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The hydrogen molecule-ion in the momentum representation

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The Hydrogen Molecule-ion in the Momentum Representation

by

Cathryn Abrams

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Executive Officer

L Massa

John Arents
Supervisory Committee

The City University of New York

ABSTRACT

The Hydrogen Molecule-ion in the Momentum Representation

by

Cathryn Abrams

Adviser: Professor John Lombardi

The ground state wave function for the hydrogen molecule-ion is derived in momentum space from a linear combination of hydrogen atom functions. The transform used is one in which the momentum variables are conjugate to corresponding position variables (r, $\cos\theta$, ϕ). The transformed wave function is shown to give the correct energies when used in the calculation of the relevant matrix elements. The calculations are greatly simplified by considering the momentum variables to be complex, which enables the use of Cauchy's residue theorem. Expressions for the potential energy operators $1/r_a$ and $1/r_b$ are derived in this momentum representation, as well as shifted Slater orbitals centered on nucleus b, which are considered as a basis for future calculations on more complex systems.

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CONTENTS

APPENDICES

1 INTRODUCTION

The subject of this thesis is an examination of the hydrogen molecule-ion in momentum space. This momentum space is reached by a modified Fourier transform proposed by DeWitt, that differs from the standard in that it includes the Jacobian determinant of the transformation matrix. The DeWitt transform has been used successfully to study the hydrogen atom [1], the helium atom [2], and Slater orbitals [2] in momentum space. The advantage of applying the DeWitt transform lies in the mathematical simplification of the transformed functions. The next step is to apply this transform to study the hydrogen molecule-ion, as well as shifted Slater orbitals (i.e., orbitals centered on nucleus b, displaced a distance R from unshifted nucleus a), with the expectation that this mathematical simplicity will be retained and encourage future work on momentum space wave functions.

A quantum system may be described by its dynamical variables, the commutator relations obeyed by the operators corresponding to these variables, and the Hamiltonian, as a function of these variables, which characterizes the motion of the system. In quantum mechanics operators representing observables are chosen to satisfy the commutation relation:

$$[q, p] = q\,p - p\,q = i\,\hbar$$

Traditionally the position coordinates $q_1, q_2, q_3, \ldots q_n$ have been used to form a complete set of commuting observables and define a $\{q\}$ representation. This is due, in part, to the fact that position is more accessible than momentum to our senses. An alternate, entirely equivalent description of a quantum system may be expressed as a function of the momentum, p, where position, q, and momentum, p, are conjugate variables.

Since either representation may be used to calculate expectation values of any observable, the choice of which representation to use can be determined merely by mathematical convenience. In the position representation, the position operator is defined by multiplication by the coordinate value and the momentum operator is defined by differentiation with respect to that coordinate. In the momentum representation, the situation is reversed; the position operator is defined by differentiation with respect to the momentum component and the momentum operator is defined by multiplication by the momentum component value.

For example, in one dimension :

	Observable:	**Position, x**	**Momentum, p**
Position Space	Operator:	$x\,\cdot$	$-i\,\hbar\,d/dx$

	Observable:	**Position, x**	**Momentum, p**
Momentum Space	Operator:	$i\,\hbar\,d/dp$	$p\,\cdot$

(where p represents the x-component of the linear momentum)

Using the operator expressions above for position and momentum in Cartesian coordinates, the position space representation of the kinetic energy operator, T, in one dimension is:

$$T = p^2/2m = (-\hbar^2/2m)(d^2/dx^2)$$

For a free particle travelling in one dimension, the Hamiltonian includes only the kinetic energy operator, since the potential energy is constant. The Schrödinger equation for a free particle is:

$$(-\hbar^2/2m)(d^2\psi(x)/dx^2) = E\psi(x)$$

The position space solution for a free particle travelling in the positive x direction in atomic units ($\hbar = 1$) is:

$$\psi(x) = e^{ikx} \qquad x>0 \qquad k = \pm\sqrt{2m\mathrm{E}}$$

The motion is completely unconfined, the energy, E, is unquantized, and a solution can be found for any nonnegative value of E. The corresponding free particle momentum space wave function, ϕ(p), obtained by applying a Fourier transform to ψ (x) = e^{ikx} is

$$\phi(p) = \int_{-\infty}^{\infty} e^{ikx} e^{-ipx} dx = i\pi\,\delta(p-k)$$

The momentum space wave function for a free particle travelling in the positive x direction is just a Dirac delta function, where the delta function is defined by:

$$\delta(p-k) = 0 \qquad p \neq k$$

$$\int_{-\infty}^{\infty} \delta(p-k)\,dp = 1$$

This function, δ(p - k), is equal to zero everywhere except at k, where it is infinite, and its integral is equal to one. The occurrence of the delta function shows that the momentum of a free particle does not change. The result that the momentum representation of a free particle is a delta function is a consequence of the Heisenberg Uncertainty Principle which states that if p is precisely known, $\Delta p \Rightarrow 0$ and the particle is equally likely to be anywhere, so that $\Delta x \Rightarrow \infty$ and vice versa.

An alternate method of obtaining a momentum wave function for a free particle involves solving the Schrödinger equation directly in momentum space.

$$\frac{p^2}{2m}\phi(p) = E\phi(p)$$

$$(p^2 - 2mE)\phi(p) = 0$$

This equation has the solution that either $p^2 = 2mE$ or $\phi(p) = 0$. Once again, we see that the solution is a delta function.

$$\phi(p) = \delta(p-k) = 0 \qquad p \neq k \qquad k = \pm\sqrt{2mE}$$

The momentum function has a nonzero value only when $p = k$. For all other values of p, it is zero. For a free particle both x and p are observables with eigenvalues extending from $-\infty$ to ∞.

The quantum mechanical harmonic oscillator is characterized by an unusual simplicity which arises from the symmetrical occurrence of momentum p, and displacement, x. Since the potential energy operator has the form

$$V(x) = \frac{1}{2}kx^2$$

(k is the force constant)

the Schrödinger wave equation is:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

With the following substitutions

$$z = \alpha x \qquad \alpha^4 = \frac{mK}{\hbar^2} \qquad \lambda = \frac{2E}{\hbar}\left(\frac{m}{k}\right)^{\frac{1}{2}} \qquad \psi(x) = \psi\left(\frac{z}{\alpha}\right) = \Psi(z)$$

the differential equation becomes

$$\frac{d^2\Psi(z)}{dz^2} + (\lambda - z^2)\Psi(z) = 0$$

The solution to the harmonic oscillator equation is

$$\Psi_n(z) = 2^{-n/2}\pi^{-1/4}(n!)^{-1/2}e^{-z^2/2}H_n(z)$$

where $H_n(z)$ are the Hermite polynomials and n is required by boundary conditions to be a nonnegative integer. In order to rewrite this differential equation in terms of p using atomic units ($\hbar = 1$) we make the substitutions

$$p^2 = -\frac{d^2}{dz^2} \qquad z^2 = -\frac{d^2}{dp^2}$$

The resulting equation in p is

$$\frac{d^2\phi(p)}{dp^2} + (\lambda - p^2)\phi(p) = 0$$

where the symmetry in p and z becomes obvious, since this is the same differential equation with z replaced by p. Therefore the harmonic oscillator wave function in momentum coordinates is identical to the wave function in position coordinates and

$$\Psi_n(z) = \phi_n(p)$$

With these examples, we have seen the complementary relationship between the Cartesian coordinates, (x, y, z) and the momentum variables, (p_x, p_y, p_z) in both the free particle and the harmonic oscillator. It is important to note that this simple relationship ($p_x = -i\hbar d/dx$, etc.) does not exist when the coordinate system is not Cartesian.

The momentum operator p_q, in a Cartesian coordinate system, is:

$$p_q = -i\hbar\partial/\partial q$$

where q = x,y, or z. However, Podolsky [3] in 1928 pointed out that this is not the correct expression for non-Cartesian coordinates. DeWitt [4] in 1952 and Gruber [5] in 1971 have shown that to properly write the expression for the momentum associated with the corresponding position variable in curvilinear coordinates requires the inclusion of the Jacobian, g, of the transformation (x, y, z) to (u, v, w), where (u, v, w) are curvilinear coordinates. It has been shown by Gruber [5] that if we define the momentum operator by $p_u = -i\hbar\partial/\partial u$, where u is a curvilinear coordinate, then p_u will not be Hermitian, but will be composed of Hermitian and anti-Hermitian parts. An operator corresponding to a measurable momentum may be constructed by using only the Hermitian part of the operator and discarding the non-Hermitian part (which corresponds to imaginary eigenvalues). Gruber [5] shows that the operator p = $-i\hbar\partial/\partial u$ has the adjoint

$$p^\dagger = -i\hbar\left(\frac{\partial}{\partial u} + \frac{1}{g}\frac{\partial g}{\partial u}\right)$$

and thus its Hermitian part is

$$p_u = \frac{1}{2}(p + p^\dagger)$$

$$= -i\hbar[\partial/\partial u + (2g)^{-1}\partial g/\partial u] \qquad (1)$$

Chand and Cassonova [6] showed this expression to be equivalent to that of DeWitt. Gruber has demonstrated its uniqueness: that is, g must be the Jacobian of the transformation. He also shows that if the expression

$$p_u = -i\hbar[\partial/\partial u]$$

is used to obtain the Hamiltonian operator in curvilinear coordinates, then this will create the wrong Hamiltonian operator. Only when (1) is used will the correct expression for the Hamiltonian be given. Correctly using the Jacobian to construct the momentum operators associated with non-Cartesian coordinates ensures that the Hamiltonian operator will be Hermitian and therefore its momentum eigenfunctions will be orthogonal and form a complete set.

The momentum space wave function ϕ(p), which is the probability amplitude in momentum space, is systematically obtained in either of two ways. The first involves directly solving the Schrödinger equation in momentum space - that is, finding the solution of the momentum space eigenvalue equation. The second method requires a knowledge of the position space wave function which is transformed by means of a three-dimensional Fourier or modified Fourier transform. The one-dimensional Fourier transform and back transform are:

$$\varphi(p) = \int dx\, e^{-ixp}\, \psi(x)$$

$$\psi(x) = \frac{1}{2\pi} \int dp\, e^{ixp}\, \varphi(p) \tag{2}$$

where ϕ(p) is the momentum space wave function and ψ(x) is the position space wave function. When the position variables are Cartesian, a Fourier transform is used. However, DeWitt showed that if the position variables are not Cartesian, (i.e.,curvilinear), then the correct transform is not a Fourier transform. For any curvilinear coordinate system the Fourier transform must be modified by including the determinant of the Jacobian transformation matrix between Cartesian (x, y, z) and curvilinear coordinates (u, v, w). The Jacobian determinant, g(u, v, w), of the coordinate transformation (x, y, z) to (u, v, w) is defined by:

$$g(u,v,w) = \begin{vmatrix} \frac{dx}{du} & \frac{dx}{dv} & \frac{dx}{dw} \\ \frac{dy}{du} & \frac{dy}{dv} & \frac{dy}{dw} \\ \frac{dz}{du} & \frac{dz}{dv} & \frac{dz}{dw} \end{vmatrix}$$

For example, if the coordinate transformation is between the Cartesian coordinates, (x, y, z), and the spherical polar coordinates, (r, θ, ϕ), where $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\theta$, $z = r \cos\theta$, then the Jacobian determinant, g(r, θ, ϕ), is:

$$g(r,\theta,\phi) = \begin{vmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi \\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi \\ \cos\theta & -r\sin\theta & 0 \end{vmatrix}$$

$$= r^2\sin\theta$$

If g(u, v, w) represents the determinant and the differential volume element is $d\tau = dx\ dy\ dz = g\ du\ dv\ dw$, then the correct transform, shown by DeWitt, is:

$$S(u,v,w,p_u,p_v,p_w) = g^{-1/2} e^{-i(up_u + vp_v + wp_w)} \tag{3}$$

There are in theory an infinite number of momentum space representations, just as there are in theory an infinite number of coordinate space representations. Many transforms are possible which connect these representations; however, the DeWitt transform defines a distinct momentum space. The momentum space representation used in this research, which is based on the DeWitt transform, is one in which each of the momentum variables is chosen canonically conjugate (defined by the commutation relation, $[\mathbf{q},\mathbf{p}] = i\hbar$) to the corresponding position variable and this defines a unique momentum space connected by a unique transform.

