Determination of the ground state of three-body systems

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The problem of determining the ground-state energy and wave function of a three-body system is considered anew. It is found that a particular Hylleraas-type expansion for the wave function arises naturally in the present approach. The main problem is seen to be the determination of the action of certain matrices on a vector representation of the trial wave function. A method is introduced which avoids the need for, and hence determination of, long algebraic expressions for matrix elements. As a result, computer programs do not have to be altered when new potentials are considered. It is merely necessary to supply the parameter values characterizing the two-body potentials, which, in general, are a linear combination of a Coulomb potential and terms which are of the form of a polynomial times a Yukawa potential.

I. INTRODUCTION

The ground state of a three-body system interacting through spin-independent two-particle potentials has, in general, an internal wave function depending only on the interparticle distances. Hylleraas introduced variational trial functions of this type for the He atom.[1] Other authors soon found such expansions useful in the calculation of the ground states of the H_2 molecule[2] and the lithium atom.[3] Subsequently, authors using electronic computors have based their calculations on Hylleraas expansions,[4-6] and there has been much related work involving four or more particles and excited states.[7-17]

The general form of the wave function of Hylleraas is

$$\psi = e^{-1/2ks} \sum c_{lmn} s^l t^m u^n , \tag{1.1}$$

where s, t, u are the linear combinations

$$s = r_1 + r_2, \quad t = r_2 - r_1, \quad u = r_{12} , \tag{1.2}$$

of the interparticle distances and k is a scale parameter. The nucleus is treated as a point source. Pekeris[18] finds it convenient to work with "perimetric coordinates" defined by

$$2u = k(r_2 + r_{12} - r_1), \quad 2v = k(r_1 + r_{12} - r_2),$$
$$w = k(r_1 + r_2 - r_{12}) . \tag{1.3}$$

Perimetric coordinates were used earlier by James and Coolidge[19] to investigate the convergence of the Hylleraas approach. The work of Pekeris and of Frost and co-workers[20-22] is directed towards an approximate series solution of the three-particle atomic problem. Numerical solutions have been given for a number of three-body atomic systems by Accad, Pekeris, and Schiff,[23] including results for excited states. The expansions used by these authors are closely related to those which will be introduced here. For another application of their methods see Elkomoss[24] where many useful references can be found. A related approach leading to compact wave functions has been investigated recently by Thakker and Smith.[25,26]

Here we consider only the ground state of three-body systems but allow more general interactions than in atomic systems. The development in the early sections is essentially not new. It serves, however, to introduce a particular notation and results needed in the later sections. It also adds a measure of completeness to the presentation. In Sec. II we consider the action of the kinetic energy operator on a wave function in which internal motion is described through a factor depending only on interparticle distances. The type of integrals which arise in applying the Raleigh-Ritz principle with a particular type of trial function are investigated in Sec. III. In Sec. IV a basic integral is evaluated. The results of Sec. IV are seen, in Sec. V, to lead naturally to "triangular" parameters and to a particular basis set for the expansion of the trial function. The actions of various operators associated with the kinetic and potential energy operators are also considered. In Sec. VI a particular ordering of the basis functions is introduced and the general procedure for computing the ground state is outlined. The procedure is shown to depend on the ability of computing the action of certain matrices on typical vectors in their domains. This is to be done without explicit formulas for the matrix elements. The details of this crucial procedure are presented in Sec. VII. In Sec. VIII the first-order approximation and other minor issues are discussed. Some general observations are included. For an approach through the computation of matrix elements see Benesch.[27]

II. KINETIC ENERGY OPERATOR

The masses and position vectors of the particles are denoted by $m_i, \vec{r}_i; 1 \leq i \leq 3$.

The kinetic energy operator K for the system is given by

$$K = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{\hbar^2}{2m_3}\nabla_3^2, \tag{2.1}$$

where $\nabla_i, 1 \leq i \leq 3$ is the gradiant operator with respect to the variable $\vec{r}_i$.

In general the wave function for this system will be a spinor function of the variables $\vec{r}_1, \vec{r}_2$, and $\vec{r}_3$. We, however, are concerned only with states of lowest internal energy. Such states will be a superposition of states described by wave functions of the form

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = F(\vec{R})\Phi(x, y, z), \tag{2.2}$$

where F is a spinor function of the center of mass position vector $\vec{R}$ defined by

$$(m_1 + m_2 + m_3)\vec{R} = m_1\vec{r}_1 + \vec{m}_2\vec{r}_2 + m_3\vec{r}_3, \tag{2.3}$$

and where x, y, z are the lengths of the vectors,

$$\vec{x} = \vec{r}_3 - \vec{r}_2, \quad \vec{y} = \vec{r}_1 - \vec{r}_3, \quad \vec{z} = \vec{r}_2 - \vec{r}_1. \tag{2.4}$$

The function Φ in (2.2) is fixed, being the internal wave function of the ground state while F is any $L^2(\vec{R})$ function whose spin state is consistent with ground-state symmetry requirements.

Introducing

$$\vec{\omega} = \vec{r}_1 - (m_2\vec{r}_2 + m_3\vec{r}_3)/(m_2 + m_3) \tag{2.5}$$

it is well known that the kinetic energy operator (2.1) may be written

$$K = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_x^2 - \frac{\hbar^2}{2m}\nabla_\omega^2, \tag{2.6}$$

where

$$M = m_1 + m_2 + m_3, \quad \mu = \frac{m_2 m_3}{m_2 + m_3}, \quad m = \frac{m_1(m_2 + m_3)}{m_1 + m_2 + m_3}. \tag{2.7}$$

