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Hyperspherical Coordinates for Triatomic Molecules

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We propose a hyperspherical coordinate system for the three-body problem. The classical and quantum Hamiltonians are derived as well as the classical equations of motion. General expressions for distances between the particles in hyperspherical coordinates are obtained. Finally, potential energy plots for the water molecule are constructed.

1. INTRODUCTION

Hyperspherical coordinates have been used extensively to describe bound states of triatomic molecules [1, 2] and the scattering of an atom by a diatomic molecule [3, 4].

A system of hyperspherical coordinates for a three-body system may be divided into internal and external coordinates: the first describe the shape of the triangle formed by the particles, the latter determine the orientation of the triangle in space. In this system of coordinates the total angular orbital momentum depends only on the external coordinates, while the potential energy surface for an isolated system and the principal moments of inertia depend only on the internal ones. Another advantage of hyperspherical coordinates is that only the hyperradius has an unlimited range; the other coordinates have finite ranges. One can take full advantage of that when working with numerical methods since only for one variable will the interval have to be narrowed.

The purpose of this paper is to present the quantum and classical Hamiltonians for three particles, using a new system of hyperspherical coordinates based on a system proposed by Öhrn and Linderberg for four particles [5]. The

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coordinates lead to a simple three-body classical Hamiltonian and classical equations of motion. The quantum Hamiltonian is also simple and the symmetry of the physical system can be used to decrease the numerical effort.

This paper is organized as follows. In Section 2 we define mass-weighted Jacobi coordinates and our system of hyperspherical coordinates. In particular, in section 2.2 we establish the form of the quantum mechanical kinetic energy functional in our system of hyperspherical coordinates. Section 3 is a classical study of the three-body problem, and expressions for the canonical momenta, principal moments of inertia, total angular momentum, and kinetic energy are obtained in this section. In Section 4, we derive the Hamilton equations of motion. Potential energy surfaces for the water molecule are built in Section 5. Our concluding remarks are given in the Section 6.

2. THE THREE-BODY PROBLEM: QUANTUM TREATMENT

2.1. Mass-Weighted Jacobi Coordinates and Hyperspherical Coordinates

Nonrelativistic quantum mechanics for a system of particles with masses $\{m_j\}$ involves the kinetic energy functional

$$T(\psi) = \int d\tau \sum_j \frac{|-i\hbar\nabla_j\psi|^2}{2m_j} \tag{1}$$

Here, we denote $\nabla_j \equiv \nabla\vec{r}_i$, and ψ is a wave function in the configuration space, with position coordinates $\{\vec{r}_j\}$.

Consider a matrix O defined by (for $k < N$) [5]

$$\left.\begin{aligned} O_{jk} &= -\left(\frac{m_j m_{k+1}}{M_k M_{k+1}}\right)^{1/2}, \qquad j \le k \\ O_{k+1,k} &= \left(\frac{M_k}{M_{k+1}}\right)^{1/2} \\ O_{jk} &= 0, \qquad j > k+1 \end{aligned}\right\} \tag{2}$$

where

$$M_1 = m_1, \qquad M_j = m_j + M_{j-1} \tag{3}$$

Applying the linear transformation to the $\vec{r}_j$ vectors, we obtain,

$$\vec{u}_k = \sum_j \vec{r}_j \left(\frac{m_1}{m}\right)^{1/2} O_{jk} \tag{4}$$

where m is the total mass of the system and j, $k = 1, 2, 3$. We call the vectors $\vec{u}_k$ the mass-weighted Jacobi coordinates.