It is interesting to note that the DeWitt transform has been virtually ignored, and practically all momentum space research uses the Fourier transform method. An advantage that the DeWitt transform has over the Fourier transform method regarding bound state problems is that there appears to be considerable simplification in the equations to be solved and the resulting eigenfunctions. In fact this simplification is evident (e.g.,H [1] and He [2]) even when compared to position space eigenfunctions and their method of solution.

In Chapter 2, some of the early work on H, He, and H_2^+ in Fourier transform momentum space relevant to the proposed research is discussed. Chapter 3 contains a discussion of previous work in momentum space using the DeWitt transform. Chapter 4 presents the actual results of this research on H_2^+ and the calculation of matrix elements S, J, and K. Shifted Slater orbitals in conjugate momentum space using the DeWitt transform are shown in Chapter 5 and Chapter 6 is a look at some important operators in conjugate momentum space. Finally, Chapter 7 contains a discussion of the research findings and proposals of future projects.

2 FOURIER TRANSFORM MOMENTUM SPACE

Most bound state problems such as those dealing with atomic and molecular structure have been solved using the position rather than the momentum representation. This is because it is intuitively easier to select coordinates which can physically describe the spatial symmetry of the potential energy function. The momentum representation has been used primarily to study scattering problems because the momentum distribution of the electrons determines the shape of the Compton line and the distribution of inelastically scattered electrons. Momentum-space work on bound state problems is based on the work of Podolsky and Pauling [7] in 1929 on the hydrogen atom. Their approach uses the spherical polar momentum variables, (P, Θ, Φ) which are functions of the Cartesian momentum variables, (p_x, p_y, p_z) and which have the same spatial relationship as (r, θ, ϕ) and (x, y, z). At the foundation of their representation exists the conjugate relationship between (p_x, p_y, p_z) and the corresponding position coordinates (x, y, z). However, their momentum variables (P, Θ, Φ) are not directly conjugate to any meaningful position variables. P is the magnitude of the total momentum, and Θ and Φ are the spherical polar angles of the momentum vector referred to the space-fixed axis system. The hydrogen atom momentum-space eigenfunctions of (P, Θ, Φ) are separable and yield products of Gegenbauer polynomials in P and momentum spherical harmonics consisting of Legendre polynomials and exponentials in Θ and Φ. These functions are widely used in conjunction with experiments designed to measure the total momentum. Fock [8] obtained the same momentum functions by solving the Fourier transformed equations in hyperspherical four dimensional coordinates. A thorough discussion of Fock's results is presented by Bethe and Salpeter [9].

Since Pauling and Podolsky's pioneering work on the hydrogen atom there have been numerous attempts to determine the Fourier transformed momentum space functions for the helium atom. Kirkpatrick, Ross and Ritland [10] used the method of Podolsky and Pauling on Slater orbitals to obtain momentum distributions in several elements. Hicks [11] applied the same transform to approximations to the correlated functions of Hylleraas [12]. McWeeny and Coulson [13] modified the functions of Podolsky and Pauling by introducing a variational parameter and later they obtained still better functions by an iterative technique resulting in correlated functions.

Cooper [14] gives an exhaustive review of early work. More recent work on atoms comes from Bayard and coworkers [15, 16] who used the same transform on Hartree-Fock functions as well as the configuration interaction functions of Weiss [17].

An examination of molecular wave functions in momentum space using a Fourier transform and momentum spherical polar coordinates began in the early 1940's. Coulson [18] transformed LCAO position space functions to obtain momentum wave functions of simple molecules (e.g., H_2^+, H_2) with only single bonds in order to understand the nature of the chemical bond in momentum space. In each case he discovered that the presence of the chemical bond resulted in: an increase in the mean component of the momentum in the direction perpendicular to the bond, a decrease in the mean component of the momentum in the direction parallel to the bond, and an increase in the mean momentum averaged over all directions. Thus in the molecule, there is a greater probability of finding a given momentum in the perpendicular direction than in the parallel direction. Next, McWeeny [19] utilized an iterative technique on an integral analog of the Schrödinger equation for H_2^+. However, after just a few iterations, he found that the mathematical problems became formidable. More recently Steinborn and coworkers [20-22] applied a Fourier transform to a linear combination of position space Slater orbitals. They used these momentum functions to derive analytic expressions for two, three, and four center integrals including overlap, Coulomb, and exchange integrals which are important in molecular orbital calculations. Lassettre [23-26] has studied atomic and molecular Fourier-transformed functions in the complex momentum plane and has found a connection between the nature and location of singularities in these functions and their atomic and molecular energies.

The momentum functions in the Fourier transformed space are functions of P, the total momentum, and the momentum density function of P is closely related to the Compton scattering profile. This relationship enables one to compare theoretical with experimental results. Epstein [27] provides a summary of this work. More recently, owing to electron momentum spectroscopy (e,2e) experiments, Brion [28] and others [29] are able to measure not only total but also orbital contributions to the Compton profile and thus provide measurements of momentum distributions in individual orbitals.

3 CONJUGATE MOMENTUM SPACE

The DeWitt transform was first applied to a bound state system by Lombardi [1] for the hydrogen atom. The momentum variables p_r, p_θ, p_ϕ were chosen properly conjugate to the spherical polar coordinates r, $\cos\theta$, ϕ. This was accomplished by determining the Jacobian determinant, g, of the transformation matrix between (x, y, z) and (r, $\cos\theta$, ϕ). The determinant, g(r, $\cos\theta$, ϕ) of this coordinate transformation is $g = r^2$. Following DeWitt [4] and Gruber [5] the momentum operators are defined using (1) which for p_r ,p_θ ,p_ϕ are:

$$p_r = -i\hbar(\partial/\partial r + 1/r)$$

$$p_\theta = -i\hbar(\partial/\partial\cos\theta) \tag{6}$$

$$p_\phi = -i\hbar(\partial/\partial\phi)$$

In momentum space, functions of the spherical polar coordinates become operators (Chapter 6). For example:

$$r \Rightarrow i\hbar\partial/\partial p_r \qquad\qquad r^{-1} \Rightarrow \frac{-i}{\hbar}\int dp_r \tag{7}$$

These expressions make it relatively easy to represent the potential energy operators in momentum space. This facility is not present in the momentum representation of Pauling and Podolsky which uses the spherical polar coordinates of the momentum vector. In that representation Coulombic potential operators are difficult to express.

Next the Hamiltonian operator is constructed in momentum space by employing the momentum operator expressions above. The resulting integro-differential equations in the momentum representation are then solved and boundary conditions are applied, leading to the correct quantum numbers. As an example of this technique, some of the steps in the transformation and solution of the radial hydrogen atom differential equation will be shown below following Lombardi [1]. Consider the radial differential equation satisfied by $R_\ell(r)$, the hydrogen atom radial wave function in atomic units:

$$\left[\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\ell(\ell+1)}{r^2}+\frac{2\mu Ze^2}{r}+2\mu E\right]R_\ell(r)=0$$

In order to examine the radial equation in momentum space, the following transformations are used:

$$-i\left(\frac{d}{dr}+\frac{1}{r}\right)\Rightarrow p_r \qquad \frac{1}{r}\Rightarrow -i\int dp_r \equiv I \qquad R_\ell(r)\Rightarrow \alpha_\ell(p_r)$$

and the integral equation obtained is:

$$\left[(p_r^2-2\mu E)\ +\ \ell(\ell+1)I^2\ +\ 2\mu Ze^2 I\right]\alpha_\ell(p_r)\ =\ 0$$

The solution to this equation is most easily found by taking taking the $(\ell+1)$th derivative, which results in a first order differential equation:

$$\left[(p_r^2-2\mu E)\frac{d}{dp_r}+2(\ell+1)p_r+2\mu Ze^2 i\right]\chi(p_r)=0$$

$$\chi(p_r)=i^\ell\frac{d^\ell}{dp_r^\ell}\alpha_\ell(p_r)$$

The solution to the p_r equation can be expressed in terms of poles in the complex plane. For $\ell=0$ states:

$$\chi(p_r) = \alpha_\ell(p_r) = \frac{(p_r + ip_0/n)^{n-1}}{(p_r - ip_0/n)^{n+1}} \tag{8}$$

where $p_0 = Za_0^{-1}$ (a_0 is the Bohr radius) and $c = 2\mu Ze^2 i$, $n = c/2\sqrt{2\mu E}$. DePrunele [30] has shown that $\alpha_\ell(p_r)$ may also be expressed in terms of hypergeometric functions for any ℓ. The angular functions for p_ϕ are given by the Dirac delta function $\delta(p_\phi \pm m)$. The momentum functions of p_θ are written in terms of Bessel functions of order integer plus one half. Thomas [31] has verified these results by means of a direct transformation from position space spherical harmomics. Actually, the momentum variables associated with the angular position variables θ,ϕ are not conjugates. For example $[\phi, L_z] = i\hbar$ is incorrect. The variable ϕ is continuous and not bounded by its domain of $[0,2\pi)$, resulting in problems at the end points. The operator ϕ actually takes the eigenfunctions out of the space. A discussion of this problem can be found in a review by Carruthers and Nieto [32]. Additional discussion on this problem is found in Lévy-Leblond [33] and Biedenharn and Louck [34]. In order to make p_θ, p_ϕ appropriately conjugate to the spherical polar angular coordinates, Lombardi [1] associates them with functions of the spherical polar angle variables, t and v, where $t=e^{i\pi\cos\theta}$, $v=e^{i\phi}$. For example, regarding the change of variable from ϕ to v, the operator $e^{i\phi}$ is everywhere invariant under $\phi \rightarrow \phi + 2\pi$ and leaves the domain invariant; however, it is not physically observable [34]. With these modifications the correct commutation relations for p_r, p_θ, p_ϕ become:

$$[p_r,r]=i \qquad [p_\theta,t]=\pi t \qquad [p_\phi,v]=v$$

It is important to point out that these substitutions have no effect on the momentum space results which may be expressed in terms of (r, t, v) as well as (r, $\cos\theta$, ϕ).

The DeWitt transform has also been used to study Slater orbitals in momentum space. In 1930 John C. Slater [35] created a set of orbitals, known as Slater orbitals, which are:

$$S_{n\ell m}(r,\theta,\phi)=N_{n\ell}r^{n-1}e^{-\zeta r}Y_\ell^m(\theta,\phi)$$

where $N_{n\ell}$ is a normalization constant and Y_ℓ^m are the spherical harmonics. The exponent ζ is a variational parameter. Slater functions have been widely used in the position representation as a basis set for quantum mechanical calculations because they are nodeless and thus facilitate the evaluation of integrals. Lombardi [2] has applied the radial DeWitt transform to find the momentum analogue of Slater-type orbitals centered on nucleus a

$$\psi(r) = Nr^{n-1}e^{-\zeta r}$$

where nucleus a is the center of the spherical polar coordinate system. Lombardi shows the transformed radial momentum Slater orbital to be:

$$\frac{N}{\sqrt{\pi}}\frac{(-i)^{n+1}n!}{(p_r-i\zeta)^{n+1}} \qquad (9)$$

At this point it is interesting to compare the radial momentum hydrogen atom functions (8) with the radial momentum Slater orbital (9). Several important features of these functions are immediately apparent. First, both functions have poles of order n + 1 . In the radial hydrogenic functions ($\ell = 0$) these poles are located at $p_r = iZ/n = \sqrt{-I}$ where I represents the ionization potential of the hydrogen atom (and the hydogenlike ions). This singularity thus represents i times the radial momentum at which ionization occurs. Similarly, in the momentum Slater functions these poles occur at $p_r = i\zeta$. In position space the parameter ζ is usually interpreted as an effective nuclear charge screened by electrons and is not necessarily equal to Z/n as in the hydrogenlike orbitals. In momentum space $i\zeta$ is mathematically the point at which the wave function has a pole, and by analogy with the hydrogen atom, can also be interpreted as i times the radial momentum at which ionization occurs. One noticeable difference in these functions is that the momentum hydrogenic functions (8) have nodes at $p_r = -iZ/n$, whereas the Slater functions are nodeless. As a result, it is considerably easier to evaluate integrals over the momentum Slater functions than the momentum hydrogenic functions. As noted previously, this simplicity is also obtained in position space.