By inverting the equations (2.3), (2.4), and (2.5) or from the interpretation of $-i\hbar\nabla_R$ as a momentum operator one finds

$$\nabla_R = \nabla_1 + \nabla_2 + \nabla_3. \tag{2.8}$$

With the aid of the relationships (2.4) for any function u depending on x, y, and z only, we have

$$\nabla_1 u = u_y\hat{y} - u_z\hat{z}, \tag{2.9}$$

$$\nabla_2 u = u_z\hat{z} - u_x\hat{x}, \tag{2.10}$$

and

$$\nabla_3 u = u_x\hat{x} - u_y\hat{y}, \tag{2.11}$$

where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors in the directions of $\vec{x}$, $\vec{y}$, and $\vec{z}$, respectively. From (2.8)–(2.11) it follows that

$$\nabla_R u = 0, \tag{2.12}$$

which is also clear from the translational invariance of u. Thus operating on (2.2) with the expression (2.6) and noting (2.12) we have

$$K(F(\vec{R})\Phi(x, y, z)) = -\frac{\hbar^2}{2M}\nabla_R^2 F(\vec{R})\Phi(x, y, z) + F(\vec{R})[K\Phi(x, y, z)]. \tag{2.13}$$

Taking the divergence of (2.9) with respect to $\vec{r}_1$ we find

$$\nabla_1^2 u = u_{yy} + u_{zz} - 2u_{yz}\hat{y}\cdot\hat{z} + (2/y)u_y + (2/z)u_z. \tag{2.14}$$

Now since $-\hat{y}\cdot\hat{z}$ is the cosine of the angle opposite the side $\vec{x}$ of the triangle formed by the vectors $\vec{x}, \vec{y}, \vec{z}$, we have

$$\hat{y}\cdot\hat{z} = (x^2 - y^2 - z^2)/2yz. \tag{2.15}$$

Thus from (2.14) and (2.15) we have

$$\nabla_1^2 u = u_{yy} + u_{zz} + \frac{y^2 + z^2 - x^2}{yz}u_{yz} + \frac{2}{y}u_y + \frac{2}{z}u_z, \tag{2.16}$$

with

$$\nabla_2^2 u = u_{zz} + u_{xx} + \frac{z^2 + x^2 - y^2}{zx}u_{zx} + \frac{2}{z}u_z + \frac{2}{x}u_x, \tag{2.17}$$

and

$$\nabla_3^2 u = u_{xx} + u_{yy} + \frac{x^2 + y^2 - z^2}{xy}u_{xy} + \frac{2}{x}u_x + \frac{2}{y}u_y, \tag{2.18}$$

being derived similarly.

Introducing

$$\rho_2 = -\hbar^2/2m_1, \quad \sigma_2 = -\hbar^2/2m_2, \quad \tau_2 = -\hbar^2/2m_3, \tag{2.19}$$

and

$$\rho_1 = \sigma_2 + \tau_2, \quad \sigma_1 = \tau_2 + \rho_2, \quad \tau_1 = \rho_2 + \sigma_2, \tag{2.20}$$

it follows from (2.1) and (2.16)–(2.18) that when operating on a function depending only on x, y, and z that the kinetic energy operator may be taken to be

$$\tilde{K} = K_1 + K_2 + 2K_3, \tag{2.21}$$

where

$$K_1 = \rho_1\frac{\partial^2}{\partial x^2} + \sigma_1\frac{\partial^2}{\partial y^2} + \tau_1\frac{\partial^2}{\partial z^2}, \tag{2.22}$$

$$K_2 = \rho_2\frac{y^2 + z^2 - x^2}{yz}\frac{\partial^2}{\partial y\partial z} + \sigma_2\frac{z^2 + x^2 - y^2}{zx}\frac{\partial^2}{\partial z\partial x} + \tau_2\frac{x^2 + y^2 - z^2}{yz}\frac{\partial^2}{\partial x\partial y}, \tag{2.23}$$

and

$$K_3=\rho_1\frac{1}{x}\frac{\partial}{\partial x}+\sigma_1\frac{1}{y}\frac{\partial}{\partial y}+\tau_1\frac{1}{z}\frac{\partial}{\partial z}\,. \tag{2.24}$$

For an alternative derivation see Frost.[28]

III. EXPECTATION INTEGRALS

In order to estimate the lowest energy of the system we consider trial wave functions of the form

$$\psi(\vec{r}_1,\vec{r}_2,\vec{r}_3)=F(\vec{R})u(x,y,z)\,, \tag{3.1}$$

where $F(\vec{R})$ is as in (2.2) and

$$u(x,y,z)=P(x,y,z)\exp[-(\alpha x+\beta y+\gamma z)/2]\,, \tag{3.2}$$

where P is the general polynomial of degree N, say, in x, y, and z. α,β,γ are constants, whose value is to be determined, but which satisfy the conditions

$$\alpha+\beta>0,\quad \beta+\gamma>0,\quad \gamma+\alpha>0\,. \tag{3.3}$$

These conditions are required, as will be shown in Sec. IV, to make (3.1) a normalizable wave function.

The Hamiltonian operator H will be restricted to the form

$$H=K+V\,, \tag{3.4}$$

where the potential energy operator V may be expressed

$$V=V_1+V_2+V_3\,. \tag{3.5}$$

Potentials V_1, V_2, and V_3 are operators of multiplication by a function of x, y, and z, respectively, which in general may be a linear combination of a Coulomb interaction and polynomial times a Yukawa interaction.

The mean energy $\langle H\rangle$ of the system with wave function (3.1) is given by

$$\langle H\rangle=\frac{\int\bar{\psi}H\psi\,d\vec{r}_1^{\,3}\,d\vec{r}_2^{\,3}\,d\vec{r}_3^{\,3}}{\int\bar{\psi}\psi\,d\vec{r}_1^{\,3}\,d\vec{r}_2^{\,3}\,d\vec{r}_3^{\,3}}\,, \tag{3.6}$$

where $\bar{\psi}$ is the complex conjugate of ψ and where an inner product over spin states is implied.

