that $n \geq -1$.

Frolov and Wardlaw [33] recently showed that,

$$J_{000}(a, b, c; k) = \frac{2}{b^2 - c^2}\left[\mathcal{L}(a + c; k) - \mathcal{L}(a + b; k)\right]. \tag{78}$$

In this case, $\mathcal{L}(p; k)$ turns out to be the Laplace transform of the spherical Bessel function $j_1(kr)$, although this procedure generalizes to any function by simply taking the Laplace transform of the specific function desired. In particular, for $j_1(kr)$ [34], [35],

$$\mathcal{L}(p; k) = \frac{1}{k^2}\left[k - p\,tan^{-1}(\frac{k}{p})\right]. \tag{79}$$

General Approach

Following the standard procedure of taking multiple derivatives within Eqn. (78) to obtain higher powers of r_1, r_2, and r_{12} [23],

$$J_{LMN}(a,b,c;k) = (-1)^{L+M+N} \frac{\partial^N}{\partial c^N} \frac{\partial^M}{\partial b^M} \frac{\partial^L}{\partial a^L} J_{000}(a,b,c;k). \tag{80}$$

Noting that only the $\mathcal{L}(p;k)$ part of $J_{000}(a,b,c;k)$ depends explicitly on a, we find that

$$J_{LMN}(a,b,c;k) = (-1)^{M+N} \frac{\partial^N}{\partial c^N} \frac{\partial^M}{\partial b^M} \left\{ \frac{2}{b^2-c^2} [\mathcal{L}_L(a+c;k) - \mathcal{L}_L(a+b;k)] \right\} \tag{81}$$

where

$$\mathcal{L}_L(p;k) = (-1)^L \frac{\partial^L}{\partial a^L} \mathcal{L}(p;k) = (-1)^L \frac{\partial^L}{\partial a^L} \frac{1}{k^2} \left[k - p\, tan^{-1}(\frac{k}{p}) \right]. \tag{82}$$

and $p = a + c$ or $a + b$. It can be shown that

$$\mathcal{L}_L(p;k) = \begin{cases} \frac{1}{k^2}\left[k - p\, tan^{-1}(\frac{k}{p})\right] & L = 0 \\ \frac{1}{k^2}\left[-\frac{kp}{p^2+k^2} + tan^{-1}(\frac{k}{p})\right] & L = 1 \\ \frac{i(L-2)!}{2k^2}\left[\frac{p+ikL}{(p+ik)^L} - \frac{p-ikL}{(p-ik)^L}\right] = & \\ -\dfrac{(L-2)!}{k\,(k^2+p^2)^L} \displaystyle\sum_{j=0}^{L}{}^{(2)} \binom{L}{j} \frac{j(L+1)}{j+1} (-1)^{j/2}\, k^j p^{L-j} & L = 2,3,4,... \\ \frac{1}{3}(L+1)!\frac{k}{p^{L+2}}\, {}_2F_1\left(\frac{L+2}{2}, \frac{L+3}{2}; \frac{5}{2}; -\frac{k^2}{p^2}\right) & L \geq 0 \end{cases}, \tag{83}$$

$$(-1)^L \frac{\partial^L}{\partial p^L} \mathfrak{L}\left(j_l(kr);p\right) = \frac{(L+l)!\Gamma(\frac{1}{2})}{2^{l+1}\Gamma(l+3/2)} \frac{k^l}{p^{l+L+1}} F\left(\frac{L+1+l}{2}, \frac{L+2+l}{2}; l+\frac{3}{2}, -\frac{k^2}{p^2}\right), \tag{84}$$

where the "(2)" on the summation sign in the last line indicates steps of two. We have included Eqn. (84) (for l not necessarily equal to 1) for completeness.