Substitution of the O_{jk} values in Eq. (4) gives

$$\vec{u}_1 = \left(\frac{m_1 m_2}{m(m_1 + m_2)}\right)^{1/2} [\vec{r}_2 - \vec{r}_1] \tag{5}$$

$$\vec{u}_2 = \frac{1}{m}\left(\frac{m_3}{m_1 + m_2}\right)^{1/2} [m_1(\vec{r}_3 - \vec{r}_1) + m_2(\vec{r}_3 - \vec{r}_2)] \tag{6}$$

and,

$$\vec{u}_3 = \frac{m_1\vec{r}_1 + m_2\vec{r}_2 + m_3\vec{r}_3}{m} \tag{7}$$

As one can see, the mass-weighted Jacobi coordinates depend on the distances between particles 1, 2, and 3. We note that $\vec{u}_3$ is the position of the center of mass of the system. As the wavefunction is translationally invariant, we have

$$\nabla_3 \psi = 0 \tag{8}$$

In order to obtain the kinetic energy function in terms of the coordinates $\vec{u}_k$, we use

$$\frac{\partial \vec{u}_k}{\partial \vec{r}_j} = \left(\frac{m_j}{m}\right)^{1/2} O_{jk} \tag{9}$$

and obtain from Eqs. (2), (3), and (9)

$$T(\psi) = \frac{(-i\hbar)^2}{2m} \int d\tau \left[\frac{\partial \psi^*}{\partial \vec{u}_1}\frac{\partial \psi}{\partial \vec{u}_1} + \frac{\partial \psi^*}{\partial \vec{u}_2}\frac{\partial \psi}{\partial \vec{u}_2} + \frac{\partial \psi^*}{\partial \vec{u}_3}\frac{\partial \psi}{\partial \vec{u}_3}\right] \tag{10}$$

Therefore, the kinetic energy functional is diagonal in the mass-weighted Jacobi coordinate system $\vec{u}_k$.

Since the vectors $\vec{u}_1$ and $\vec{u}_2$ define the internal and rotational motion of the system, we write

$$T(\psi) = \frac{(-i\hbar)^2}{2m} \int d\tau \left[\frac{\partial \psi^*}{\partial \vec{u}_1}\frac{\partial \psi}{\partial \vec{u}_1} + \frac{\partial \psi^*}{\partial \vec{u}_2}\frac{\partial \psi}{\partial \vec{u}_2}\right]$$

The cartesian components of the vectors $\vec{u}_k$, in terms of a fixed reference system, are

$$\vec{u}_1 = u_{1x}\hat{\imath} + u_{1y}\hat{\jmath} + u_{1z}\hat{k} \tag{11}$$

$$\vec{u}_2 = u_{2x}\hat{\imath} + u_{2y}\hat{\jmath} + u_{2z}\hat{k} \tag{12}$$

We define a set of hyperspherical coordinates as [5]

$$\begin{pmatrix} u_{1x} & u_{2x} \\ u_{1y} & u_{2y} \\ u_{1z} & u_{2z} \end{pmatrix} = D(\alpha\beta\gamma) \begin{pmatrix} \rho \sin\theta \cos\phi & 0 & 0 \\ 0 & \rho \sin\theta \sin\phi & 0 \\ 0 & 0 & \rho \cos\theta \end{pmatrix} \times \begin{pmatrix} v_{11} & v_{12} \\ v_{21} & v_{22} \\ v_{31} & v_{32} \end{pmatrix} \tag{13}$$

where

$$D(\alpha\beta\gamma) = D_1(\alpha)D_2(\beta)D_3(\gamma) \tag{14}$$

with

$$D_1(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{15}$$

$$D_2(\beta) = \begin{pmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{pmatrix} \tag{16}$$

and

$$D_3(\gamma) = \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{17}$$

$D(\alpha\beta\gamma)$ is an orthogonal matrix and α, β, and γ are the Euler angles. In order to define the Euler angles, let $X'Y'Z'$ be a system of orthogonal axes, and let XYZ be a rotating system of axes. The orientation of XYZ relative to $X'Y'Z'$ at any instant is specified by the three Euler angles α, β, and γ. Initially, the axes XYZ coincide with the $X'Y'Z'$ axes in the initial position K'. The α, β, and γ angles, are defined by three elementary consecutive rotations (right hand) [7]: (i) a rotation by α ($0 \leq \alpha \leq 2\pi$) around the Z' axis, followed by (ii) a rotation by β ($0 \leq \beta \leq \pi$) around the new Y' axis, which is also known as the line of nodes, and (iii) finally, a rotation by γ ($0 \leq \gamma \leq 2\pi$) around the Z axis.