4 H_2^+ IN MOMENTUM SPACE

Using the DeWitt transform the hydrogen atom has been represented in conjugate momentum space [1]. The question arises whether the DeWitt transform could be applied to study the momentum space analog of olecular orbitals formed from a linear combination of atomic orbitals. The following section describes this method in which the hydrogen-like wave functions $e^{-\alpha r_a}$, $e^{-\alpha r_b}$, centered on nucleus a and nucleus b respectively, are used as basis functions for the calculation of the wave function for H_2^+ in conjugate momentum space.

The hydrogen molecule-ion is the simplest single electron molecule. The Schrödinger equation for H_2^+ is:

$$\left(-\nabla^2-\frac{2}{r_a}-\frac{2}{r_b}\right)\Psi=E'\Psi$$

$$E'=E-\frac{2}{R}$$

where r_a is the distance of the electron from nucleus a, r_b is the distance of the electron from nucleus b, and R is the nucleus-nucleus separation. The

Hamiltonian operator includes the kinetic energy operator of the electron and the potential energy of the electron in the field of nucleus a and nucleus b. The nuclei are stationary. Atomic units are used and distances are measured in terms of a_0, the radius of the first Bohr orbit in hydrogen. Energies are measured in rydbergs. The nuclear repulsion term is included in E′.

The Schrödinger equation for the hydrogen molecule-ion, has an exact solution in the position representation using prolate spheroidal coordinates,

$$x = \frac{R}{2}\sqrt{(\mu^2 - 1)(1 - \nu^2)}\cos\phi \qquad \mu = \frac{(r_a + r_b)}{R}$$

$$y = \frac{R}{2}\sqrt{(\mu^2 - 1)(1 - \nu^2)}\sin\phi \qquad \nu = \frac{(r_a - r_b)}{R}$$

$$z = \frac{R}{2}\mu\nu$$

where ϕ is the azimuthal angle and R is the distance between the two nuclei a and b. Although this representation is of limited use because the solutions are complicated and it has little application to other than small diatomic molecules, it is still worthwhile to examine the momentum representation that is constructed from momentum variables conjugate to the prolate spheroidal coordinates. The first step is to find the Jacobian of the transformation matrix (x, y, z) to (μ, ν, ϕ). The volume element is:

$$d^3q = \frac{R^3}{8}(\mu^2 - \nu^2)\,d\mu\,d\nu\,d\phi$$

$$g(\mu,\nu,\phi) = \frac{R^3}{8}(\mu^2 - \nu^2)$$

The Jacobian is a function of both variables μ and ν and it is not separable. This means that the conjugate momentum operators are functions of both variables.

$$p_\mu = -i\hbar\left(\frac{\partial}{\partial\mu} + \frac{\mu}{\mu^2-\nu^2}\right)$$

$$p_\nu = -i\hbar\left(\frac{\partial}{\partial\nu} - \frac{\nu}{\mu^2-\nu^2}\right)$$

$$p_\phi = -i\hbar\frac{\partial}{\partial\phi}$$

The Schrödinger equation, separable in position space prolate spheroidal coordinates, is shown below, where A is a separation constant.

$$\Psi(\mu,\nu,\varphi) = M(\mu)N(\nu)\Phi(\varphi)$$

$$\frac{d}{d\mu}\left[(\mu^2-1)\frac{d}{d\mu}\right] + \left(A + 2R\mu - \rho^2\mu^2 - \frac{m^2}{\mu^2-1}\right)M(\mu) = 0$$

$$\frac{d}{d\nu}\left[(1-\nu^2)\frac{d}{d\nu}\right] + \left(-A + \rho^2\nu^2 - \frac{m}{1-\nu^2}\right)N(\nu) = 0$$

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi$$

$$\rho^2 = -R^2E'/4 \qquad E' = E - 2/R$$

However, when the conjugate momentum operators are substituted into the Hamiltonian operator in order to perform the transformation to momentum space, the resulting momentum equations are not separable into equations of a single variable. For example, if the following transformations are substituted in the μ equation:

$$p_\mu = -i\hbar\left(\frac{\partial}{\partial\mu} + \frac{\mu}{\mu^2 - \nu^2}\right)$$

$$p_\mu^2 = -\hbar^2\left(\frac{\partial^2}{\partial\mu^2} + \frac{2\mu}{\mu^2 - \nu^2}\frac{\partial}{\partial\mu} - \frac{\nu^2}{(\mu^2 - \nu^2)^2}\right)$$

$$\mu = i\frac{\partial}{\partial p_\mu} \qquad \mu^2 = -\frac{\partial^2}{\partial p_\mu^2} \qquad \mu^{-1} = -i\int dp_\mu$$

a sixth order partial differential equation results that mixes the variables μ and ν, and cannot be solved analytically in conjugate momentum space.

As a consequence of this difficulty, an alternate route to H_2^+ in momentum space had to be considered. One possibility was to continue the investigation with a momentum space constructed from the prolate spheroidal coordinates but abandon the DeWitt transform. This choice would enable us to generate separable differential equations because we would no longer need the Jacobian (which was not separable) to define the momentum operators. One drawback, however, was that the momentum variables would not be conjugate to nor have any meaningful uncertainty relationship with the prolate spheroidal coordinates. Calculation shows that the Fourier transform of the function N(ν) over a finite range is the same prolate spheroidal function over an infinite range. For example, the function $N(\nu)$ can be expanded in a linear combination of the associated Legendre polynomials, which are orthogonal in the range $|\nu| < 1$. The Fourier transform of $N(\nu)$ is the same function; however, the range of the momentum variable is $-\infty < p_\nu < \infty$. Hille [36] shows that the momentum functions, the associated Legendre functions, are no longer orthogonal to one another when the domain of the variable is infinite because the corresponding integrals are not convergent. Overall, this approach did not seem very interesting since it would: <1> generate momentum functions more difficult to work with than the position space functions; <2> give little insight into the DeWitt transform and conjugate momentum space. Therefore, rather than pursue a study of H_2^+ in momentum space derived from prolate spheroidal coordinates, an investigation of the hydrogen molecule-ion using a momentum space analog of molecular orbitals formed from a linear combination of atomic orbitals was undertaken. A momentum space LCAO approach is based on a momentum space connected to position space by a DeWitt transform with momentum variables conjugate to the spherical polar coordinates of the hydrogen atom. This is a method of much wider applicability and in the next section it is used to solve H_2^+ approximately using a linear combination of atomic momentum orbitals to construct a molecular momentum wave function.

H_2^+ --The LCAO Approach

The simplest LCAO approximation (linear combination of atomic orbitals) for the ground state of H_2^+ is the function

$$1\sigma_g = e^{-r_a} + e^{-r_b}$$

The hydrogen atom wave functions e^{-r_a}, e^{-r_b} centered on nucleus a and b respectively are used as basis functions. This is not a bad approximation when the internuclear distance, R, is large; however, it is inadequate for smaller distances. In order to make it into a good approximation at all distances, an orbital exponent, α, is introduced, to set up the function $e^{-\alpha r_a} + e^{-\alpha r_b}$. The exponent, α, is treated as a variational parameter depending on R. By varying α from 1 when R is large to 2 when R=0, this turns out to be a good description of the wave function at all distances. The wave function is set up by normalizing the function $e^{-\alpha r_a} + e^{-\alpha r_b}$, computing the average values of the Hamiltonian for a given nuclear distance R, and varying α to minimize energy. From the variation principle we are assured that this is the value of α which will give the best approximation to the true energy for the assumed form of the wave function.

The next few sections involve calculations. The following methods will be used in order to transform the LCAO functions to conjugate momentum space. First, we begin with the $1s_b$ wave function $e^{-\alpha r_b}$, in which $Y_{0,0}(\theta_b, \phi_b) = 1$.

$$r_b = (r_a^2 - 2Rr_a\cos\theta_a + R^2)^{\frac{1}{2}}$$

$$e^{-\alpha r_b} = e^{-\alpha(r_a^2 - 2Rr_a\cos\theta_a + R^2)^{\frac{1}{2}}}$$

Since ultimately we will be calculating matrix elements S, J, K, we will also need the $1s_a$ wave function, $e^{-\alpha r_a}$, with $Y_{0,0}(\theta_a, \phi_a) = 1$. We obtain the matrix elements by integrating the wave function with respect to θ_a, ϕ_a in position space.

$$f(r_a) = \int_0^{2\pi} d\phi_a \int_{-1}^{1} d\cos\theta_a \, e^{-\alpha(r_a^2 - 2r_aR\cos\theta_a + R^2)^{\frac{1}{2}}}$$

The resulting radial function, $f(r_a)$, is transformed to momentum space using the DeWitt transform.

$$F(p_r) = \int dr_a \frac{e^{-ir_ap_r}}{r_a} r_a^2 f(r_a)$$

The momentum wave function, $F(p_r)$ is then used in the calculation of matrix elements S(overlap), J(Coulomb), and K(exchange). Shifted Slater orbitals centered on nucleus b are also transformed to momentum space following the procedure outlined above.

An alternate method, referred to as the direct transform method, of computing the momentum wave function, begins with the $1s_b$ function $e^{-\alpha r_b}$. The function, centered on atom b, is expanded in position space as a sum of separable functions centered on atom a. The expanded function is then directly transformed to momentum space using the DeWitt transform. As a last step, in order to demonstrate that the direct transform result agrees with the result of the first method, an integration is performed in momentum space with respect to the momentum angular function $\beta_\ell^m(p_\theta)$. The direct transform result is shown to be in agreement with the momentum result from the first transform method.

Momentum Representation of $e^{-\alpha r_a}$

In this section the momentum representation of $e^{-\alpha r_a}$ is shown using the DeWitt transform. The DeWitt transform differs from a Fourier transform by including the factor $1/r_a$.

The Radial DeWitt Transform of $e^{-\alpha r_a}$

$$\int_0^\infty dr_a r_a^2 \frac{e^{-ir_a p_{r_a}}}{r_a} \psi(r_a) \tag{10}$$

$$= \int_0^\infty dr_a r_a^2 \frac{e^{-ir_a p_{r_a}}}{r_a} e^{-\alpha r_a} \tag{11}$$

$$= \frac{-1}{(p_{r_a} - i\alpha)^2} \tag{12}$$

We compare the unnormalized radial momentum function in (12) with that found by Lombardi [1] for the hydrogen atom,

$$\frac{1}{(p_{r_a} - ip_0)^2}$$

They are identical except for: 1) a negative sign in (12) which stems from a phase difference in the transform ($e^{\pm i\pi p}$) and 2) a difference in the labeling of constants with $\alpha = p_0$.

Note: A number of integrals which have been compiled by Gradshteyn and Ryshik [37] will be required in the sections that follow and we will refer to them as GR along with the appropriate reference number.

Momentum Representation of $e^{-\alpha r_b}$

The radial DeWitt transform is applied to $e^{-\alpha r_b}$ to give the radial momentum wave function, $F(p_r)$. The integration is over a hybrid space ($\cos\theta_a$, ϕ, p_r) where $\phi_a = \phi_b$. We will be integrating with respect to $\cos\theta_a$, ϕ in position space first, before applying the radial DeWitt transform to $f(r_a)$. The coordinate system is centered on nucleus a. We use the substitution:

$$r_b = \sqrt{r_a^2 + R^2 - 2r_a R\cos\theta}$$

$$e^{-\alpha r_b} = e^{-\alpha(r_a^2 + R^2 - 2r_a R\cos\theta)^{\frac{1}{2}}}$$

We consider the $\ell = 0$ case in which $Y_{0,0}(\theta_b, \phi_b) = 1$,

$$\int_{-1}^{1} d\cos\theta_a \, e^{-\alpha(r_a^2 + R^2 - 2r_a R\cos\theta_a)^{\frac{1}{2}}} \int_0^{2\pi} d\phi_a N_{\phi_a}^* N_{\phi_b} \tag{13}$$

$$N_{\phi_a}^* = N_{\phi_b} = \frac{1}{\sqrt{2\pi}}$$

where the N's represent normalization constants.

Integration with respect to $\cos\theta$, ϕ gives the unnormalized radial wave function, $f(r_a)$: (Appendix B)

$$f(r_a) = \frac{1}{\alpha R r_a}\left[e^{-\alpha|r_a-R|}\left(|r_a-R|+\frac{1}{\alpha}\right) - e^{-\alpha|r_a+R|}\left(|r_a+R|+\frac{1}{\alpha}\right)\right] \qquad (14)$$

The radial DeWitt transform is applied to f(r_a):

$$F(p) = \int_0^\infty dr r^2 \frac{e^{-irp}}{r}\frac{1}{\alpha R r}\left[e^{-\alpha|r-R|}\left(|r-R|+\frac{1}{\alpha}\right) - e^{-\alpha|r+R|}\left(|r+R|+\frac{1}{\alpha}\right)\right]$$

(14a)

where we have used r = r_a, p = p_r.