Next, we use the Leibniz product rule for multiple derivatives [36],

$$\begin{aligned} J_{LMN}(a,b,c;k) &= (-1)^{M+N} \sum_{N'=0}^{N} \sum_{M'=0}^{M} \begin{pmatrix} N \\ N' \end{pmatrix} \begin{pmatrix} M \\ M' \end{pmatrix} \frac{\partial^{N'}}{\partial c^{N'}} \frac{\partial^{M'}}{\partial b^{M'}} \frac{2}{b^2-c^2} \\ &\quad \times \frac{\partial^{N-N'}}{\partial c^{N-N'}} \frac{\partial^{M-M'}}{\partial b^{M-M'}} \left[\mathcal{L}_L(a+c;k) - \mathcal{L}_L(a+b;k)\right], \end{aligned} \tag{85}$$

and define the function

$$F_{MN}(b,c) = (-1)^{M+N} \frac{\partial^N}{\partial c^N} \frac{\partial^M}{\partial b^M} \frac{2}{b^2-c^2}. \tag{86}$$

It can be shown that

$$F_{MN}(b,c) = 2M!N! \sum_{M'=0}^{M} \sum_{N'=0}^{N} (-1)^{N'} \frac{\begin{pmatrix} M-M'+N' \\ N' \end{pmatrix}}{(b-c)^{M-M'+N'+1}} \frac{\begin{pmatrix} N-N'+M' \\ M' \end{pmatrix}}{(b+c)^{N-N'+M'+1}}. \tag{87}$$

Thus,

$$J_{LMN}(a,b,c;k) =$$
$$\sum_{N'=0}^{N}\sum_{M'=0}^{M}\begin{pmatrix} N \\ N' \end{pmatrix}\begin{pmatrix} M \\ M' \end{pmatrix} F_{M'N'}(b,c)(-1)^{N-N'+M-M'}\frac{\partial^{N-N'}}{\partial c^{N-N'}}\frac{\partial^{M-M'}}{\partial b^{M-M'}}\mathcal{L}_L(a+c;k)$$
$$-\sum_{N'=0}^{N}\sum_{M'=0}^{M}\begin{pmatrix} N \\ N' \end{pmatrix}\begin{pmatrix} M \\ M' \end{pmatrix} F_{M'N'}(b,c)(-1)^{N-N'+M-M'}\frac{\partial^{N-N'}}{\partial c^{N-N'}}\frac{\partial^{M-M'}}{\partial b^{M-M'}}\mathcal{L}_L(a+b;k). \tag{88}$$

Looking at the term $\frac{\partial^{M-M'}}{\partial b^{M-M'}}\mathcal{L}_L(a+c;k)$, we note that $\mathcal{L}_L(a+c;k)$ is not a function of b. Thus, this term is zero unless $M-M'=0$. Likewise, for the term $\frac{\partial^{N-N'}}{\partial c^{N-N'}}\mathcal{L}_L(a+b;k)$, we see that $N-N'=0$. Therefore,

$$\begin{aligned} J_{LMN}(a,b,c;k) = \sum_{N'=0}^{N}\begin{pmatrix} N \\ N' \end{pmatrix} F_{MN'}(b,c)(-1)^{N-N'}\frac{\partial^{N-N'}}{\partial c^{N-N'}}\mathcal{L}_L(a+c;k) \\ -\sum_{M'=0}^{M}\begin{pmatrix} M \\ M' \end{pmatrix} F_{M'N}(b,c)(-1)^{M-M'}\frac{\partial^{M-M'}}{\partial b^{M-M'}}\mathcal{L}_L(a+b;k). \end{aligned} \tag{89}$$

This finally produces the formula desired for this study

$$\begin{aligned} J_{LMN}(a,b,c;k) \quad = \quad & \sum_{N'=0}^{N}\begin{pmatrix} N \\ N' \end{pmatrix} F_{MN'}(b,c)\mathcal{L}_{L+N-N'}(a+c;k) \\ & -\sum_{M'=0}^{M}\begin{pmatrix} M \\ M' \end{pmatrix} F_{M'N}(b,c)\mathcal{L}_{L+M-M'}(a+b;k). \end{aligned} \tag{90}$$

This procedure can be generalized to any integral of the form

$$J_{LMN}(a,b,c;k) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} f(kr_1) r_1^L r_2^M r_{12}^N e^{-ar_1-br_2-cr_{12}}. \qquad (91)$$

as long as one can find the Laplace transform of $f(kr_1)$.