We define the hyperradius as

$$\rho^2 = \sum_{i=1}^{2} (u_{ix}^2 + u_{iy}^2 + u_{iz}^2) = \sum_{i=1}^{2} |\vec{u}_i|^2 \tag{18}$$

The principal values of the moment of inertia are given by [5]

$$\left.\begin{aligned} I_1 &= m\rho^2(1 - \sin^2\theta\cos^2\phi) \\ I_2 &= m\rho^2(1 - \sin^2\theta\sin^2\phi) \\ I_3 &= m\rho^2(1 - \cos^2\theta) \end{aligned}\right\} \tag{19}$$

For a system of three particles in the XZ plane ($Y = 0$), $I_2 = I_1 + I_3$ [6] is constant. This occurs, necessarily, when $\phi = 0$, so

$$\left.\begin{aligned} I_1 &= m\rho^2\cos^2\theta \\ I_2 &= m\rho^2 \\ I_3 &= m\rho^2\sin^2\theta \end{aligned}\right\} \tag{19a}$$

Thus, the system of hyperspherical coordinates becomes

$$\begin{pmatrix} u_{1x} & u_{2x} \\ u_{1y} & u_{2y} \\ u_{1z} & u_{2z} \end{pmatrix} = D(\alpha\beta\gamma)\begin{pmatrix} \rho\sin\theta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \rho\cos\theta \end{pmatrix}\begin{pmatrix} v_{11} & v_{12} \\ v_{21} & v_{22} \\ v_{31} & v_{32} \end{pmatrix} \tag{20}$$

As we are dealing with six degrees of freedom, the V matrix must contain one degree of freedom labeled σ. Defining

$$V = \begin{pmatrix} \cos\sigma & \sin\sigma \\ 0 & 0 \\ -\sin\sigma & \cos\sigma \end{pmatrix} \tag{21}$$

and substituting Eqs. (14) and (21) in Eq. (20), we obtain the components of $\vec{u}_1$ and $\vec{u}_2$ in terms of the hyperspherical coordinates.

In order to calculate the value of the potential energy surface in hyperspherical coordinates is necessary to know the distance between the particles. From Eqs. (5)–(7) we get

$$|\vec{r}_2 - \vec{r}_1| = \rho\left(\frac{m(m_1 + m_2)}{m_1 m_2}\right)^{1/2}(\sin^2\theta\cos^2\sigma + \cos^2\theta\sin^2\sigma)^{1/2} \tag{22}$$

$$\begin{aligned} |\vec{r}_3 - \vec{r}_1| = \rho\left(\frac{m}{m_1 + m_2}\right)^{1/2}\Bigg[&\left(\frac{m}{m_3}\right)(\sin^2\theta\sin^2\sigma + \cos^2\theta\cos^2\sigma) \\ &+ 2\left(\frac{mm_2}{m_1 m_3}\right)^{1/2}(\sin^2\theta\sin\sigma\cos\sigma - \cos^2\theta\sin\sigma\cos\sigma) \\ &+ \left(\frac{m_2}{m_1}\right)(\sin^2\theta\sin^2\sigma + \cos^2\theta\cos^2\sigma)\Bigg]^{1/2} \end{aligned} \tag{23}$$

and

$$|\vec{r}_3 - \vec{r}_2| = \rho\left(\frac{m}{m_1 + m_2}\right)^{1/2}\left[\left(\frac{m}{m_3}\right)(\sin^2\theta \sin^2\sigma + \cos^2\theta \cos^2\sigma) + 2\left(\frac{mm_1}{m_2m_3}\right)^{1/2}(\sin^2\theta \sin\sigma \cos\sigma - \cos^2\theta \sin\sigma \cos\sigma) + \left(\frac{m_1}{m_2}\right)(\sin^2\theta \cos^2\sigma + \cos^2\theta \sin^2\sigma)\right]^{1/2} \quad (24)$$