From (2.4) and (2.5) we have

$$\vec{y}=\vec{\omega}-\frac{m_2}{m_2+m_3}\vec{x} \tag{3.7}$$

and

$$\vec{z}=\vec{\omega}+\frac{m_3}{m_2+m_3}\vec{x}\,. \tag{3.8}$$

Thus the function u of (3.1) depends only on $\vec{x}$ and $\vec{\omega}$. We also note from (2.3)–(2.5) that the associated Jacobians satisfy

$$\frac{\partial((\vec{R})_i,(\vec{x})_i,(\vec{\omega})_i)}{\partial((\vec{r}_1)_i,(\vec{r}_2)_i,(\vec{r}_3)_i)}=1,\quad 1\leq i\leq 3\,, \tag{3.9}$$

where the subscript i indicates the ith Cartesian coordinate. Reexpressing (3.6) in terms of the integration variables $\vec{R}$, $\vec{x}$, $\vec{\omega}$ and using (2.13), (3.17), and (3.5) we find

$$\langle H\rangle=\frac{\int F(\vec{R})\left(\frac{-\hbar^2\nabla_R^2}{2M}\right)F(\vec{R})\,d^3\vec{R}}{\int F(\vec{R})F(\vec{R})\,d^3\vec{R}}+\frac{\int\bar{u}Hu\,d^3\vec{x}\,d^3\vec{\omega}}{\int\bar{u}u\,d^3\vec{x}\,d^3\vec{\omega}}\,. \tag{3.10}$$

Since the operator $-\nabla_R^2$ is positive definite, the first term on the right in (3.10) is positive but by a suitable choice of F may be made arbitrarily small. Since we are seeking the greatest lower bound to all expressions of the form (3.10), we will assume

$$\langle H\rangle=\frac{\int\bar{u}Hu\,d^3\vec{x}\,d^3\vec{y}}{\int\bar{u}u\,d^3\vec{x}\,d^3\vec{y}}\,, \tag{3.11}$$

where we have used (3.7). Comparing (3.2) with (3.11) and noting that H involves terms of the form (2.23) it is evident we need to be able to evaluate integrals of the form

$$\int\frac{Q(x,y,z)}{xy}\exp(-\alpha x-\beta y-\gamma z)\,d^3\vec{x}\,d^3\vec{y}\,, \tag{3.12}$$

where Q is a polynomial, in order to evaluate (3.11).

IV. BASIC INTEGRAL

To facilitate the evaluation of integrals of the type (3.12) consider the integral

$$I(\alpha,\beta,\gamma)=\int\frac{\exp(-\alpha x-\beta y-\gamma z)}{xyz}\,d^3\vec{x}d^3\vec{y}\,. \tag{4.1}$$

We shall show that

$$I(\alpha,\beta,\gamma)=\frac{16\pi^2}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}\,. \tag{4.2}$$

To introduce powers of x, y, and z into the integrand of (4.1) we simply differentiate the equation an appropriate number of times with respect to the parameters α,β,γ which in view of its simple form (4.2) is straightforward. The integral (3.12) can then be calculated by expressing it as a linear combination of such integrals.

To establish the formula (4.2) let the polar coordinates of $\vec{x}$ be (x,θ',ϕ') and let $\vec{k}$ be a unit vector in the polar direction. For $\vec{y}$ introduce polar coordinates (y,θ,ϕ) depending on $\vec{x}$ in the following manner; $\vec{x}$ is the polar direction for $\vec{y}$ and $\vec{k}\times\vec{x}$ is in the direction of the "y axis" for $\vec{y}$. (4.1) now yields

$$I(\alpha,\beta,\gamma)=\int_{-\pi}^{\pi}d\phi'\int_{0}^{\pi}d\theta'\int_{0}^{\infty}dx\int_{-\pi}^{\pi}d\phi\int_{0}^{\pi}d\theta\int_{0}^{\infty}dy\,\sin\theta'\sin\theta\frac{xy}{z}\exp(-\alpha x-\beta y-\gamma z), \tag{4.3}$$

where

$$z=(x^2+y^2-2xy\cos\theta)^{1/2}. \tag{4.4}$$

Integrating out the variables θ', ϕ', and ϕ from (4.3) and noting from (4.4) that for fixed x and y

$$dz=(xy/z)\sin\theta\,d\theta, \tag{4.5}$$

we have

$$I(\alpha,\beta,\gamma)=8\pi^2\int_0^\infty dx\int_0^\infty dy\int_{|x-y|}^{x+y}\exp(-\alpha x-\beta y-\gamma z)\,dz, \tag{4.6}$$

or after integration with respect to z

$$I(\alpha,\beta,\gamma)=\frac{8\pi^2}{\gamma}\int_0^\infty dx\left(\int_0^x\exp[-(\alpha+\gamma)x-(\beta-\gamma)y]\,dy+\int_x^\infty\exp[-(\alpha-\gamma)x-(\beta+\gamma)y]\,dy-\int_0^\infty\exp[-\alpha+\gamma)x-(\beta+\gamma)y]\,dy\right). \tag{4.7}$$

Computing the elementary integrals in (4.7) yields

$$I(\alpha,\beta,\gamma)=\frac{8\pi^2}{\gamma}\frac{1}{\beta-\gamma}\frac{1}{\alpha+\gamma}-\frac{1}{\alpha+\beta}+\frac{1}{\beta+\gamma}\frac{1}{\alpha+\beta}-\frac{1}{\beta+\gamma}\frac{1}{\alpha+\gamma}, \tag{4.8}$$

which after simplification results in (4.2). The conditions (3.3) are seen to be sufficient to carry out the integration steps. That this remains true when a polynomial factor $Q(x,y,z)$ is introduced into the integrand of (4.1) may be argued as follows. It is sufficient to consider the case in which

$$Q(x,y,z)=x^l y^m z^n, \tag{4.9}$$

but

$$x^l y^m z^n<1+x^j+y^j+z^j, \tag{4.10}$$

where

$$j=l+m+n. \tag{4.11}$$

If a factor x^j is introduced into the integrand of (4.1) the manipulations leading to (4.7) can be carried out as before. Only on the last step from (4.7) to (4.8) would there be a change and it is clear that this can be carried through. From the symmetry of the integral a factor y^j or z^j also causes no problem. It follows from (4.10) that any polynomial can be introduced.