We may remove the absolute value signs:

$$|r-R| = r-R \ (R<r<\infty)$$

$$R-r \ (0<r\leq R)$$

$$|r+R| = r+R \ (0<r<\infty)$$

Integration with respect to the coordinate r results in three integrals, where the first integration is from 0 to R, the second is from R to ∞, and the third is from 0 to ∞.

$$F(p) = \frac{1}{\alpha R}\left[\int_0^R dr\, e^{-irp} e^{-\alpha(R-r)}\left(R - r + \frac{1}{\alpha}\right) + \right.$$

$$\int_R^\infty dr\, e^{-irp} e^{-\alpha(r-R)}\left(r - R + \frac{1}{\alpha}\right) -$$

$$\left.\int_0^\infty dr\, e^{-irp} e^{-\alpha(r+R)}\left(r + R + \frac{1}{\alpha}\right)\right] \qquad (15)$$

The following integration formulas are used to evaluate the integrals:

$$\int_R^\infty x^n e^{-\alpha x} dx = n!\, e^{-\alpha R} \sum_{k=0}^{n} \frac{1}{k!} \frac{R^k}{\alpha^{n-k+1}} \qquad (16a)$$

$$\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}} \qquad (16b)$$

$$\int_0^R x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}} - n!\, e^{-\alpha R} \sum_{k=0}^{n} \frac{1}{k!} \frac{R^k}{\alpha^{n-k+1}} \qquad (16c)$$

(GR 3.351.1)

The result is:

$$F(p) = \frac{1}{\alpha R}\left[\left(e^{-\alpha R} - e^{-iRp}\right)\left(\frac{1}{(p+i\alpha)^2} + \frac{1}{(p-i\alpha)^2}\right) - \right.$$
$$\left. \frac{i}{\alpha}\left((\alpha R+1)e^{-\alpha R} - e^{-iRp}\right)\left(\frac{1}{(p+i\alpha)} - \frac{1}{(p-i\alpha)}\right)\right] \qquad (17)$$

F(p) represents $e^{-\alpha r_b}$ in conjugate momentum space (the radial portion which contains a contribution from integrating with respect to the angular coordinates in position space); the $1s_b$ momentum wave function.

The momentum function corresponding to $e^{-\alpha r_b}$ (17) has several important features that are not present in the unshifted momentum function corresponding to $e^{-\alpha r_a}$ (12). First, there is a new pole in the lower half plane at $p = -i\alpha$. Both the shifted and the unshifted functions have a pole in the upper half plane at $p = i\alpha$, but in the shifted transformed function a new pole appears. The new pole reflects a contribution from the wave function $e^{\alpha r_a}$ which becomes important in the range of $0 < r < R$, where it remains finite. It is useful to utilize the interpretation of Coulomb-like operators (e.g., $1/r_a$, $1/r_b$; Chapter 6) in momentum space as momentum transfer operators [42]. Then attractive or repulsive forces may be considered to impart momentum by means of an impulse. If the impulse is coming from the direction of positive r, then the pole is $p = i\alpha$. If the impulse is coming from the opposite direction, then the pole is $p = -i\alpha$. If the pole $p = i\alpha$ represents i times the momentum at which ionization occurs, then the opposite pole represents a momentum of the same magnitude but opposite direction. The behavior of the functions $1/(p - i\alpha)^2$ and $1/(p - i\alpha)$ for values of p in the upper half plane are connected with $e^{-\alpha r_b}$ for $r_a \geq R$. The behavior of the functions $1/(p + i\alpha)^2$ and $1/(p + i\alpha)$ for values of p in the lower half plane are connected with $e^{-\alpha r_b}$ for $r_a < R$ [38]. Second, we see the terms $\frac{e^{-\alpha R} - e^{-iRp}}{R}$ which appear in the numerator of the shifted function (17). These terms are absent in the unshifted function; however, they resemble terms found in the work of Coulson [18] on the hydrogen molecule-ion in momentum space. These are geometric terms and they consist of a constant and an oscillating term.

These terms limit the extent to which $e^{\alpha r_a}$ contributes to the LCAO momentum function. They allow in the transformed function only the part integrated from $0 \leq r \leq R$ where $e^{\alpha r_a}$ remains finite. The term $e^{-\alpha R}$ arises from the transform when we integrate with respect to r with $r = 0$ as one limit. The term e^{-iRp} arises from the transform when we integrate with respect to r with r = R as one limit. The term e^{-iRp} makes it possible to back transform the functions $1/(p+i\alpha)$ and $1/(p+i\alpha)^2$ to position space to obtain $\frac{e^{\alpha r_a}}{r_a}$, $e^{\alpha r_a}$. Lastly, it is important to examine the shifted momentum function (17) when R ⇒ 0. In the limit when R approaches zero the factor $\frac{e^{-\alpha R}-e^{-iRp}}{R}$ approaches $i(p + i\alpha)$.

$$\lim_{R\to 0}\frac{e^{-\alpha R}-e^{-iRp}}{R}=i(p+i\alpha)$$

When $i(p + i\alpha)$ is multiplied by the remaining terms in (17) as R → 0, the pole in the lower half plane disappears and (17) approaches

$$\frac{-2}{(p-i\alpha)^2}$$

which is (twice) the unnormalized hydrogen atom momentum function (Appendix A). As R → 0, the distance between nuclei a and b approaches zero. Therefore nucleus b approaches nucleus a and the shifted function becomes (twice) the unshifted function.

As a test of the shifted momentum wave function, the following integrals including:

<1> S (Charge Overlap)

<2> J (Coulomb Attraction)

<3> K (Exchange)

are calculated below using (17) in place of $e^{-\alpha r_b}$.

Charge Overlap (S)

The charge overlap, S, arises from the product of the two atomic orbitals, $e^{-\alpha(r_a+r_b)}$. The integral is large only when the orbitals overlap strongly. The maximum charge density occurs along the line joining the two nuclei and falls off away from that line. S is equal to zero when the internuclear distance is large because then the atomic orbitals do not overlap sufficiently. As the internuclear distance goes to zero, the overlap charge distribution approaches the same spherical shape as the atomic distributions and S approaches unity.

CALCULATION OF CHARGE OVERLAP (S)

$$S=\int\phi_a^*\phi_b d\tau \tag{18}$$

$$S=\frac{\alpha^3}{\pi}\int e^{-\alpha r_a}e^{-\alpha r_b}d\tau \tag{19}$$

S will be determined by performing a radial integration entirely in momentum space. In order to accomplish this, we need the momentum representations for the LCAO functions $e^{-\alpha r_a}$ (12) and $e^{-\alpha r_b}$ (17).

First, we replace $e^{-\alpha r_a}$ with its representation in momentum space,

$$-\frac{1}{(p-i\alpha)^2}$$

and use the complex conjugate

$$-\frac{1}{(p+i\alpha)^2}$$

in the integral. Next, we replace $e^{-\alpha r_b}$ in the integral with its representation in momentum space (17). Finally, we replace the volume element dτ with dp and integrate in momentum space to obtain S.

$$S = \frac{1}{\alpha R}\frac{\alpha^3}{\pi}\int_{-\infty}^{\infty}\frac{-dp}{(p+i\alpha)^2} \quad \times$$

$$\left[\frac{(e^{-\alpha R}-e^{-iRp})}{(p+i\alpha)^2} - \frac{i}{\alpha(p+i\alpha)}\left(e^{-\alpha R}(\alpha R+1) - e^{-iRp}\right)\right.$$

$$\left. + \frac{(e^{-\alpha R}-e^{-iRp})}{(p-i\alpha)^2} + \frac{i}{\alpha(p-i\alpha)}\left(e^{-\alpha R}(\alpha R+1) - e^{-iRp}\right)\right] \qquad (20)$$

In conjugate momentum space, we consider p a complex variable. The resulting integrals are easily evaluated using Cauchy's theorem, where the path of integration surrounds the singularity, ±iα. Cauchy's fundamental integral theorem states that if f(z) is an analytic function inside and on C, a simple closed contour, and a is any point inside C, then the nth derivative of f(z) at z = a is given by

$$f^{n}(a)=\frac{n!}{2\pi i}\oint_{c}\frac{f(z)}{(z-a)^{n+1}}dz \qquad n=1,2,3...$$

where C is traversed in the positive or counterclockwise sense.

For example, consider one of the integrals occurring in the calculation of charge overlap (20).

$$I_s=\int_{-\infty}^{\infty}dp\frac{e^{-iRp}}{(p+i\alpha)^4}$$

This integral represents an integration along the entire length of the real axis, of the function

$$f(z)=\frac{e^{-iRz}}{(z+i\alpha)^4}$$

a function with a pole at z = -iα of order 4. A contour is chosen that includes a semicircle, C_Γ, in the lower half plane and the real p axis which extends from (-Γ, Γ) where $\Gamma \Rightarrow \infty$. Integrating f(z) clockwise around the boundary of the semicircular region we have:

$$\int_{-\Gamma}^{\Gamma} \frac{e^{-iRp}}{(p+i\alpha)^4}\,dp + \int_{C_\Gamma} \frac{e^{-iRz}}{(z+i\alpha)^4}\,dz = \frac{-2\pi i}{n!} f^{III}(-i\alpha)$$

$$z = p + i\eta$$

where η is an arbitrary negative real number.

From the expression for f(z), we see that

$$\frac{-2\pi i}{n!} f^{III}(-i\alpha) \;=\; -2\pi i(iR^3 e^{-\alpha R}) \;=\; \frac{\pi R^3}{3} e^{-\alpha R}$$

Therefore, I_s becomes:

$$I_s \;=\; \int_{-\Gamma}^{\Gamma} \frac{e^{-iRp}}{(p+i\alpha)^4}\,dp \;=\; \frac{\pi R^3}{3} e^{-\alpha R} - \int_{C_\Gamma} \frac{e^{-iRz}}{(z+i\alpha)^4}\,dz$$

Now we examine the integrand on the right as an analytic function of the complex variable $z = p + i\eta$ and investigate the behavior of

$f(z) = \dfrac{e^{-iRz}}{(z+i\alpha)^4}$ in the complex plane. Apart from the singularity at the point $z = -i\alpha$ where the function goes to infinity, the function is regular everywhere in the lower half complex plane. In addition, since R is positive $e^{-iR(p+i\eta)} = e^{-iRp}\, e^{R\eta}$ goes strongly to zero along any ray of the lower half-plane ($\eta < 0$). Therefore we can close the path of integration over the infinite semicircle $\Gamma = \infty$ of the lower half-plane and by Cauchy's integral theorem, this integral vanishes as $\Gamma \to \infty$. It follows that:

$$I_s = \lim_{\Gamma\to\infty} \int_{-\Gamma}^{\Gamma} \frac{e^{-iRp}}{(p+i\alpha)^4}\, dp = \frac{\pi R^3}{3} e^{-\alpha R}$$

We use Cauchy's theorem to evaluate the remaining integrals in (20).

$$S = \frac{\alpha^3}{\pi} \frac{1}{\alpha R} \frac{\pi R}{\alpha^2} e^{-\alpha R} \left(1 + \alpha R + \frac{\alpha^2 R^2}{3} \right)$$

$$= e^{-\alpha R} \left(1 + \alpha R + \frac{\alpha^2 R^2}{3} \right) \tag{21}$$

Expression (21) for the overlap integral, S, is identical to that obtained by Slater [39], using the position space representation. The function exhibits the correct behavior because it goes to zero when R becomes infinite and approaches unity as R goes to zero. This confirms that the momentum wave function (17) accurately represents the transform of the $1s_b$ wave function, $e^{-\alpha r_b}$.