Conclusion

We have confirmed that by using Hylleraas coordinates, the three body system of helium could be solved via the variational principle, and it generates very accurate results for ground state energies and wavefunctions, which are the starting points for calculations of photodetachment. We then developed an approach that is successful at obtaining closed form analytical formulas for three body integrals containing any function $f(kr_1)$, provided one can find the Laplace transform of the function. Our interest in obtaining these formulas was the application to calculation of photodetachment in three-body atoms. However, such integrals are of interest in many problems in the areas of atomic and nuclear physics. While solutions to these integrals have heretofore been evaluated numerically, the computational load is greatly reduced with an analytical result.

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Appendix

Derivation of the Hamiltonian in Hylleraas Coordinates

We start with the Hamiltonian

$$H = -\frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - (\frac{Z}{r_1} + \frac{Z}{r_1} - \frac{1}{r_{12}}) \tag{92}$$

The Laplacian is defined as

$$\begin{aligned} \nabla^2_{r_1} &= \tfrac{\partial^2}{\partial x_1^2} + \tfrac{\partial^2}{\partial y_1^2} + \tfrac{\partial^2}{\partial z_1^2} \\ \nabla^2_{r_2} &= \tfrac{\partial^2}{\partial x_2^2} + \tfrac{\partial^2}{\partial y_2^2} + \tfrac{\partial^2}{\partial z_2^2}. \end{aligned} \tag{93}$$

We would like to transform into coordinates

$$\begin{aligned} r_1^2 &= x_1^2 + y_1^2 + z_1^2 \\ r_2^2 &= x_2^2 + y_2^2 + z_2^2 \\ r_{12}^2 &= (x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2. \end{aligned} \tag{94}$$

We start with the chain rule

$$\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial r_1}\frac{\partial r_1}{\partial x_1} + \frac{\partial \psi}{\partial r_2}\frac{\partial r_2}{\partial x_1} + \frac{\partial \psi}{\partial r_{12}}\frac{\partial r_{12}}{\partial x_1}. \tag{95}$$

The three derivatives we need are:

$$\frac{\partial r_1}{\partial x_1} = \frac{1}{2}(x_1^2 + y_1^2 + z_1^2)^{-1/2} 2x_1 = \frac{x_1}{r_1}, \tag{96}$$

$$\frac{\partial r_2}{\partial x_1} = 0, \tag{97}$$

$$\frac{\partial r_{12}}{\partial x_1} = \frac{1}{2}((x_2 - x_1)^2 + (y_2 - y_1) + (z_2 - z_1)^2)^{-1/2} 2(x_2 - x_1)(-1) = -\frac{x_2 - x_1}{r_{12}}. \quad (98)$$

Thus,

$$\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial r_1} \frac{x_1}{r_1} + \frac{\partial \psi}{\partial r_2} 0 + \frac{\partial \psi}{\partial r_{12}} \left(-\frac{x_2 - x_1}{r_{12}} \right). \quad (99)$$

However, we still need the second derivative. Applying the chain rule once more, we find

$$\frac{\partial^2 \psi}{\partial x_1^2} = \frac{\partial \psi}{\partial r_1} \frac{\partial}{\partial x_1} \left(\frac{x_1}{r_1} \right) + \frac{\partial^2 \psi}{\partial x_1 dr_1} \frac{x_1}{r_1} + \frac{\partial \psi}{\partial r_{12}} \frac{\partial}{\partial x_1} \left(-\frac{x_2 - x_1}{r_{12}} \right) + \frac{\partial^2 \psi}{\partial x_1 dr_{12}} \left(-\frac{x_2 - x_1}{r_{12}} \right). \quad (100)$$