The integral (4.1) has been evaluated previously by Calais and Löwdin,[29] as an example of their method for the evaluation of integrals with separable integrands.

V. EXPANSION OF THE WAVE FUNCTION

Although the integral $I(\alpha,\beta,\gamma)$ is a simple function of its parameters, it is convenient to introduce new "triangular" parameters by

$$r=\tfrac{1}{2}(\beta+\gamma),\quad s=\tfrac{1}{2}(\gamma+\alpha),\quad t=\tfrac{1}{2}(\alpha+\beta), \tag{5.1}$$

in terms of which the original parameters are given by

$$\alpha=s+t-r,\quad \beta=t+r-s,\quad \gamma=r+s-t. \tag{5.2}$$

Corresponding to the "triangular" parameters (5.1) we introduce "triangular" variables by

$$X=y+z-x,\quad Y=z+x-y,\quad Z=x+y-z, \tag{5.3}$$

in terms of which the original variables are given by

$$x=\tfrac{1}{2}(Y+Z),\quad y=\tfrac{1}{2}(Z+X),\quad z=\tfrac{1}{2}(X+Y). \tag{5.4}$$

Introducing the parameters (5.1) into (4.2) we find

$$I(\alpha,\beta,\gamma)=2\pi^2/rst, \tag{5.5}$$

while substituting (5.2) into (4.1) and using (5.3) gives

$$I(\alpha,\beta,\gamma)=\int\frac{\exp(-rX-sY-tZ)}{xyz}d^3\vec{\mathbf{x}}\,d^3\vec{\mathbf{y}}. \tag{5.6}$$

The advantage of the "triangle" parameters and variables is now clear. If we operate on (5.5) and (5.6) with

$$\left(-\frac{\partial}{\partial r}\right)^l\left(-\frac{\partial}{\partial s}\right)^m\left(-\frac{\partial}{\partial t}\right)^n$$

we find

$$\int X^l Y^m Z^n\frac{\exp(-rX-sY-tZ)}{xyz}d^3\vec{\mathbf{x}}\,d^3\vec{\mathbf{y}}=\frac{2\pi^2 l!\,m!\,n!}{r^{l+1}s^{m+1}t^{n+1}}. \tag{5.7}$$

A formula for the integral differing from (4.1) by an extra factor $x^l y^m z^n$ in the integrand is not so

easily obtained from (4.1) and (4.2). Recursive formulas for the evaluation of those integrals have, however, been given by Sack, Roothaan, and Kolos.[30] It follows from (5.4) and (5.3) that a polynomial in x,y,z is also a polynomial in X,Y,Z and conversely, and since conversion both ways is possible, the degrees must be the same. Thus the trial wave function (3.2) may be expressed

$$u(x,y,z)=Q(X,Y,Z)\exp[-(rX+sY+tZ)/2], \tag{5.8}$$

where Q is the general polynomial of degree N in X,Y,Z.

A suitable basis for the class of functions of the form (5.8) is the set $\{\chi_{lMn}\}$, defined by

$$\chi_{lmn}(X,Y,Z)=\frac{(rst)^{1/2}}{\pi\sqrt{2}}(rX)^l(sY)^M(tZ)^n \times\exp[-(rX+sY+tZ)/2]. \tag{5.9}$$

Introducing the notation

$$\langle l_1m_1n_1|O|l_2m_2n_2\rangle=\int\frac{\chi_{l_1m_1n_1}}{xyz}O\chi_{l_2n_2n_2}d^3\vec{x}\,d^3\vec{y} \tag{5.10}$$

where O is an operator, it follows from (5.7) and (5.9) that

$$\langle l_1m_1n_1|1|l_2m_2n_2\rangle=(l_1+l_2)!\,(m_1+m_2)!\,(n_1+n_2)!\,. \tag{5.11}$$

Now with the trial function u expanded as a linear combination of the functions (5.9) it follows from (3.11) that we are interested in Eq. (5.10) in the the cases when O is the operator xyz or $xyzH$. Decomposing H in the form (3.4) the cases $xyzK$ and $xyzV$ will be of interest. Recalling that on functions of the form (5.8) K is equivalent to the operator $\tilde{K}$ defined by (2.19)–(2.24) it is observed that $xyz\tilde{K}$ is a polynomial in the six operators $x,y,z,\partial/\partial x,\partial/\partial y,\partial/\partial z$. Accordingly we are concerned with the action of these operators on the basis functions (5.9). Noting from (5.3) that

$$\frac{\partial}{\partial x}=\frac{\partial}{\partial Y}+\frac{\partial}{\partial Z}-\frac{\partial}{\partial X},\quad \frac{\partial}{\partial y}=\frac{\partial}{\partial Z}+\frac{\partial}{\partial X}-\frac{\partial}{\partial Y},$$
$$\frac{\partial}{\partial z}=\frac{\partial}{\partial X}+\frac{\partial}{\partial Y}-\frac{\partial}{\partial Z} \tag{5.12}$$

and using (5.4) we find

$$2x\chi_{lmn}=(1/s)\chi_{lm+1n}+(1/t)\chi_{lmn+1}, \tag{5.13}$$

$$2y\chi_{lmn}=(1/t)\chi_{lmn+1}+(1/r)\chi_{l+1mn}, \tag{5.14}$$

$$2z\chi_{lmn}=(1/r)\chi_{l+1mn}+(1/s)\chi_{lm+1n}, \tag{5.15}$$

and

$$\frac{\partial}{\partial x}\chi_{lmn}=-\tfrac{1}{2}(s+t-r)\chi_{lmn}+ms_{lm-1n} +nt\chi_{lmn-1}-lr\chi_{l-1mn}, \tag{5.16}$$

$$\frac{\partial}{\partial y}\chi_{lmn}=-\tfrac{1}{2}(t+r-s)\chi_{lmn}+nt\chi_{lmn-1} +lr\chi_{l-1mn}-ms\chi_{lm-1n}, \tag{5.17}$$

$$\frac{\partial}{\partial z}\chi_{lmn}=-\tfrac{1}{2}(r+s-t)\chi_{lmn}+lr\chi_{l-1mn} +ms\chi_{lm-1n}-nt\chi_{lmn-1}. \tag{5.18}$$