Calculation of Coulomb Integral (J)

The Coulomb integral, for the H_2^+ LCAO approximation, represents the average electrostatic interaction energy at nucleus b arising from a spherically symmetric charge distribution whose density is $e^{-2\alpha r_a}$ centered about nucleus a.

$$J = \int \phi_a^* \frac{2}{r_b} \phi_a d\tau \tag{22}$$

$$J = \int e^{-\alpha r_a} \frac{2}{r_b} e^{-\alpha r_a} d\tau \tag{23}$$

In order to calculate J, we first need to transform $\frac{1}{r_b} \times e^{-\alpha r_a}$ to momentum space. We begin with the operator $\frac{1}{r_b}$ and integrate with respect to the angular part (cos θ) in position space. Then we perform the radial transform of the operator, $\frac{1}{r_b}$ × the wave function, $e^{-\alpha r_a}$.

$$\frac{1}{r_b} = \frac{1}{\sqrt{r_a{}^2 - 2r_a R\cos\theta + R^2}}$$

First we integrate with respect to cosθ:

$$\int_0^\infty dr_a r_a{}^2 \frac{e^{-ir_a p_a}}{r_a} e^{-\alpha r_a} \int_{-1}^{1} \frac{d\cos\theta}{\sqrt{r_a{}^2 - 2r_a R\cos\theta + R^2}} \qquad (24)$$

$$\int_{-1}^{1} \frac{d\cos\theta}{\sqrt{r_a{}^2 - 2r_a R\cos\theta + R^2}} = \left(\begin{array}{ll} \dfrac{2}{r_a} & (R < r_a < \infty) \\ \dfrac{2}{R} & (0 < r_a \leq R) \end{array} \right) \qquad (25)$$

We place (25) in (24) and now apply the radial transform to $\frac{1}{r_b} e^{-\alpha r_a}$

$$I_J = \int_0^\infty dr_a r_a^2 \frac{e^{-ir_a p_a}}{r_a} e^{-\alpha r_a} \times \left(\begin{array}{ll} \dfrac{2}{r_a} & (R < r_a < \infty) \\ \dfrac{2}{R} & (0 < r_a \leq R) \end{array} \right) \qquad (26)$$

$$= \frac{2}{R}\int_0^R dr_a r_a^2 \frac{e^{-ir_a p} e^{-\alpha r_a}}{r_a} \quad + \quad 2\int_R^\infty dr_a r_a^2 \frac{e^{-ir_a p} e^{-\alpha r_a}}{r_a^2} \tag{27}$$

$$= \frac{2ie^{-R(ip+\alpha)}}{p-i\alpha} + \frac{2e^{-R(ip+\alpha)}}{R(p-i\alpha)^2} - \frac{2}{R(p-i\alpha)^2} - \frac{2ie^{-R(ip+\alpha)}}{p-i\alpha} \tag{28}$$

The last term in (28) arises from the second integral R $\leq$ r $<$ ∞, and the remaining three terms arise from the first 0 $<$ r $<$ R. Combining terms we obtain:

$$I_J = \frac{2}{R}\frac{(e^{-R(ip+\alpha)}-1)}{(p-i\alpha)^2} \tag{29}$$

To complete the integration in momentum space we multiply by the momentum representation of $e^{-\alpha r_a}$, (12), and take its complex conjugate, which is:

$$-\frac{1}{(p+i\alpha)^2} \tag{30}$$

We substitute the momentum functions (29) and (30) in the integral (23).

$$J = \frac{4}{R}\int_{-\infty}^{\infty} dp \frac{-1}{(p+i\alpha)^2} \frac{(e^{-R(ip-\alpha)}-1)}{(p-i\alpha)^2} \tag{31}$$

Using Cauchy's theorem, we integrate around a semicircle in the lower half-plane and the real p axis (-Γ, Γ) that surrounds the singularity at the point $p = -i\alpha$. Using this contour, the integral over the semicircle vanishes as $\Gamma \rightarrow \infty$ since the integrand goes to zero along any ray of the lower half-plane, as shown in the calculation of S. Evaluating the residue we then obtain,

$$J = \frac{-2\pi e^{-2\alpha R}}{R\alpha^3} - \frac{2\pi e^{-2\alpha R}}{\alpha^2} + \frac{2\pi}{R\alpha^3} \tag{32}$$

$$= \frac{2\pi}{R\alpha^3}(1-e^{-2\alpha R}(\alpha R+1)) \tag{33}$$

The result in (33) for J is identical to that obtained by Slater [39] using the position space representation.

Calculation of Exchange Integral (K)

The K integral is usually referred to as a resonance or exchange integral, because the two wave functions involved differ from one another in the interchange of electrons. Here however, although the integral contains the two wave functions a and b, it is really not an exchange integral since there is only one electron.

$$K = \int \phi_b^* \frac{2}{r_a} \phi_a d\tau$$

$$K = \int d\tau \; e^{-\alpha r_b} \frac{2}{r_a} \, e^{-\alpha r_a} \tag{34}$$

We transform $\frac{2}{r_a} \, e^{-\alpha r_a}$ to momentum space.

$$2\int_0^\infty dr_a \; r_a^2 \; \frac{e^{-\alpha r_a}}{r_a} \; \frac{e^{-ir_a p_a}}{r_a} = 2\int_0^\infty dr_a e^{-r_a(\alpha - ip_a)} = \frac{-2i}{p-i\alpha} \tag{35}$$

The integral above was evaluated using (16b).

The function $e^{-\alpha r_b}$ in momentum space is shown in (17); however, to perform the integration in (34) we need the complex conjugate, which is:

$$\frac{1}{\alpha R}\left[(e^{-\alpha R}-e^{+iRp})\left(\frac{1}{(p-i\alpha)^2}+\frac{1}{(p+i\alpha)^2}\right)+\right.$$

$$\left.\frac{i}{\alpha}((\alpha R+1)e^{-\alpha R}-e^{+iRp})\left(\frac{1}{(p-i\alpha)}-\frac{1}{(p+i\alpha)}\right)\right] \tag{36}$$

where i has been replaced with -i. Now we are ready to perform the integration in momentum space. We place the transformed functions (35) and (36) in the K integral (34) and apply Cauchy's theorem:

$$K = \frac{-2i}{\alpha R}\int_{-\infty}^{\infty} dp\left[(e^{-\alpha R}-e^{+iRp})\left(\frac{1}{(p-i\alpha)^2}+\frac{1}{(p+i\alpha)^2}\right)+\right.$$

$$\left.\frac{i}{\alpha}((\alpha R+1)e^{-\alpha R}-e^{+iRp})\left(\frac{1}{(p-i\alpha)}-\frac{1}{(p+i\alpha)}\right)\right]\frac{1}{(p-i\alpha)} \tag{37}$$

We choose a contour of integration which surrounds the singularity at $p = i\alpha$ that includes a semicircle in the upper half plane and the real p axis, which extends from $(-\Gamma, \Gamma)$ where $\Gamma \Rightarrow \infty$.

$$K = \frac{\pi R}{\alpha}e^{-\alpha R}(\alpha R+1) \tag{38}$$

Expression (38) for K is identical to that obtained by Slater [39] using the position representation. This confirms that the momentum representation of $e^{-\alpha r_b}$ is correct and can successfully be used in the above integrals to determine S, J, and K.

Direct Transform of $e^{-\alpha r_b}$

Another approach to H_2^+ in momentum space involves representing $e^{-\alpha r_b}$ as $e^{-\alpha|\vec{r}_a-\vec{R}|}$. The main idea is to take an atomic orbital located at atom b and rewrite it in terms of functions centered about an atomic position a. The atomic orbital at b is represented by an expansion in r_a and R where each function in the expansion depends on one vector only and each is a function of definite angular momentum.

To begin this procedure we start with the function $e^{-\alpha r_b}$, where r_b is the distance from atom b and consider the $\ell=0$ case, where $Y(\theta_b,\phi_b)=1$. We use the substitution (law of cosines)

$$r_b=\sqrt{r_a^2+R^2-2r_aR\cos\theta}$$

and the "Summation Theorem" for Bessel Functions (GR 8.532.1)

$$\frac{Z_\nu(mr_b)}{r_b^\nu}=2^\nu m^{-\nu}\Gamma(\nu)\sum_{k=0}^{\infty}(\nu+k)\frac{J_{\nu+k}(mr_a)}{r_a^\nu}\frac{Z_{\nu+b}(mR)}{R^\nu}C_k^\nu(\cos\theta) \qquad (39)$$

for all $r_a < R$.

$Z_\nu(r)$ are arbitrary Bessel functions and are solutions of the differential equation

$$\frac{d^2Z_\nu}{dz^2}+\frac{1}{z}\frac{dZ_\nu}{dz}+(1-\frac{\nu^2}{z^2})Z_\nu=0$$

(GR 8.401)

$J_\nu(r)$ are Bessel functions of the first kind

$$J_\nu(z)=\frac{z^\nu}{2^\nu}\sum_{k=0}^{\infty}(-1)^k\frac{z^{2k}}{2^{2k}k!\,\Gamma(\nu+k+1)} \qquad [|\arg z|<\pi]$$

(GR 8.402)

and $C_k^\nu(\cos\theta)$ are Gegenbauer functions which are generalizations of the Legendre functions. We may disregard the restriction that $r_a < R$, since r_a and R are interchangeable in the expression for r_b. We take the smaller of the two, $\min(r_a,R)$ in J and the larger of the two, $\max(r_a,R)$ in Z. We choose $m=i$ and $\nu=-1/2$;

$$Z_\nu(mr_b)=H_\nu^{(1)}(ir_b)=\frac{2}{\pi i}e^{-\pi\nu i/2}K_\nu(r_b) \qquad (40)$$

(GR 8.407.1)

$H_\nu^{(1)}(ir)$ are Bessel functions of the third kind or Hankel functions which are linear combinations of Bessel functions of the first and second kind. $K_\nu(r)$ are modified Bessel functions of imaginary argument. Hankel functions are related to the modified Bessel functions, K_ν, as shown in (40).

K_ν has a simple expression when $\nu = \pm 1/2$:

$$K_{\pm 1/2}(r_b) = \sqrt{\frac{\pi}{2r_b}}\, e^{-r_b} \tag{41}$$

(GR 8.4693);

We rearrange (41)

$$e^{-\alpha r_b} = \sqrt{\frac{2\alpha r_b}{\pi}}\, K_{-1/2}(\alpha r_b) = \sqrt{\frac{2\alpha}{\pi}}\, \frac{K_{-1/2}(\alpha r_b)}{{r_b}^{-1/2}} = e^{-i\pi/4}\, i \sqrt{\frac{\alpha\pi}{2}}\, \frac{H^{(-1)}_{-1/2}(i\alpha r_b)}{{r_b}^{-1/2}}$$

where r_b is replaced by αr_b.

Now we use equation (39) where we have chosen ν=-1/2 and simplify.

$$e^{-\alpha r_b} = -2\alpha\sqrt{i}\sum_{k=0}^{\infty} (k-1/2)\sqrt{r_a R}\, e^{-i\pi k/2}$$

$$\times\, J_{k-1/2}(i\alpha \min(r_a,R))\, K_{k-1/2}(\alpha \max(r_a,R))\, C_k^{-1/2}(\cos\theta) \tag{42}$$

Angular Functions--Gegenbauer Functions

Below is shown the relation between the Gegenbauer functions, $C_k^{\nu}(t)$ and the Legendre functions,

$$C_k^{-1/2}(t) = \frac{\Gamma(k-1)\Gamma(0)}{\Gamma(-1)\Gamma(k+1)}(1/4(t^2-1))^{1/2}P_{k-1}^{1}(t)$$

(GR 8.936.1) (λ=-1/2 and t=cosθ)

In order to evaluate the expression

$$\frac{\Gamma(0)}{\Gamma(-1)}$$

it is necessary to use an identity that is derived from the Weierstrass infinite product definition of $\Gamma(z)$ [40]:

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin\pi z}$$

We approximate $\Gamma(0)$ by letting $z = 1 + \epsilon$, (then $1 - z = -\epsilon$), and we approximate $\Gamma(-1)$ by letting $z = 2 + \epsilon$, (then $1 - z = -1 - \epsilon$). We now expand $\sin\pi z$ and take the limit as $\epsilon \to 0$, recalling that $\Gamma(1) = \Gamma(2) = 1$.

$$\Gamma(1+\epsilon)\Gamma(-\epsilon) = \frac{\pi}{\sin\pi(1+\epsilon)}$$

$$\Gamma(2+\epsilon)\Gamma(-1-\epsilon) = \frac{\pi}{\sin\pi(2+\epsilon)}$$

$$\frac{\Gamma(0)}{\Gamma(-1)} = \lim_{\epsilon\to 0}\frac{\sin\pi(2+\epsilon)}{\sin\pi(1+\epsilon)}$$