As the Jacobian of the coordinates transformation is

$$J = \rho^5 \sin\theta \cos\theta(2\cos^2\theta - 1)\sin\beta$$

the volume element $d\tau$ is given by

$$d\tau = \rho^5 \sin\theta \cos\theta(2\cos^2\theta - 1)\sin\beta \, d\rho \, d\theta \, d\alpha \, d\beta \, d\gamma \, d\sigma \quad (25)$$

and the range of the coordinates can be obtained. $0 \leq \rho < \infty$, $0 \leq \theta \leq \pi/4$, and $0 \leq \sigma \leq 2\pi$.

2.2. Quantum Mechanical Kinetic Energy Functional in Hyperspherical Coordinates

Equation (10) be written in the following form,

$$T(\psi) = \int_0^\infty \int_0^{\pi/4} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} \sum_{ia} \frac{|-i\hbar \, \partial\psi/\partial u_{ia}|^2}{2m} \times \rho^5 \sin\theta \cos\theta(2\cos^2\theta - 1)\sin\beta \, d\rho \, d\theta \, d\alpha \, d\beta \, d\gamma \, d\sigma \quad (26)$$

with $\psi = \psi(u_{ia})$ and $u_{ia} = u_{ia}(\rho, \theta, \alpha, \beta, \gamma, \sigma)$.

We proceed now to obtain the kinetic energy functional in terms of hyperspherical coordinates. We write

$$\frac{\partial\psi}{\partial u_{ia}} = \frac{\partial\psi}{\partial\rho}\frac{\partial\rho}{\partial u_{ia}} + \frac{\partial\psi}{\partial\theta}\frac{\partial\theta}{\partial u_{ia}} + \frac{\partial\psi}{\partial\alpha}\frac{\partial\alpha}{\partial u_{ia}} + \frac{\partial\psi}{\partial\beta}\frac{\partial\beta}{\partial u_{ia}} + \frac{\partial\psi}{\partial\gamma}\frac{\partial\gamma}{\partial u_{ia}} + \frac{\partial\psi}{\partial\sigma}\frac{\partial\sigma}{\partial u_{ia}} \quad (27)$$

and, in order to obtain the components $\partial/\partial u_{ia}$ in terms of hyperspherical coordinates, we define, using Eq. (20),

$$U = DQV \quad (28)$$

Differentiating U, we have

$$\partial U = \partial DQV + D\,\partial QV + DQ\,\partial V \quad (28a)$$

Multiplying from the left by D^T and from the right by V^T, we get

$$D^T\,\partial UV^T = D^T\,\partial DQVV^T + D^TD\,\partial QVV^T + D^TDQ\,\partial VV^T \tag{28b}$$

Using the fact that $VV^T = 1$ and $D^TD = 1$, we obtain

$$D^T\,\partial UV^T = D^T\,\partial DQ + \partial Q + Q\partial VV^T \tag{29}$$

Substituting in Eq. (26) the values of $\partial\rho/\partial u_{ia}$, $\partial\alpha/\partial u_{ia}$, $\partial\beta/\partial u_{ia}$, $\partial\gamma/\partial u_{ia}$, and $\partial\sigma/\partial u_{ia}$ obtained from Eq. (29) and using Eq. (27), we obtain after simplifications,