With the potential as in (3.5) it is clear that $xyzV$ will in general involve terms which are polynomials times an exponential factor, $e^{-2\eta x}$ say. To compute matrix elements involving this factor we absorb a factor $e^{-\eta x}$ into the basis functions (5.9). Thus noting from (5.1) that it is convenient to introduce

$$\tilde{s}=s+\eta,\quad \tilde{t}=t+\eta, \tag{5.19}$$

we find from (5.9) that

$$e^{-\eta x}\chi_{lmn}=(s/\tilde{s})^{m+1/2}(t/\tilde{t})^{n+1/2}\tilde{\chi}_{lmn}, \tag{5.20}$$

where $\tilde{\chi}_{lmn}$ is defined identically to χ_{lmn} through (5.9) with the exception that s and t are replaced by $\tilde{s}$ and $\tilde{t}$. The effect of operating on $\tilde{\chi}_{lmn}$ with x, y, or z is given by formulas of the form (5.13)–(5.15) with $\tilde{s}$ and $\tilde{t}$ replacing s and t. Similar considerations apply in absorbing factors $e^{-\eta y}$ and $e^{-\eta z}$.

VI. VARIATIONAL PROBLEM

Since the basis functions $\{\chi_{lmn}\}$ involve a triple subscript some method of ordering must be devised. Introducing

$$\tilde{l}=l+m+n+1,\quad \tilde{m}=m+n+1,\quad \tilde{n}=n+1, \tag{6.1}$$

to each triplet (l,m,n) we associate a triplet $(\tilde{l},\tilde{m},\tilde{n})$ in a one to one manner. Thus by ordering the triplets $\{(\tilde{l},\tilde{m},\tilde{n})\}$ we induce an ordering on the triplets $\{(l,m,n)\}$. Noting that l,m,n can be any non-negative integers it follows from (6.1) that

$$\tilde{l}\geq\tilde{m}\geq\tilde{n}\geq 1, \tag{6.2}$$

are the only limits on the triplets $\{(\tilde{l},\tilde{m},\tilde{n})\}$. Ordering the triples $\{(\tilde{l},\tilde{m},\tilde{n})\}$ lexically we find that the triplet $(\tilde{l},\tilde{m},\tilde{n})$ is that kth member of the sequence where

$$k=\tfrac{1}{6}(\tilde{l}-1)\tilde{l}(\tilde{l}+1)+\tfrac{1}{2}(\tilde{m}-1)\tilde{m}+\tilde{n}. \tag{6.3}$$

It is convenient, therefore, to introduce

$$\chi_k=\chi_{lmn}, \tag{6.4}$$

where k is defined through (6.1) and (6.3).

In the notation of (6.4) the trial wave function (5.8) has the expansion

$$u(x,y,z)=\sum_{k=1}^{N_0} c_k\chi_k(X,Y,Z)\,, \tag{6.5}$$

where N_0 is related to the degree N of the polynomial Q in (5.8) by

$$N_0=(N+1)(N+2)(N+3)/6\,. \tag{6.6}$$

Introducing the notation $\vec{c}$ for the column vector with components c_k and A and B for matrices with elements defined by

$$A_{k_1k_2}=\langle l_1m_1n_1\,|\,xyzH\,|\,l_2m_2n_2\rangle \tag{6.7}$$

and

$$B_{k_1k_2}=\langle l_1m_1n_1\,|\,xyz\,|\,l_2m_2n_2\rangle\,, \tag{6.8}$$

where k_1 and k_2 are related to the triplets (l_1,m_1,n_1), (l_2,m_2,n_2) through equations similar to (6.1) and (6.3), it follows from (3.11) and (5.10) that

$$\langle H\rangle=\vec{c}^{\,\dagger}A\vec{c}/\vec{c}^{\,\dagger}B\vec{c}\,. \tag{6.9}$$

Since from (6.4) and (5.9) the basis functions $\{\chi_k\}$ are real and linearly independent, it follows from (5.10), (6.7), and (6.8) that A and B are real symmetric matrices and that B is positive definite.

Our objective then is to minimize $\langle H\rangle$ of (6.9) with respect to $\vec{c}$. This is done using a standard approach.[31-33] The vector $\vec{c}$ is assumed to be real with $c_1>0$ and normalized so that

$$\vec{c}^{\,T}B\vec{c}=1\,. \tag{6.10}$$

An initial choice for $\vec{c}$ is made by setting $c_k=0$ for $k\geq 2$. A sequence of improved choices is then found through iteration of the following procedure. Denote by $\Delta\vec{c}$ the vector whose nth component is $\partial/\partial c_n\langle H\rangle$, $1\leq n\leq N_0$. Its components are computed from (6.9), or since $\vec{c}$ is real from

$$\langle H\rangle=\vec{c}^{\,T}A\vec{c}/\vec{c}^{\,T}B\vec{c}\,. \tag{6.11}$$

Introduce a function $f(t)$ by replacing $\vec{c}$ in (6.11) by $\vec{c}+t\Delta\vec{c}$. We then have

$$f(t)=\frac{A_0+2A_1t+A_2t^2}{B_0+2B_1t+B_2t^2}\,, \tag{6.12}$$

where

$$\begin{aligned}&A_0=\vec{c}^{\,T}A\vec{c},\quad A_1=(\Delta\vec{c})^TA\vec{c},\quad A_2=(\Delta\vec{c})^TA\Delta\vec{c}\,;\\ &B_0=\vec{c}^{\,T}B\vec{c},\quad B_1=(\Delta\vec{c})^TB\vec{c}^{\,T},\quad B_2=(\Delta\vec{c})^TB\Delta\vec{c}\,.\end{aligned} \tag{6.13}$$