After simplifying, the result is

$$\frac{\Gamma(0)}{\Gamma(-1)} = -1$$

Further simplification of the remaining gamma functions gives

$$\frac{\Gamma(k-1)}{\Gamma(k+1)} = \frac{(k-2)!}{k!} = \frac{1}{k(k-1)}$$

We use the following recursion relation for the Legendre functions:

$$\sqrt{1-t^2}\,P_\nu^{\mu+1}(t) = \frac{1}{2\nu+1}\left[(\nu-\mu)(\nu-\mu+1)P_{\nu+1}^{\mu}(t) - (\nu+\mu)(\nu+\mu+1)P_{\nu-1}^{\mu}(t)\right]$$

(GR 8.735.5)

Substitute ν = k - 1 and μ = 0; let t = cos θ; simplify:

$$C_k^{-1/2}(\cos\theta) = \frac{-i(P_k^0(\cos\theta) - P_{k-2}^0(\cos\theta))}{2(2k-1)} \tag{43}$$

We will use (43) to replace the Gegenbauer functions with the Legendre functions in equation (42). After simplification, $e^{-\alpha r_b}$ (ℓ = 0) becomes:

$$e^{-\alpha r_b} = \frac{-i^{3/2}}{2}\sum_{k=0}^{\infty} \alpha\sqrt{r_a R}\, e^{-i\pi k/2} J_{k-1/2}(i\alpha \min(r_a,R))\, K_{k-1/2}(\alpha \max(r_a,R))$$

$$\times \quad \left(P_k^0(\cos\theta) - P_{k-2}^0(\cos\theta)\right) \tag{44}$$

Transformation to Momentum Space

DeWitt Radial Transform

The radial functions, to be transformed to momentum space, are Bessel functions of half-integer order. These functions are the only Bessel functions that can be expressed in terms of elementary functions. For example, the general expression in terms of elementary functions is:

$$J_{n+1/2} = (-1)^n \left(\frac{2}{\pi}\right)^{1/2} z^{n+1/2} \left(\frac{d}{zdz}\right)^n \frac{\sin z}{z} \qquad n = 0,1,2...$$

We are now ready to transform the radial functions $J_{k-1/2}(i\alpha r)$ and $K_{k-1/2}(\alpha r)$ to momentum space using the DeWitt transform.

$$I_r = \int_0^\infty dr\, r^2 \sqrt{r} \frac{e^{-irp}}{r} J_{k-1/2}(i\,\alpha \min(r,R))\, K_{k-1/2}(\alpha \max(r,R))$$

Let $r = r_a$. The integral I_r is divided into two integrals, I_{r1} $(r < R)$ and I_{r2} $(r > R)$.

$$K_{k-1/2}(\alpha R)\int_0^R dr\, r\sqrt{r}\, e^{-irp} J_{k-1/2}(i\alpha r) \quad + \qquad I_{r1} \ (r<R)$$

$$J_{k-1/2}(i\alpha R)\int_R^\infty dr\, r\sqrt{r}\, e^{-irp} K_{k-1/2}(\alpha r) \qquad I_{r2} \ (r>R)$$

We will utilize the following expansions for $K_{k-1/2}(\alpha r)$ and $J_{k-1/2}(i\alpha r)$, (GR 8.468, GR 8.462).

$$K_{k-1/2}(\alpha r) = \sqrt{\frac{\pi}{2r}}\, e^{-\alpha r} \sum_{m=0}^{k-1} \alpha^{-m} \gamma_k^m(r) \tag{45}$$

$$J_{k-1/2}(i\alpha r) = \frac{1}{\sqrt{2\pi i\alpha r}}\left[e^{i\alpha r} \sum_{m=0}^{k-1} i^{-k} \alpha^{-m} \gamma_k^m(r) \quad + \right. \\ \left. e^{-i\alpha r} \sum_{m=o}^{k-1} (-1)^{m-k} i^{-k} \alpha^{-m} \gamma_k^m(r) \right] \tag{46}$$

We introduce the function $\gamma_k^m(\alpha r)$

$$\gamma_k^m(\alpha r) = \frac{\alpha^{-m}(k+m-1)!}{m!(k-m-1)!(2r)^m}$$

The two integrals I_{r1} and I_{r2} are rewritten to include the expansions in (45) and (46).

$$I_{r1} = \frac{1}{\sqrt{2\pi i\alpha}} K_{k-1/2}(\alpha R) \sum_{m=0}^{k-1} \left[i^{m-k} \int_0^R dr\, r\, \gamma_k^m(i\alpha r) e^{-r(ip+\alpha)} \right. +$$

$$\left. (-i)^{m-k} \int_0^R dr\, r\, \gamma_k^m(ir) e^{-r(ip-\alpha)} \right]$$

$$I_{r2} = \sqrt{\frac{\pi}{2\alpha}} J_{k-1/2}(i\alpha R) \sum_{m=0}^{k-1} \int_R^{\infty} dr\, r\, \gamma_k^m(\alpha r) e^{-r(ip+\alpha)}$$

$I_{r1} + I_{r2}$ can be resolved to give a simplified expression for $e^{-\alpha r_b}$ ($\ell = 0$):

$$e^{-\alpha r_b} = \sum_k^{\infty} \frac{i^{1-k}}{4} e^{\frac{-i\pi k}{2}} \{P_k^0(\cos\theta) - P_{k-2}^0(\cos\theta)\} \quad \times$$

$$\sum_{m'=0}^{k-1} \sum_{m=0}^{k-1} \alpha^{-m'} \alpha^{-m}\, r\, \gamma_k^{m'}(R)\, \gamma_k^m(r) \quad \times \tag{47}$$

$$\left[\frac{(e^{-\alpha R} + (-1)^{m'-k} e^{-iRp})}{ip+\alpha} + \frac{(-1)^{m-k}(e^{-\alpha R} - e^{-iRp})}{ip-\alpha} \right]$$

When we evaluate the product of factors $\gamma_k^m(r)$ x r roduct for $\ell = 0$, (where m = 0 or 1 and m′ = 0 or 1), the product simplifies to multipication by a constant or by r in the case ($m = 0$, $m' = 1$). Since multiplication by r has a simple momentum represention, r ⇒ id/dp, this operation will be performed in momentum space for the case ($m = 0$, $m' = 1$).

Transform of Angular Functions

Lombardi [1] has shown that the hydrogen atom momentum angular functions, $\beta(p_\theta)$ are connected to the Legendre functions by a Fourier transform.

$$\int_{-1}^{1} d(\cos\theta)\, e^{-i\cos\theta p_\theta} P_k^0(\cos\theta) = \beta_\ell^m(p_\theta)$$

$$\beta_\ell^m(p_\theta) = \sum_{j=E(m/2)}^{E(\ell/2)} a_j p_\theta^{-(m+1)/2} J_{j-(m-1)/2}(p_\theta)$$

The generalized hydrogen momentum wave function centered on nucleus b is shown in (48). It is the same representation as in (47) with the Legendre functions replaced by the momentum angular functions $\beta_\ell^m(p_\theta)$.

$$\begin{aligned} e^{-\alpha r_b} &= \sum_{k}^{\infty} \frac{i^{1-k}}{4} e^{\frac{-i\pi k}{2}} \left(\beta_k^0(p_\theta) - \beta_{k-2}^0(p_\theta)\right) \quad \times \\ & \sum_{m'=0}^{k-1} \sum_{m=0}^{k-1} \alpha^{-m'} \alpha^{-m}\, r\, \gamma_k^{m'}(R)\, \gamma_k^m(r) \quad \times \\ & \left[\frac{(e^{-\alpha R} + (-1)^{m'-k} e^{-iRp})}{ip+\alpha} + \frac{(-1)^{m-k}(e^{-\alpha R} - e^{-iRp})}{ip-\alpha}\right] \end{aligned} \tag{48}$$

At this point it is useful to examine (48) when $R \Rightarrow 0$. We see immediately that the term on the right containing the pole at $p = i\alpha$, vanishes when $R \Rightarrow 0$. Examining the term on the left, we see that for the cases when the exponential term $m' - k$ is even, the pole at $p = -i\alpha$ remains. This is the pole that is found in the momentum representation of the hydrogen atom. Therefore (48) is exhibiting the correct behavior as $R \Rightarrow 0$, since $e^{-\alpha r_b} \Rightarrow e^{-\alpha r_a}$.

In order to compare the results of this transform, where $e^{-\alpha r_b}$ was expanded in sums over Bessel functions and Legendre functions, with the results from the earlier transform it is necessary to integrate with respect to the unnormalized angular functions, $\beta_k^0(p_\theta)$. The momentum angular functions are orthogonal and multiplying by $\beta_k^0(p_\theta)$ and integrating gives contributions from $k = 0$ and $k = 2$.

$$\underset{k\,=\,0}{\int \beta_k^0(p_\theta)\,\beta_k^0(p_\theta)\,dp_\theta} = \underset{k\,=\,2}{\int \beta_{k-2}^0(p_\theta)\,\beta_{k-2}^0(p_\theta)\,dp_\theta} = \frac{2}{\pi}\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}\,dx = 2$$

$$\int \beta_k^0(p_\theta)\,\beta_{k-2}^0(p_\theta)\,dp_\theta = 0$$

There is only one $k = 0$ term ($m=0$, $m'=0$) which cancels one of the four $k=2$ ($m=0$, $m'=0$) terms. The remaining three terms from $k = 2$ all contribute: (m=0, m′=1), (m=1, m′=0), and (m=1, m′=1).

$$(m=0,m'=1)\Rightarrow\frac{r}{\alpha R}\left[\frac{e^{-\alpha R}}{ip+\alpha}-\frac{e^{-iRp}}{ip+\alpha}+\frac{e^{-\alpha R}}{ip-\alpha}-\frac{e^{-iRp}}{ip-\alpha}\right] \tag{49}$$

$$(m=1,m'=0)\Rightarrow\frac{1}{\alpha}\left[\frac{e^{-\alpha R}}{ip+\alpha}+\frac{e^{-iRp}}{ip+\alpha}-\frac{e^{-\alpha R}}{ip-\alpha}+\frac{e^{-iRp}}{ip-\alpha}\right] \tag{50}$$

$$(m=1,m'=1)\Rightarrow\frac{1}{\alpha^2 R}\left[\frac{e^{-\alpha R}}{ip+\alpha}-\frac{e^{-iRp}}{ip+\alpha}-\frac{e^{-\alpha R}}{ip-\alpha}+\frac{e^{-iRp}}{ip-\alpha}\right] \tag{51}$$

Now we multiply by r in (49); this operation was postponed until now.

$$r\Rightarrow i\frac{d}{dp}$$

$$(m=0,m'=1)\Rightarrow\frac{i}{\alpha R}\frac{d}{dp}\left[\frac{e^{-\alpha R}}{ip+\alpha}-\frac{e^{-iRp}}{ip+\alpha}+\frac{e^{-\alpha R}}{ip-\alpha}-\frac{e^{-iRp}}{ip-\alpha}\right]$$

After simplification the result is:

$$\frac{1}{2\alpha R}\left[(e^{-\alpha R}-e^{-iRp})\left(\frac{1}{(p+i\alpha)^2}+\frac{1}{(p-i\alpha)^2}\right)-\frac{i}{\alpha}((\alpha R+1)e^{-\alpha R}-e^{-iRp})\left(\frac{1}{(p+i\alpha)}-\frac{1}{(p-i\alpha)}\right)\right] \tag{52}$$

Collecting constants, including the factor 2 arising from the multiplication by the angular function, $\beta_0^0(p\theta)$, and simplifying, (52) is the unnormalized radial DeWitt transform of $e^{-\alpha r_b}$ and it agrees with the previous result (17) (except for the 1/2 factor). (This constant arises because of a difference in the procedure of the two transform methods. The direct transform involved a transform of the angular functions to momentum space. The first method integrated with respect to the angular functions in position space.) Normalization will correct this discrepancy. The normalization constant, which applies to equation (17) is found by solving the equation:

$$N^2\int F^*(p)F(p)dp = 1$$

$$N = \frac{\alpha R}{2}\sqrt{\frac{\alpha^3}{\pi}}$$

where F(p) is represented by equation (17).