$$\begin{aligned} T(\psi) = \int_0^\infty \int_0^{\pi/4} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \int_0^{2\pi} \Bigg\{ & \frac{1}{2m} \left| -i\hbar\,\frac{\partial\psi}{\partial\rho} \right|^2 + \frac{1}{2I_2} \Bigg| -i\hbar\,\frac{\partial\psi}{\partial\theta} \Bigg|^2 + \frac{|J_1\psi|^2}{2I_1} \\ & + \frac{I_2|J_2\psi|^2}{2(I_3 - I_1)^2} + \frac{|J_3\psi|^2}{2I_3} + \frac{I_2}{2(I_3 - I_1)^2} \Bigg| - i\hbar\,\frac{\partial\psi}{\partial\sigma} \Bigg|^2 \\ & - \sin 2\theta\,\frac{I_2J_2\psi}{(I_3 - I_1)^2} \left(-i\hbar\,\frac{\partial\psi}{\partial\sigma} \right) \Bigg\} \\ & \times \rho^5 \sin\theta \cos\theta (2\cos^2\theta - 1) \sin\beta\, d\rho\, d\theta\, d\alpha\, d\beta\, d\gamma\, d\sigma \end{aligned} \tag{30}$$

where J_1, J_2, and J_3 are given by

$$\begin{aligned} J_1 &= -i\hbar \left(\frac{-\cos\gamma}{\sin\beta}\,\frac{\partial}{\partial\alpha} + \sin\gamma\,\frac{\partial}{\partial\beta} + \cot\beta\cos\gamma\,\frac{\partial}{\partial\gamma} \right) \\ J_2 &= -\hbar \left(\frac{\sin\gamma}{\sin\beta}\,\frac{\partial}{\partial\alpha} + \cos\gamma\,\frac{\partial}{\partial\beta} - \cot\beta\sin\gamma\,\frac{\partial}{\partial\gamma} \right) \\ J_3 &= -i\hbar\,\frac{\partial}{\partial\gamma} \end{aligned} \tag{31}$$

and I_1, I_2, and I_3 are given by Eqs. (19).

3. CLASSICAL TREATMENT

3.1. Angular Momentum

The Cartesian components of the angular momentum are defined as [7]

$$L_\lambda = \frac{\partial T}{\partial\omega_\lambda} \tag{32}$$

where T is the classical kinetic energy of the system, ω_λ is the angular velocity of the molecule, and $\lambda = (X, Y, Z)$.

The generalized conjugate linear momentum for the Euler angles is defined by [7]

$$p_\nu = \frac{\partial T}{\partial \dot{\nu}} \tag{33}$$

where $\nu = (\alpha, \beta, \gamma, \rho, \theta, \sigma)$. Using Eqs. (32) and (33), we obtain

$$p_\nu \sum_\lambda \frac{\partial \omega_\lambda}{\partial \dot{\nu}} L_\lambda \tag{34}$$

Let P be an arbitrary point in space and let the Cartesian components of P in the two systems XYZ and $X'Y'Z'$ be given by the two column matrix vectors $\vec{r}$ and $\vec{r}'$, respectively. These vectors are related by the orthogonal rotation matrix D,

$$\vec{r}' = D\vec{r} \tag{35}$$

where D is given by Eq. (14) and the matrices of elementary rotations are given by Eqs. (15)–(17).

The inverse transformation of coordinates is given by

$$\vec{r} = D^{-1}\vec{r}' \tag{36}$$

Change of orientation of the XYZ axes in relation to $X'Y'Z'$ axes is a function of time, $D = D(t)$ [8], therefore $\alpha = \alpha(t)$, $\beta = \beta(t)$ and $\gamma = \gamma(t)$. The infinitesimal rotation associated with $\vec{\omega}$ is composed of three sucessive rotations with angular velocities $\omega_\alpha = \dot{\alpha}$, $\omega_\beta = \dot{\beta}$, and $\omega_\gamma = \dot{\gamma}$.