The denominator of (6.12) is positive definite and $f(t)$ is found to be stationary when

$$2\begin{vmatrix}A_1 & A_2\\ B_1 & B_2\end{vmatrix}t^2-\begin{vmatrix}A_2 & A_0\\ B_2 & B_0\end{vmatrix}t+\begin{vmatrix}A_0 & A_1\\ B_0 & B_1\end{vmatrix}=0\,. \tag{6.14}$$

The root of (6.14) which makes $f(t)$ a minimum is substituted in the expression $\vec{c}+t\Delta\vec{c}$ to yield a vector which when normalized to satisfy the condition (6.10) becomes the next choice of $\vec{c}$ in the sequence.

Although this procedure is conceptually simple it is of course necessary to be able to compute $\Delta\vec{c}$ and the coefficients (6.13). By taking the gradiant of (6.11) we find

$$\Delta\vec{c}=2B_0^{-2}\{B_0A\vec{c}-A_0B\vec{c}\}\,. \tag{6.15}$$

Examination of (6.13) and (6.15) shows that if we have a way of computing $A\vec{d}$ and $B\vec{d}$ from a typical vector $\vec{d}$ then we will be able to accomplish our objective. Thus if we first compute $A\vec{c}$ and $B\vec{c}$, A_0 and B_0 are easily found, followed by $\Delta\vec{c}$ from (6.15). This immediately allows the computation of A_1 and B_1. Finally, A_2 and B_2 are easily computed if we first compute $A\Delta\vec{c}$ and $B\Delta\vec{c}$.

The question of how we compute $A\vec{d}$ and $B\vec{d}$ from a typical vector $\vec{d}$ is the subject of the next section. The author's procedure for the determination of these vectors is an important part of this paper. Its merits are discussed in the concluding paragraph.

VII. OPERATOR ALGORITHMS

The preceding section describes a method of finding a vector $\vec{c}$ which minimizes the expectation value of H with respect to the wave function (6.5), the expression to be minimized being given by (6.11). As noted above the unresolved question is how are we to compute the vectors $A\vec{d}$ and $B\vec{d}$ from a typical vector $\vec{d}$.

Although $\vec{d}$ is a vector with N_0 components, it is convenient to regard it as an infinitely dimensional vector of which all but the first N_0 components are zero.

It follows from the definitions (6.7) and (6.8) that the action of A and B on the vector $\vec{c}$ is closely related to the action of $xyzH$ and xyz on $u(x,y,z)$ of (6.5). It turns out that the terms of H which have an exponential factor require special treatment which will be discussed later. For the moment we will assume H has no such terms. With this assumption both xyz and $xyzH$ are polynomials in the operators $x, y, z, \partial/\partial x, \partial/\partial y, \partial/\partial z$.

Since the action of each of these on a basis function results in a finite linear combination of basis functions, this is also true of $xyzH$ and xyz. Let us denote the vectors whose components are the coefficients in the expansion of $xyzHu(x,y,z)$ and $xyzu(x,y,z)$, in the manner of (6.5), by $\vec{a}$ and $\vec{b}$, respectively. Both $\vec{a}$ and $\vec{b}$ will have more than N_0 components. The vectors $A\vec{c}$ and $B\vec{c}$ are simply related to $\vec{a}$ and $\vec{b}$. Introducing

$$G_{k_1k_2}=\langle l_1m_1n_1|1|l_2m_2n_2\rangle\,, \tag{7.1}$$

and noting that the kth components of $A\vec{c}$ and $B\vec{c}$ are obtained by forming the inner product of χ_k with $xyzHu(x,y,z)$ and $xyzu(x,y,z)$, respectively, we find

$$(A\vec{c})_k = \sum_j G_{kj}\, a_j \quad \text{and} \quad (B\vec{c})_k = \sum_j G_{kj}\, b_j \,. \tag{7.2}$$

Here $1 \leq k \leq N_0$ while j ranges over all values for which the summand is nonzero. $(A\vec{c})_k$ and $(B\vec{c})_k$ denote the kth components of $A\vec{c}$ and $B\vec{c}$, respectively. By inner product of two functions $u_1(x,y,z)$ and $u_2(x,y,z)$ we mean

$$\int \frac{u_1(x,y,z)u_2(x,y,z)}{xyz}\; d^3\vec{x}\, d^3\vec{y}\,, \tag{7.3}$$

as in (5.10).

We note that as a consequence of (5.11), the definition (7.1) can be replaced by

$$G_{k_1k_2} = (l_1+l_2)!\,(m_1+m_2)!\,(n_1+n_2)!\;. \tag{7.4}$$

Our problem thus reduces to the computation of $\vec{a}$ and $\vec{b}$ from $\vec{c}$.

As observed above the operators $xyzH$ and xyz are polynomials in the "simple" operators x, y, z, $\partial/\partial x, \partial/\partial y, \partial/\partial z$. Thus if we have a procedure for finding the new coefficients in the expansion of the wave function obtained by operating with any of these on a typical function of the form

$$u(x,y,z) = \sum_{k=1}^{N_\nu} d_k \chi_k(X,Y,Z)\,, \tag{7.5}$$

where

$$N_\nu = (N+\nu+1)(N+\nu+2)(N+\nu+3)/6\,, \tag{7.6}$$

we will be able by a combination of applying these procedures and forming linear combinations of resulting vectors arrive at both $\vec{a}$ and $\vec{b}$. The reason for introducing N_ν, which is a generalization of N_0 defined in (6.6), needs explanation. First it will be noted that if $N_\nu < k \leq N_{\nu+1}$ then $\chi_k(X,Y,Z)$ has a monomial factor of degree $N+\nu+1$. Thus if $u(x,y,z)$ of (7.5) is multipled by x, y, or z the expansion of the resulting function will involve a sum of $N_{\nu+1}$ terms. Acting with $\partial/\partial x$, $\partial/\partial y$, or $\partial/\partial z$ on the other hand does not alter the number of terms in the expansion, as is easily deduced from Eqs. (5.16)–(5.18).