5 SHIFTED SLATER ORBITALS

Radial DeWitt Transform of $r_b^{n-1}e^{-\beta r_b}$:

In this section, we show the transform to momentum space of a shifted Slater orbital $r_b^{n-1}e^{-\beta r_b}$, centered on nucleus b, with $Y(\theta_b, \phi_b) = 1$. Nucleus b is located a distance R from nucleus a. In order to apply the DeWitt transform, the function centered about nucleus b is rewritten as a linear combination of terms of functions centered about nucleus a. We will be integrating in a hybrid space ($\cos\theta_a$, ϕ_a, p_r), as defined previously. First, we integrate with respect to the angular coordinates in position space, followed by integration in momentum space, with respect to the momentum radial variable, p_r. We use the substitution

$$r_b = \sqrt{r_a^2 + R^2 - 2 r_a R \cos\theta}$$

The radial DeWitt transform is:

$$I_{SL} = \int_0^\infty dr r^2 \frac{e^{-irp}}{r} \int_{-1}^{1} (r^2 + R^2 - 2rR\cos\theta)^{(n-1)/2} e^{-\alpha(r^2+R^2-2rR\cos\theta)1/2} d\cos\theta$$

where $r = r_a$ and $p = p_r$.

Now we integrate with respect to $\cos\theta$ in position space and use (GR 2.321.2) to evaluate I_{SL}.

$$= \frac{1}{\beta R} \int_0^\infty dr e^{-irp} \left[e^{-\beta|r-R|} |r-R|^n + \sum_{k=1}^{n} \frac{(-1)^k n(n-1)\ldots(n-k+1)(|r-R|)^{n-k}}{(-\beta)^k} \right.$$

$$\left. - e^{-\beta|r+R|} |r+R|^n + \sum_{k=1}^{n} \frac{(-1)^k n(n-1)\ldots(n-k+1)(|r+R|)^{n-k}}{(-\beta)^k} \right]$$

Remove absolute value signs:

$$|r - R| = r - R \quad (R \leq r < \infty)$$

$$R - r \quad (0 < r < R)$$

$$|r + R| = r + R \quad (0 < r < \infty)$$

Integration with respect to r results in three integrals: I_{SL1}, I_{SL2} and I_{SL3}.

$$\sqrt{\frac{\beta^3}{\pi}\frac{1}{\beta R}} \qquad x$$

$$\left[\int_R^\infty dr\, e^{-irp} e^{-\beta(r-R)} \left((r-R)^n + \sum_{k=1}^{n} \frac{(-1)^k n(n-1)\ldots(n-k+1)(r-R)^{n-k}}{(-\beta)^k} \right) \right. +$$

$$\int_0^R dr\, e^{-irp} e^{-\beta(R-r)} \left((R-r)^n + \sum_{k=1}^{n} \frac{(-1)^k n(n-1)\ldots(n-k+1)(R-r)^{n-k}}{(-\beta)^k} \right) -$$

$$\left. \int_0^\infty dr\, e^{-irp} e^{-\beta(r+R)} \left((r+R)^n + \sum_{k=1}^{n} \frac{(-1)^k n(n-1)\ldots(n-k+1)(r+R)^{n-k}}{(-\beta)^k} \right) \right]$$

The first integral, I_{SL1}, is easily evaluated using (16a). The result is:

$$I_{SL1} = e^{-iRp} \left(\frac{n!}{(\beta + ip)} + \sum_{k=1}^{n} \frac{(-1)^k n(n-1)\ldots(n-k+1)\,(n-k)!}{(-\beta)^k (\beta + ip)^{n-k+1}} \right)$$

The second integral, I_{SL2}, may be evaluated using equation (16c). The result is:

$$I_{SL2} = \frac{e^{-iRp}n!}{(\beta - ip)^{n+1}} - e^{-R\beta}n!\sum_{k=0}^{n}\frac{1}{k!}\frac{R^k}{(\beta - ip)^{n-k+1}} \quad +$$

$$\sum_{k=1}^{n}\frac{(-1)^k n(n-1)...(n-k+1)}{(-\beta)^k} \quad \times$$

$$\left(\frac{e^{-iRp}(n-k)!}{(\beta - ip)^{n-k+1}} - e^{-R\beta}\sum_{k=0}^{n-k}\frac{(n-k)!}{k!}\frac{R^k}{(\beta - ip)^{n-2k+1}}\right)$$

The third integral, I_{SL3}, is evaluated using (16b). The result is:

$$I_{SL3} = -\frac{n!e^{-\beta R}}{(\beta + ip)^{n+1}}\left(1 + (\beta + ip)R + \frac{1}{2!}((\beta + ip)R)^2 + ...\frac{1}{n!}((\beta + ip)R)^n\right) \quad -$$

$$\sum_{k=1}^{n}\frac{(-1)^k n(n-1)...(n-k-1)}{(-\beta)^k}\frac{(n-k)!\,e^{-\beta R}}{(\beta + ip)^{n-k+1}} \quad \times$$

$$\left(1 + (\beta + ip)R + \frac{1}{2!}((\beta + ip)R)^2 + ...\frac{1}{(n-k)!}((\beta + ip)R)^{n-k}\right)$$

We may evaluate the solutions above for a particular n.

For example, for the case n=1

$$I_{SL} = \frac{1}{\beta R}\left[\int_0^R dr\, e^{-irp} e^{-\beta(R-r)}\left(R-r+\frac{1}{\beta}\right) + \int_R^\infty dr\, e^{-irp} e^{-\beta(r-R)}\left(r-R+\frac{1}{\beta}\right) - \int_0^\infty dr\, e^{-irp} e^{-\beta(r+R)}\left(r+R+\frac{1}{\beta}\right)\right]$$

For n=1, $r_b^{n-1} e^{-\beta r_b}$ reduces to $e^{-\beta r_b}$. The result shown below in (53) is the same as in (17) where β is replaced by α.

$$= \frac{1}{\beta R}\left[\left(e^{-\beta R} - e^{-iRp}\right)\left(\frac{1}{(p+i\beta)^2} + \frac{1}{(p-i\beta)^2}\right) - \frac{i}{\beta}\left((\beta R+1)e^{-\beta R} - e^{-iRp}\right)\left(\frac{1}{(p+i\beta)} - \frac{1}{(p-i\beta)}\right)\right] \tag{53}$$

6 OPERATORS IN MOMENTUM SPACE

Potential Operator $1/r_a$ in Momentum Space

According to Messiah [41] the correct way to represent V(p) the momentum representation of the potential energy operator, W(r) is :

$$V(p'-p)=\int_0^\infty W(r)e^{-i(p'-p)r}r^2dr$$

$$V(p)_{op}=\int_{-\infty}^{p}[V(p'-p)]\,dp'$$

Using the DeWitt transform V(p′-p) would be represented by:

$$V(p'-p)=\int_0^\infty W(r)\frac{e^{-i(p'-p)r}}{r^2}r^2dr$$

$$=\int_0^\infty (1/r_a)e^{-i(p'-p)r_a}dr_a$$

when W(r) = $1/r_a$

This integral diverges unless the range of integration is extended to (-∞,∞).

We take its principal value:

$$V(p'-p) = \frac{1}{2}\lim_{\epsilon\to 0}\left[\int_{-\infty}^{-\epsilon}\frac{e^{i(p-p')r_a}}{r_a}dr_a \quad + \quad \int_{\epsilon}^{\infty}\frac{e^{i(p-p')r_a}}{r_a}dr_a\right]$$

and integrate around a closed contour consisting of a semicircle in the upper half plane and the real axis which extends from $(-\Gamma,\Gamma)$ where $\Gamma \Rightarrow \infty$, with an infinitely small semicircle $(-\epsilon,\epsilon)$ where $\epsilon \Rightarrow 0$, drawn around the singularity at 0. The result is:

$$V(p'-p) = -i\pi$$

$$V(p) = -i\pi\int_{-\infty}^{p}dp'$$

$$\frac{1}{r_a} \Rightarrow i\pi\int_{-\infty}^{p}dp'$$

It has been suggested [42] that $1/r_a$ acts as a momentum transfer operator. It transfers momentum from nucleus a to the electron and vice versa.

Another way to show that $1/r_a$ is an integral operator in conjugate momentum space is to recognize that the operators are reciprocals

$$\frac{1}{r_a} \times r_a = 1$$

Since $r_a = i\partial/\partial p$, $1/r_a$ must represent the inverse operation which is integration. In addition a constant of integration must be properly chosen to ensure that the operators are reciprocals.

The DeWitt transform may be used to demonstrate the effect of the operator $1/r_a$ on $e^{-\alpha r_a}$. Transform the operator, $1/r_a$ x the wave function, $e^{-\alpha r_a}$:

$$\frac{1}{r_a} \times e^{-\alpha r_a} = \int_0^\infty dr_a r_a^2 \frac{e^{-ir_a p_a}}{r_a} \frac{e^{-\alpha r_a}}{r_a} = \frac{1}{ip+\alpha} = \frac{-i}{p-i\alpha}$$

To see what meaning $1/r_a$ has as an operator on the hydrogen atom momentum wave function examine $\frac{-i}{p-i\alpha}$ and ask, what operation on the momentum wave function, $\frac{-1}{(p-i\alpha)^2}$, was done to give $\frac{-i}{p-i\alpha}$? The answer is $-i\int_{-\infty}^{p} dp'$ which reveals that $1/r_a$ is acting as an integral operator on the momentum wave function.

Potential Operator $1/r_b$ in Momentum Space

The radial DeWitt transform of the operator $1/r_b$ to momentum space will be shown below following the procedure for the calculation of J:($\ell = 0$)

$$\frac{1}{r_b} = \frac{1}{\sqrt{r_a^2 - 2r_a R\cos\theta + R^2}}$$

We integrate over $\cos\theta$:

$$\int_{-1}^{1} \frac{d\cos\theta}{\sqrt{r_a^2 - 2r_a R\cos\theta + R^2}} = \begin{array}{ll} \dfrac{2}{r_a} & (R<r_a<\infty) \\ \dfrac{2}{R} & (0<r_a<R) \end{array}$$

$$\frac{1}{r_b} = \frac{1}{\min(r_a,R)}$$

$$V(p'-p) = \int_0^\infty \frac{e^{-i(p'-p)r_a}}{r_a^2} \frac{1}{\min(r_a,R)} r_a^2 dr_a$$

$$V(p'-p) = \int_0^\infty \frac{e^{-i(p'-p)r_a}}{R} dr_a + \int_0^\infty \frac{e^{-i(p'-p)r_a}}{r_a} dr_a$$

$$V(p'-p) = \frac{e^{i(p'-p)R} - 1}{iR(p'-p)} - Ei(-i(p'-p)R)$$

where Ei(x) is the exponential-integral function defined by:

$$Ei(x) = \int_{-\infty}^{x} \frac{e^{u}}{u} du$$

$$-Ei(-x) = \int_{x}^{\infty} \frac{e^{-u}}{u} du$$

The operator $1/r_b$ is represented below.

$$\left[\frac{1}{r_b}\right]_{op} = \int_{-\infty}^{p} dp' \left[\frac{e^{-i(p'-p)R} - 1}{iR(p'-p)} - Ei(-i(p'-p)R)\right]$$

It has been suggested [42] that the operator $1/r_b$ is a momentum transfer operator. This operator represents a transfer of momentum from nucleus b to the electron and vice versa. In order to show the effect the operator $1/r_b$ has on the hydrogen atom momentum wave function, we transform the operator,

$1/r_b$ x the wave function, $e^{-\alpha r_a}$. We follow the procedure above for the calculation of J, the Coulomb integral. In order to represent $\frac{1}{r_b}\times e^{-\alpha r_a}$ in momentum space, we recall the steps of integrating with respect to cos*θ* in position space before applying the radial DeWitt transform.