The components of $\vec{\omega}$ according to Eq. (36) are

$$\begin{pmatrix} (\omega_\alpha)_x \\ (\omega_\alpha)_y \\ (\omega_\alpha)_z \end{pmatrix} = D^{-1}\begin{pmatrix} 0 \\ 0 \\ \dot{\alpha} \end{pmatrix} = \begin{pmatrix} -\sin\beta\cos\gamma\dot{\alpha} \\ \sin\beta\sin\gamma\dot{\alpha} \\ \cos\beta\dot{\alpha} \end{pmatrix} \tag{37}$$

$$\begin{pmatrix} (\omega_\beta)_x \\ (\omega_\beta)_y \\ (\omega_\beta)_z \end{pmatrix} = D_3^{-1}(\gamma)D_2^{-1}(\beta)\begin{pmatrix} 0 \\ \dot{\beta} \\ 0 \end{pmatrix} = \begin{pmatrix} \sin\gamma\dot{\beta} \\ \cos\gamma\dot{\beta} \\ 0 \end{pmatrix} \tag{38}$$

and

$$\begin{pmatrix} (\omega_\gamma)_x \\ (\omega_\gamma)_y \\ (\omega_\gamma)_z \end{pmatrix} = D_3^{-1}(\gamma)\begin{pmatrix} 0 \\ 0 \\ \dot{\gamma} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \dot{\gamma} \end{pmatrix} \tag{39}$$

According to Eqs. (37)–(39),

$$(\vec{\omega})_{xyz} = (-\dot{\alpha}\sin\beta\cos\gamma + \dot{\beta}\sin\gamma)\vec{i} + (\dot{\alpha}\sin\beta\sin\gamma + \dot{\beta}\cos\gamma)\vec{j} + (\dot{\alpha}\cos\beta + \dot{\gamma})\vec{k} \tag{40}$$

Using Eqs. (34) and (40), we obtain

$$\left.\begin{aligned} L_x &= -\frac{\cos\gamma}{\sin\beta}\,p_\alpha + \sin\gamma p_\beta + \cot\beta\cos\gamma p_\gamma \\ L_y &= \frac{\sin\gamma}{\sin\beta}\,p_\alpha + \cos\gamma p_\beta - \cot\beta\sin\gamma p_\gamma \\ L_z &= p_\gamma \end{aligned}\right\} \tag{41}$$

Equation (41) are equivalents to Eqs. (31) in the quantum case.

3.2. The Kinetic Energy

The hyperspherical coordinate system defined in Eq. (28), can be written as

$$(u_{ia})_{x'y'z'} = D(u_{ia})_{xyz} \tag{42}$$

or

$$(u_{ia})_{xyz} = D^{-1}(u_{ia})_{x'y'z'}$$

where,

$$(u_{ia})_{xyz} = QV \tag{43}$$

The kinetic energy in terms of the Jacobi coordinates in a fixed frame is

$$T = \frac{1}{2}\,m(|\vec{\dot{u}}_1|^2 + |\vec{\dot{u}}_2|^2) \tag{44}$$

The derivatives of the Jacobi vectors in relation to time in the $X'Y'Z'$ and XYZ systems are related by

$$\left(\frac{d\vec{u}_i}{dt}\right)_{x'y'z'} = \left(\frac{d\vec{u}_i}{dt}\right)_{xyz} + \vec{\omega}\times(\vec{u}_i)_{xyz} \tag{45}$$