If the Hamiltonian H is expressed as a sum of operators, its expectation value is the sum of the expectation values of these operators. This decomposition holds for the matrix A defined in (6.7), and for the numerator of (6.11). Thus if the $xyzV$ can be expressed as a sum of terms each of which is a product polynomial in x, y, and z and an exponential factor in x, y, or z, then their contributions to the numerator of (6.11) can be computed independently.

Let us consider the typical term

$$V_i = P(x)e^{-2\eta x}/x\,, \tag{7.7}$$

where $P(x)$ is polynomial in x then

$$xyzV_i = yzP(x)e^{-2\eta x}\,. \tag{7.8}$$

The objective here, when forming matrix elements such as (5.10), is to absorb the exponential factor of (7.8) into the basis functions on either side. The result of this absorption is given in (5.19) and (5.20).

It follows from (5.20) that if we operate on (6.5) with $e^{-\eta x}$ that we get

$$e^{-\eta x}u(x,y,z) = \sum_{k=1}^{N_0} \tilde{c}_k \tilde{\chi}_k(X,Y,Z)\,, \tag{7.9}$$

where

$$\tilde{c}_k = (\tilde{s}/s)^{m+1/2}(\tilde{t}/t)^{n+1/2} c_k\,. \tag{7.10}$$

The principle effect of the absorption operator $e^{-\eta x}$ is thus the replacement of the vector $\vec{c}$ with the vector $\tilde{\vec{c}}$ whose components are given by (7.10). A second effect is that when computing the effects of the polynomial $yzP(x)$ on $\tilde{c}$, it is necessary to use the parameters $r, \tilde{s}, \tilde{t}$ rather than r, s, t. Let us call the resulting set of coefficients $\tilde{\vec{a}}$. These now must be operated on with the $N_0 \times N_\nu$ matrix G whose elements given by (7.4). N_ν is the dimension of $\tilde{\vec{a}}$. We now have

$$\vec{c}^{\,T} A(V_i)\vec{c} = \tilde{\vec{c}}^{\,T} G \tilde{\vec{a}}\,, \tag{7.11}$$

where $A(V_i)$ is that part of A arising from V_i. But the absorption factors of (7.10) can easily be transferred to the vector $G\tilde{\vec{a}}$, and we have

$$(A(V_i)\vec{c})_k = (\tilde{s}/s)^{m+1/2}(\tilde{t}/t)^{n+1/2}(G\tilde{\vec{a}})_k\,. \tag{7.12}$$

In summary, to accommodate an exponential, we simply include an absorption operation before and after the other operations and use modified parameters.

A few minor points are in order. The normalization (5.9) of $\chi_{lmn}(X,Y,Z)$ may not be ideal if N is too large, leading to unwieldy values for $G_{k_1k_2}$, and to small numbers for c_k. To avoid this, an additional factor such as $l!m!n!$ should be included in the denominator of (5.9). If this is done (5.11) will be altered and in consequence (7.4) will be replaced by

$$G_{k_1k_2} = g_{i_1i_2} g_{m_1m_2} g_{n_1n_2}\,, \tag{7.13}$$

where

$$g_{nm} = \binom{n+m}{n}\,. \tag{7.14}$$

The matrix elements $G_{k_1k_2}$ should be computed as needed from a look-up table containing the bino-

mial coefficients g_{nm}.

One final question remains: what values should be chosen for the parameters r, s, and t. This question is taken up in Sec. VIII.

VIII. FIRST-ORDER APPROXIMATION

In order to carry out the procedures of Secs. VI and VII some choice of values for the parameters $r, s; t$ must be made. Since our objective is to minimize the expression (3.11) we should ideally choose these parameters so that (6.9) is as small as possible. Such a choice would be difficult to determine and would depend on the value of N_0 in (6.5). Accordingly we will choose these parameters so that (6.9) is close to a minimum for the simplest case, $N_0 = 1$. For this case it follows from (6.1)–(6.8) that (6.9) reduces to

$$\langle H\rangle = \langle 000|xyzH|000\rangle / \langle 000|xyz|000\rangle . \tag{8.1}$$

To find a rough minimum for (8.1) one can use any standard numerical method, calculating (8.1) for different parameter values by the methods of Sec. VII. If only the first-order estimate (8.1) is of interest, this expression can be evaluated with the aid of formulas. We note Eqs. (5.16)–(5.18) simplify in the case when l,m,n are zero, so that formulas for the various contributions to (8.1) are not too complicated.

Using (5.11) and (5.13)–(5.18) we find after some algebra

$$\langle 000|xyz|000\rangle = \frac{(r+s)(s+t)(t+r)-rst}{4(rst)^2} , \tag{8.2}$$

$$\langle 000|xyz\frac{\partial^2}{\partial x^2}|000\rangle = \frac{(s+t-r)^2}{16(rst)^2} \times[(r+s)(s+t)(t+r)-rst] , \tag{8.3}$$

$$\langle 000|x(y^2+z^2-x^2)\frac{\partial^2}{\partial y\partial z}|000\rangle = \frac{(t+r-s)(r+s-t)}{8(rst)^2} \times[st(s+t)+r(s^2+st+t^2)-r^2(s+t)] , \tag{8.4}$$

and

$$\langle 000|yz\frac{\partial}{\partial x}|000\rangle = -\frac{(s+t-r)}{8(rst)^2} \times[(rst)(r+s+t)-2(st)^2] . \tag{8.5}$$

For a potential energy, which is a superposition of Yukawa's, it is useful to also have

$$\langle 000|yze^{-2\eta x}|000\rangle = \frac{st[r(r+s+t+2\eta)-2(s+\eta)(t+\eta)]}{4[r(s+\eta)(t+\eta)]^2} , \tag{8.6}$$

where use has been made of (7.12).