The derivatives we need are as follows:

$$\frac{\partial}{\partial x_1} \left(\frac{x_1}{r_1} \right) = \frac{1}{r_1} + x_1 \left[-\frac{1}{2} (x_1^2 + y_1^2 + z_1^2)^{-3/2} 2x_1 \right] = \frac{1}{r_1} - \frac{x_1^2}{r_1^3}, \quad (101)$$

$$\begin{aligned} \frac{\partial}{\partial x_1} \left(-\frac{x_2 - x_1}{r_{12}} \right) &= \frac{1}{r_{12}} - (x_2 - x_1) \\ &\quad \times \left[-\frac{1}{2} ((x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2)^{-3/2} 2(x_2 - x_1)(-1) \right] \\ &= \frac{1}{r_{12}} - \frac{(x_2 - x_1)^2}{r_{12}^3}, \end{aligned} \quad (102)$$

$$\begin{aligned} \frac{\partial^2 \psi}{\partial x_1 dr_1} &= \frac{\partial^2 \psi}{\partial r_1^2} \frac{\partial r_1}{\partial x_1} + \frac{\partial^2 \psi}{\partial r_2 \partial r_1} \frac{\partial r_2}{\partial x_1} + \frac{\partial^2 \psi}{\partial r_{12} \partial r_1} \frac{\partial r_{12}}{\partial x_1} \\ &= \frac{\partial^2 \psi}{\partial r_1^2} \frac{x_1}{r_1} + \frac{\partial^2 \psi}{\partial r_2 \partial r_1} 0 + \frac{\partial^2 \psi}{\partial r_{12} \partial r_1} \left(-\frac{x_2 - x_1}{r_{12}} \right), \end{aligned} \quad (103)$$

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial x_1 \partial r_{12}} &= \frac{\partial^2\psi}{\partial r_1 \partial r_{12}}\frac{\partial r_1}{\partial x_1} + \frac{\partial^2\psi}{\partial r_2 \partial r_{12}}\frac{\partial r_2}{\partial x_1} + \frac{\partial^2}{\partial r_{12}^2}\frac{\partial r_{12}}{\partial x_1} \\
&= \frac{\partial^2\psi}{\partial r_1 \partial r_{12}}\frac{x_1}{r_1} + \frac{\partial^2\psi}{\partial r_2 \partial r_{12}}0 + \frac{\partial^2}{\partial r_{12}^2}\left(-\frac{x_2 - x_1}{r_{12}}\right),
\end{aligned} \tag{104}
$$

and

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial x_1^2} = & \frac{\partial\psi}{\partial r_1}\left(\frac{1}{r_1} - \frac{x_1^2}{r_1^3}\right) \\
&+ \left(\frac{\partial^2\psi}{\partial r_1^2}\frac{x_1}{r_1} + \frac{\partial^2\psi}{\partial r_{12}\partial r_1}\left(-\frac{x_2 - x_1}{r_{12}}\right)\right)\frac{x_1}{r_1} + \frac{\partial\psi}{\partial r_{12}}\left(\frac{1}{r_{12}} - \frac{(x_2 - x_1)^2}{r_{12}^3}\right) \\
&+ \left(\frac{\partial^2\psi}{\partial r_1 \partial r_{12}}\frac{x_1}{r_1} + \frac{\partial^2}{\partial r_{12}^2}\left(-\frac{x_2 - x_1}{r_{12}}\right)\right)\left(-\frac{x_2 - x_1}{r_{12}}\right).
\end{aligned} \tag{105}
$$