We use the substitution:

$$\frac{1}{r_b} = \frac{1}{\sqrt{r_a^2-2r_aR\cos\theta+R^2}}$$

$$\int_0^\infty dr_a r_a^2 \frac{e^{-ir_ap_r}}{r_a} e^{-\alpha r_a} \int_{-1}^1 \frac{d\cos\theta}{\sqrt{r_a^2-2r_aR\cos\theta+R^2}}$$

Integrate with respect to cos*θ*:

$$\int_{-1}^1 \frac{d\cos\theta}{\sqrt{r_a^2-2r_aR\cos\theta+R^2}} = \begin{matrix} \frac{2}{r_a} & (R \le r_a \le \infty) \\ \frac{2}{R} & (0 \le r_a \le R) \end{matrix}$$

Radial Transform to Momentum Space of $\frac{1}{r_b} \times e^{-\alpha r_a}$:

$$\frac{2}{R}\int_0^R dr\, r^2 \frac{e^{-irp}e^{-\alpha r}}{r} + 2\int_R^\infty dr\, r^2 \frac{e^{-irp}e^{-\alpha r}}{r^2}$$

$$= \frac{2ie^{-R(ip+\alpha)}}{p-i\alpha} + \frac{2e^{-R(ip+\alpha)}}{R(p-i\alpha)^2} - \frac{2}{R(p-i\alpha)^2} - \frac{2ie^{-R(ip+\alpha)}}{p-i\alpha}$$

$$= \frac{-2}{R}(e^{-R(ip+\alpha)}-1)\frac{-1}{(p-i\alpha)^2} \qquad (54)$$

To see what meaning $1/r_b$ has as an operator on the hydrogen atom momentum space wave function examine (54) and ask what operation was done on the momentum wave function, $\frac{-1}{(p-i\alpha)^2}$? The answer is

$$\frac{1}{r_b} = \frac{-2}{R}(e^{-R(ip+\alpha)}-1)$$

which means that $1/r_b$ is acting as a multiplicative operator on the radial momentum wave function in this momentum space. In fact for $\ell=0$ states, $1/r_b$ acts as a multiplicative operator on all test functions $e^{-\alpha r}$ where α is positive. It also acts as a multiplicative operator on Slater orbitals $r^{n-1}e^{-\beta r}$, β positive.

7 CONCLUDING REMARKS

Both position and momentum representations are equally capable of describing a quantum mechanical system. They correspond to different choices of basis in the Hilbert space of eigenfunctions. Why then are quantum mechanical problems for bound state systems most often studied in the position representation? One reason lies in the mathematical difficulties arising from the complicated form of the potential energy function in the momentum representation. The DeWitt transform to momentum space applied to the hydrogen [1] and helium atoms [2], in which the momentum variables (p_r, p_θ, p_ϕ), were chosen conjugate to the position variables, (r, $\cos\theta$, ϕ), has revealed that considerable simplification is obtained in the resulting Schrödinger equation and its solutions. The objectives of this research have been:

<1> to extend the DeWitt transform to represent the hydrogen molecule-ion in momentum space using a LCAO approach with hydrogen atom wave functions as basis;

<2> to calculate the relevant matrix elements S, J, and K;

<3> to find a momentum representation for the shifted LCAO $1s_b$ function, $e^{-\alpha r_b}$ $(\ell=0)$;

<4> to identify and explain the origin of an additional pole in the complex plane that appears in the momentum representation of $e^{-\alpha r_b}$ $(\ell=0)$ but is absent in the momentum representaion of $e^{-\alpha r_a}$ $(\ell=0)$;

<5> to identify and explain the origin of numerator terms $e^{-\alpha R}-e^{-iRp}$ which appear in the momentum representation of $e^{-\alpha r_b}$ $(\ell=0)$ but are absent in the momentum representation of $e^{-\alpha r_a}$ $(\ell=0)$;

<6> to represent shifted Slater orbitals in conjugate momentum space $(\ell=0)$;

<7> to represent the potential energy operators $1/r_a$, $1/r_b$ in conjugate momentum space.

In this research, an accurate approximation for the ground state of the hydrogen molecule-ion in the momentum representation has been found using two different procedures, both of which are based on the DeWitt transform. The first procedure involved the use of a hybrid space $(\cos\theta_a, \phi_a, p_r)$, in which integration with respect to the angular coordinates was carried out in position space, followed by integration in momentum space with respect to the momentum radial variable, p_r. An alternate procedure, referred to as the direct transform method, represented the atomic orbital at nucleus b by an expansion in Bessel functions of r_a and R. Both procedures give rise to the same wave function which is then used to calculate matrix elements S, J, and K. The momentum representation used is one in which the momentum variables were chosen to be conjugate to the spherical polar coordinates in position space. This choice of representation differs from the earlier work of Pauling and Podolsky [7] upon which all previous work on the hydrogen molecule-ion is based. Although the interval of interest for observable quantities involves only real values of the momentum, the integrations required were greatly simplified by considering the momentum variable, p_r, to be complex, enabling the use of residue theories. The momentum representation of the shifted LCAO $1s_b$ function, $e^{-\alpha r_b}$, $\ell = 0$, was shown to have poles of first and second order along the imaginary axis and these poles were located at $\pm i\alpha$, where α was the variational parameter. These poles distinguish the shifted atomic b function from the unshifted atomic a function, $e^{-\alpha r_a}$, $\ell = 0$, in which the latter has only one pole of second order located at $+i\alpha$. The additional pole at $-i\alpha$ represents the function, $e^{\alpha r_a}$, which makes a contribution when $0 < r < R$. If the pole at $p = i\alpha$ signifies i times the momentum at which ionization occurs, then the opposite pole, at $p = -i\alpha$, signifies a momentum of the same magnitude but opposite direction. The momentum representation of $e^{-\alpha r_b}$, is futher distingushed from the momentum representation of $e^{-\alpha r_a}$ by the presence of the numerator terms $e^{-\alpha R} - e^{-iRp}$. These terms limit the extent to which $e^{\alpha r_a}$ contributes to the LCAO momentum function. They allow in the transformed function only the part integrated from $0 \leq r \leq R$ where $e^{\alpha r_a}$ remains finite. The term $e^{-\alpha R}$ arises from the transform when we integrate with respect to r with $r = 0$ as one limit. The term e^{-iRp} arises from the transform when we integrate with respect to r with $r = R$ as one limit. The term e^{-iRp} makes it possible to back transform the functions $1/(p + i\alpha)$ and $1/(p + i\alpha)^2$ to position space to obtain $\frac{e^{\alpha r_a}}{r_a}$, $e^{-\alpha r_a}$. We have also shown a momentum representation of a shifted Slater orbital, $r_b^{n-1} e^{-\beta r_b}$, $Y(\theta_b, \phi_b) = 1$, centered on nucleus b. The procedure involved integrating in a hybrid space $(\cos\theta, \phi, p_r)$, as discussed previously, and resulted in functions which may be evaluated for a particular value of n.

One of the advantages of working in this momentum representation is that operators are easily expressed. For example, Lombardi [1] has shown simple expressions for the operators r_a and $1/r_a$ where the first represents the operation of partial differentiation, $i\hbar\partial/\partial p_a$, and the second represents the operation of integration, $-i/\hbar \int dp_a$. In this research we have shown the derivation of these simple operator expressions in addition to developing a representation for the operator $1/r_b$. A general integral expression has been derived for this operator. A simple example arises for the operator $1/r_b$ for $\ell=0$ states. In this case, we have integrated with respect to the angular coordinate, $\cos\theta$, in position space before the transform to momentum space and we found that the operator $1/r_b$ acting on the wave function, $e^{-\alpha r_a}$, reduces to multiplication by $\frac{-2}{R}(e^{-R(ip+\alpha)} - 1)$.

Future work using this momentum representation could involve extending the current research to more complex molecules. Using the shifted Slater orbital momentum expressions that have been derived, it is possible to consider $\ell = 0$ states with $n > 1$. As demonstrated in this research, for $\ell = 0$ states the momentum radial functions consist of simple poles in the complex plane and integrals of these functions can be easily evaluated using Cauchy's theorem. Also, using the associated Legendre addition theorems (GR 8.794.1), which separate integration variables, we could find momentum representations of simple molecules of one electron shared by three nuclei. Following along the lines of Steinborn and coworkers [20-22], we could also develop a general formalism for $\ell > 0$ states. We expect that states of greater angular momentum ($\ell > 0$) would not introduce additional poles in the complex plane [24].

APPENDIX A

We will show that in the limit R → 0 , (17) approaches (12).

$$\lim_{R\to 0} \frac{1}{\alpha R}\left[(e^{-\alpha R} - e^{-iRp})\left(\frac{1}{(p+i\alpha)^2} + \frac{1}{(p-i\alpha)^2}\right)\right.$$

$$\left. - \quad \frac{i}{\alpha}((\alpha R + 1)e^{-\alpha R} - e^{-iRp})\left(\frac{1}{(p+i\alpha)} - \frac{1}{(p-i\alpha)}\right)\right]$$

We break up (17) into fractions and take the limit as R approaches zero.

We will use the indicated limit shown below in our evaluation.

$$\lim_{R\to 0} \frac{e^{-\alpha R} - e^{-iRp}}{R} = i(p+i\alpha)$$

$$\langle 1\rangle \lim_{R\to 0} \frac{1}{\alpha}\left(\frac{e^{-\alpha R} - e^{-iRp}}{R}\right)\left(\frac{1}{(p+i\alpha)^2} + \frac{1}{(p-i\alpha)^2}\right) = \frac{i}{\alpha(p+i\alpha)} + \frac{i(p+i\alpha)}{\alpha(p-i\alpha)^2}$$

$$\langle 2\rangle \lim_{R\to 0} -\frac{i}{\alpha^2}\left(\frac{e^{-\alpha R} - e^{-iRp}}{R}\right)\left(\frac{1}{(p+i\alpha)} - \frac{1}{(p-i\alpha)}\right) = \frac{1}{\alpha^2} - \frac{(p+i\alpha)}{\alpha^2(p - i\alpha)}$$

$$\langle 3\rangle \lim_{R\to 0} \frac{-ie^{-\alpha R}}{\alpha}\left(\frac{1}{(p+i\alpha)} - \frac{1}{(p-i\alpha)}\right) = \frac{-i}{\alpha(p+i\alpha)} + \frac{i}{\alpha(p-i\alpha)}$$

After taking the limit , we are left with the following:

$$\frac{i}{\alpha(p+i\alpha)} + \frac{i(p+i\alpha)}{\alpha(p-i\alpha)^2} + \frac{1}{\alpha^2}$$

$$+ \frac{-(p+i\alpha)}{\alpha^2(p-i\alpha)} + \frac{-i}{\alpha(p+i\alpha)} + \frac{i}{\alpha(p-i\alpha)}$$

We find a common denominator $\alpha^2(p-i\alpha)^2$ and add all the fractions.

$$\frac{\underline{i\alpha(p+i\alpha) + (p-i\alpha)^2 - (p-i\alpha)(p+i\alpha) + i\alpha(p-i\alpha)}}{\alpha^2(p-i\alpha)^2}$$

The numerator simplifies to - $2\alpha^2$ and canceling α^2 in both numerator and denominator leaves just

$$\frac{-2}{(p-i\alpha)^2}$$

APPENDIX B

Integration over cos*θ* in position space to obtain f(r_a):

$$\int_{-1}^{1} d\cos\theta_a e^{-\alpha(r_a^2+R^2-2r_aR\cos\theta_a)^{\frac{1}{2}}}$$

Substitute: $a = r_a^2 + R^2$; $b = -2r_aR$; $x = \cos\theta$;

$y = (a + bx)^{1/2}$; $dy = \frac{b}{2}(a + bx)^{-1/2}dx = b/2y$;

$$= 2/b\int_{\sqrt{a-b}}^{\sqrt{a+b}} dy\, y e^{-2y}$$

Integrate by parts: $= 2/b\left[e^{-\alpha y}\left(\frac{-y}{\alpha} - \frac{1}{\alpha^2}\right)\right]_{\sqrt{a-b}}^{\sqrt{a+b}}$

$$= -2/b\left[\frac{e^{-\alpha\sqrt{a+b}}}{\alpha}\left(\sqrt{a+b} + \frac{1}{\alpha}\right) - \frac{e^{-\alpha\sqrt{a-b}}}{\alpha}\left(\sqrt{a-b} + 1\right)\right]$$

Substitute: $a \mp b = (r_a \pm R)^2$

$$\sqrt{a \mp b} = |r_a \pm R|$$

We may remove the absolute value signs:

$$\begin{aligned} |r_a - R| &= r_a - R \ (R \le r_a < \infty) \\ &\quad R - r_a \ (0 < r_a < R) \\ |r_a + R| &= r_a + R \ (0 < r_a < \infty) \end{aligned}$$

$$f(r_a) = \frac{1}{\alpha R r_a}\left[e^{-\alpha |r_a - R|}\left(|r_a - R| + \frac{1}{\alpha}\right) - e^{-\alpha |r_a + R|}\left(|r_a + R| + \frac{1}{\alpha}\right)\right] \qquad (14)$$

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