Similar formulas can be obtained by simultaneously cyclically permuting x, y, z and r, s, t.

For an exponential potential we note

$$\langle 000|xyze^{-2\eta x}|000\rangle = \frac{st[(r+s+\eta)(s+t+2\eta)(t+r+\eta)-r(s+\eta)(t+\eta)]}{4(s+\eta)^3(t+\eta)^3r^2} . \tag{8.7}$$

Powers of x can be introduced into (8.7) by differentiating with respect to η.

CONCLUSION

The introduction of "triangular parameters" and "variables" into an Hylleraas expansion leads to a well-defined and straightforward problem when applied to the ground state of a three-body system for a large class of interesting potentials. In general, the solution of such problems through the direct derivation and use of formulas can be quite lengthy. The alternative methods of calculation of matrix elements through use of algorithms for basic operators, as presented here, should be a viable and work-reducing alternative. This may be true even for the first-order approximation of this section, especially if a number of alternative potentials are to be considered. This advantage derives from the fact that it is not necessary to reprogram to modify recursion formulas each time a new potential is to be considered, since the action of the various potential terms is constructed by the programs from the descriptive parameters. In fact, the action of all operators is constructed from subprograms for the action of the simple operators $x, y, z, \partial/\partial x, \partial/\partial y, \partial/\partial z$ and for the action of an exponential factor. No significant gain in computer efficiency is anticipated. Although the procedures developed here give an alternative way of approaching three-body atomic problems, the results should turn out to be the same as those of Accad, Pekeris, and Schiff.[23] These authors preferred an expansion using a product of Legendre polynomials instead of the monomial factor we have introduced in (5.9). This, however, does not work out well for potentials involving an exponential factor. The present approach should be useful in non-

atomic three-body problems of nuclear physics and in quark models. Programs for its application are currently being developed. It should not be difficult to generalize the procedures to include excited states, since this has been done for the atomic problem.[23,25,26] The results of Calais and Löwdin[29] should be helpful in this endeavor. Thakkar and Smith[25,26] work with an expansion of the form $\sum c_k \exp(-\alpha_k X - \beta_k Y - \gamma_k Z)$, resulting by optimal choice of parameters, in accurate results with fewer terms than Pekeris.[23] There are, of course, four parameters per term. The procedures introduced here could be adapted to such an expansion, since the evaluation matrix elements for H can be carried out in much the same way $\vec{c}^T A \vec{c}$ is computed here.

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[1]E. A. Hylleraas, Z. Phys. 48, 469 (1928); 54, 347 (1929); 65, 209 (1930).
[2]H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 829 (1933).
[3]H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936).
[4]J. F. Hart and G. Herzberg, Phys. Rev. 106, 79 (1957).
[5]E. Hylleraas and J. Midtdal, Phys. Rev. 103, 829 (1956); 109, 1013 (1958).
[6]J. E. Midtdal, Phys. Rev. 138, A1010 (1965); Phys. Math. Univ. Oslo, No. 32 (1966).
[7]E. Holøien and S. Geltman, Phys. Rev. 153, 81 (1967).
[8]Y. Öhrn and J. Nordling, Ark. Fys. 31, 471 (1966).
[9]S. Larsson, Phys. Rev. 169, 49 (1968); Phys. Rev. A 6, 1786 (1971).
[10]J. F. Perkins, Phys. Rev. A 5, 514 (1972).
[11]L. Szász and J. Byrne, Phys. Rev. 158, 34 (1967).
[12]R. F. Gentner and E. A. Burke, Phys. Rev. 176, 63 (1968).
[13]J. S. Sims and S. Hagstrom, Phys. Rev. A 4, 908 (1971).
[14]W. Kolos and L. Wolniewics, J. Chem. Phys. 41, 3663 (1964); Rev. Mod. Phys. 35, 473 (1963).
[15]M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. 43, 1727 (1965).
[16]L. Százy and G. McGinn, J. Chem. Phys. 56, 1019 (1972).
[17]T. Ahlenius and S. Larsson, Phys. Rev. A 8, 1 (1973).
[18]C. L. Pekeris, Phys. Rev. 112, 1649 (1958); 115, 1216 (1959).
[19]H. M. James and A. S. Coolidge, Phys. Rev. 51, 857 (1937).
[20]A. A. Frost, J. Chem. Phys. 41, 478 (1964).
[21]A. A. Frost, M. Inokuti, and J. P. Lowe, J. Chem. Phys. 41, 482 (1964).
[22]A. A. Frost, D. K. Harris, and J. D. Scaryle, J. Chem. Phys. 41, 489 (1964).
[23]Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A 2, 516 (1970).
[24]S. G. Elkomoss, Phys. Rev. B 4, 3411 (1971); 6, 3913 (1972).
[25]Ajit J. Thakkar and Vedene H. Smith, Jr., Phys. Rev. A 15, 1 (1977).
[26]Ajit J. Thakkar and Vedene H. Smith, Jr., Phys. Rev. A 15, 16 (1977).
[27]R. Benesch, Phys. Rev. A 6, 573 (1972).
[28]A. A. Frost, Theor. Chem. Acta 1, 36 (1962).
[29]J. L. Calais and P. O. Löwdin, J. Mol. Spectrosc. 8, 203 (1962).
[30]R. A. Sack, C. C. J. Roothaan, and W. Kolos, Rev. Mod. Phys. 8, 1093 (1967).
[31]M. R. Hestenes and W. Karush, J. Res. Natl. Bur. Stand. 47, 45 (1951).
[32]M. R. Hestenes and W. Karush, J. Res. Natl. Bur. Stand. 47, 471 (1951).
[33]C. F. Bender, A. Pipano, R. P. Hosteny, and I. Shavitt, J. Comput. Phys. 11, 90 (1973).