This produces the result for the second derivative

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial x_1^2} &= \frac{\partial^2\psi}{\partial r_1^2}\frac{x_1^2}{r_1^2} + \frac{\partial\psi}{\partial r_1}\left(\frac{1}{r_1} - \frac{x_1^2}{r_1^3}\right) + \frac{\partial^2\psi}{\partial r_{12}^2}\frac{(x_2 - x_1)^2}{r_{12}^2} \\
&\quad + \frac{\partial\psi}{\partial r_{12}}\left(\frac{1}{r_{12}} - \frac{(x_2 - x_1)^2}{r_{12}^3}\right) \\
&\quad + 2\frac{\partial^2\psi}{\partial r_1 \partial r_{12}}\frac{x_1(x_1 - x_2)}{r_1 r_{12}}.
\end{aligned} \tag{106}
$$

One needs to repeat this procedure for all second derivatives of the Laplacian ($\frac{\partial^2\psi}{\partial x_1^2}$, $\frac{\partial^2\psi}{\partial y_1^2}$, $\frac{\partial^2\psi}{\partial z_1^2}$, $\frac{\partial^2\psi}{\partial x_2^2}$, $\frac{\partial^2\psi}{\partial y_2^2}$, $\frac{\partial^2\psi}{\partial z_2^2}$). One finds the others to be

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial y_1^2} &= \frac{\partial^2\psi}{\partial r_1^2}\frac{y_1^2}{r_1^2} + \frac{\partial\psi}{\partial r_1}\left(\frac{1}{r_1} - \frac{y_1^2}{r_1^3}\right) + \frac{\partial^2\psi}{\partial r_{12}^2}\frac{(y_2 - y_1)^2}{r_{12}^2} \\
&\quad + \frac{\partial\psi}{\partial r_{12}}\left(\frac{1}{r_{12}} - \frac{(y_2 - y_1)^2}{r_{12}^3}\right) \\
&\quad + 2\frac{\partial^2\psi}{\partial r_1 \partial r_{12}}\frac{y_1(y_1 - y_2)}{r_1 r_{12}},
\end{aligned} \tag{107}
$$

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial z_1^2} &= \frac{\partial^2\psi}{\partial r_1^2}\frac{z_1^2}{r_1^2} + \frac{\partial\psi}{\partial r_1}\left(\frac{1}{r_1} - \frac{z_1^2}{r_1^3}\right) + \frac{\partial^2\psi}{\partial r_{12}^2}\frac{(z_2 - z_1)^2}{r_{12}^2} \\
&\quad + \frac{\partial\psi}{\partial r_{12}}\left(\frac{1}{r_{12}} - \frac{(z_2 - z_1)^2}{r_{12}^3}\right) \\
&\quad + 2\frac{\partial^2\psi}{\partial r_1 \partial r_{12}}\frac{z_1(z_1 - z_2)}{r_1 r_{12}},
\end{aligned} \tag{108}
$$

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial x_2^2} = \; = \;& \frac{\partial^2\psi}{\partial r_1^2}\frac{x_2^2}{r_1^2} + \frac{\partial\psi}{\partial r_1}\left(-\frac{1}{r_1} - \frac{x_2^2}{r_1^3}\right) + \frac{\partial^2\psi}{\partial r_{12}^2}\frac{(x_2-x_1)^2}{r_{12}^2} \\
& + \frac{\partial\psi}{\partial r_{12}}\left(-\frac{1}{r_{12}} - \frac{(x_2-x_1)^2}{r_{12}^3}\right) \\
& + 2\frac{\partial^2\psi}{\partial r_1\partial r_{12}}\frac{x_2(x_2-x_1)}{r_1 r_{12}},
\end{aligned} \tag{109}
$$

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial y_2^2} = \;& \frac{\partial^2\psi}{\partial r_1^2}\frac{y_2^2}{r_1^2} + \frac{\partial\psi}{\partial r_1}\left(-\frac{1}{r_1} - \frac{y_2^2}{r_1^3}\right) + \frac{\partial^2\psi}{\partial r_{12}^2}\frac{(y_2-y_1)^2}{r_{12}^2} \\
& + \frac{\partial\psi}{\partial r_{12}}\left(-\frac{1}{r_{12}} - \frac{(y_2-y_1)^2}{r_{12}^3}\right) \\
& + 2\frac{\partial^2\psi}{\partial r_1\partial r_{12}}\frac{y_2(y_2-y_1)}{r_1 r_{12}},
\end{aligned} \tag{110}
$$

and

$$
\begin{aligned}
\frac{\partial^2\psi}{\partial z_2^2} = \;& \frac{\partial^2\psi}{\partial r_1^2}\frac{z_2^2}{r_1^2} + \frac{\partial\psi}{\partial r_1}\left(-\frac{1}{r_1} - \frac{z_2^2}{r_1^3}\right) + \frac{\partial^2\psi}{\partial r_{12}^2}\frac{(z_2-z_1)^2}{r_{12}^2} \\
& + \frac{\partial\psi}{\partial r_{12}}\left(-\frac{1}{r_{12}} - \frac{(z_2-z_1)^2}{r_{12}^3}\right) \\
& + 2\frac{\partial^2\psi}{\partial r_1\partial r_{12}}\frac{z_2(z_2-z_1)}{r_1 r_{12}}.
\end{aligned} \tag{111}
$$

Combining these together and noting that

$$
r_1^2 - r_2^2 + r_{12}^2 = 2\left[x_1(x_1-x_2) + y_1(y_1-y_2) + z_1(z_1-z_2)\right] \tag{112}
$$

yields

$$
\begin{aligned}
-\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 = \;& -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} \\
& - \frac{r_1^2-r_2^2+r_{12}^2}{2r_1r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}} - \frac{r_2^2-r_1^2+r_{12}^2}{2r_2r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}.
\end{aligned} \tag{113}
$$

Thus, the Hamiltonian in r_1, r_2, r_{12} basis is,

$$
\boxed{\begin{aligned} H = & -\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2} - \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} \\ & -\frac{r_1^2-r_2^2+r_{12}^2}{2r_1r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2-r_1^2+r_{12}^2}{2r_2r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} \\ & -(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}}). \end{aligned}} \tag{114}
$$

The volume element in this coordinate system is

$$
V = 8\pi^2 \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12}\, r_1 r_2 r_{12}. \tag{115}
$$

One might also like to transform into the Hylleraas s, t, u basis,

$$
\begin{aligned} s &= r_1 + r_2 \\ t &= r_1 - r_2 \\ u &= r_{12} \end{aligned} \tag{116}
$$

which implies

$$
\begin{aligned} r_1 &= \frac{1}{2}(s+t) \\ r_2 &= \frac{1}{2}(s-t) \\ r_{12} &= u. \end{aligned} \tag{117}
$$

We can use the same chain rule procedure as before,

$$
\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial s}\frac{\partial s}{\partial r_1} + \frac{\partial \psi}{\partial t}\frac{\partial t}{\partial r_1} + \frac{\partial \psi}{\partial u}\frac{\partial u}{\partial r_1}. \tag{118}
$$

We will leave the details to the reader. The result is

$$\boxed{\begin{aligned} H \quad = \quad & -\frac{\partial^2}{\partial s^2} - \frac{\partial^2}{\partial u^2} - \frac{\partial^2}{\partial t^2} \\ & -\frac{4s}{s^2-t^2}\frac{\partial}{\partial s} - \frac{4s}{t^2-s^2}\frac{\partial}{\partial t} - \frac{2}{u}\frac{\partial}{\partial u} \\ & -\frac{2s(u^2-t^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial s\partial u} - \frac{2t(s^2-u^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial t\partial u} \\ & -\left(\frac{4sZ}{s^2-t^2} - \frac{1}{u}\right). \end{aligned}} \tag{119}$$

The volume element in this coordinate system is

$$V = 2\pi^2 \int_0^\infty ds \int_0^s du \int_0^u dt\, u(s^2 - t^2). \tag{120}$$