Using Eqs. (40) and Eqs. (45) and simplifying, we have

$$\begin{aligned} T = {} & \tfrac{1}{2}m\dot{\rho}^2 + \tfrac{1}{2}m\rho^2\dot{\sigma}^2 + \tfrac{1}{2}m\rho^2\dot{\theta}^2 + 2m\rho^2\dot{\beta}\dot{\sigma}\sin\theta\cos\theta\cos\gamma \\ & + 2m\rho^2\dot{\alpha}\dot{\sigma}\sin\theta\cos\theta\sin\beta\sin\gamma + \tfrac{1}{2}m\rho^2\dot{\alpha}^2(\sin^2\gamma \\ & + \cos^2\theta\cos^2\gamma\sin^2\beta + \cos^2\beta\cos^2\gamma - \cos^2\theta\cos^2\beta) \end{aligned}$$

$$+ \tfrac{1}{2}m\rho^2\dot{\beta}^2(\sin^2\theta\cos^2\theta + \cos^2\theta) + \tfrac{1}{2}m\rho^2\dot{\gamma}^2\sin^2\theta$$
$$+ m\rho^2\dot{\alpha}\dot{\beta}\sin\beta\sin\gamma\cos\gamma\sin^2\theta + m\rho^2\dot{\alpha}\dot{\gamma}\cos\beta\sin^2\theta) \quad (46)$$

which is the kinetic energy in hyperspherical coordinates.

3.3. The Moments of Inertia

The product and moments of inertia in the body fixed coordinates frame (XYZ) are given by

$$I_{xx} = m\,(u_{1y}^2 + u_{1z}^2 + u_{2y}^2 + u_{2z}^2) \quad (47)$$
$$I_{yy} = m\,(u_{1x}^2 + u_{1z}^2 + u_{2x}^2 + u_{2z}^2) \quad (48)$$
$$I_{zz} = m(u_{1x}^2 + u_{1y}^2 + u_{2x}^2 + u_{2y}^2) \quad (49)$$
$$I_{xy} = -m\,(u_{1y}u_{1x} + u_{2y}u_{2x}) \quad (50)$$
$$I_{xz} = -m\,(u_{1z}u_{1x} + u_{2z}u_{2x}) \quad (51)$$
$$I_{yz} = -m\,(u_{1z}u_{1y} + u_{2z}u_{2y}) \quad (52)$$

We define the body-fixed system having the following features:

$$I_{xy} = I_{yx} = I_{xz} = I_{zx} = I_{yz} = I_{zy} = 0$$

Applying Eqs. (47)–(49), we have

$$\left.\begin{aligned} I_{xx} &= I_1 = m\rho^2\cos^2\theta \\ I_{yy} &= I_2 = m\rho^2 \\ I_{zz} &= I_3 = m\rho^2\sin^2\theta \end{aligned}\right\} \quad (53)$$

Note that I_1, I_2, and I_3 are the same as in Eq. (19). Only three of the six coordinates are independent in the XYZ system.

4. THE CLASSICAL EQUATIONS OF MOTION

Equations (33) and (46) give rise to

$$\left.\begin{aligned}
p_\rho &= m\dot\rho \\
p_\theta &= m\rho^2\dot\theta \\
p_\alpha &= 2m\rho^2\dot\sigma \sin\theta\cos\theta\sin\beta\sin\gamma + m\rho^2\dot\alpha(\sin^2\gamma + \cos^2\theta\cos^2\gamma \\
&\quad \times \sin^2\beta + \cos^2\beta\cos^2\gamma - \cos^2\theta\cos^2\beta) + m\rho^2\dot\beta\sin\beta\sin\gamma\cos\gamma \\
&\quad \times \sin^2\theta + m\rho^2\dot\gamma\cos\beta\sin^2\theta \\
p_\beta &= 2m\rho^2\dot\sigma\sin\theta\cos\theta\cos\gamma + m\rho^2 \\
&\quad \times \dot\beta(\sin^2\theta\cos^2\gamma + \cos^2\theta) + m\rho^2\dot\alpha\sin\beta\sin\gamma\cos\gamma\sin^2\theta \\
p_\gamma &= m\rho^2\dot\gamma\sin^2\theta + m\rho^2\dot\alpha\cos\beta\sin^2\theta \\
p_\sigma &= m\rho^2\dot\sigma + 2m\rho^2\dot\beta\sin\theta\cos\theta\cos\gamma \\
&\quad + 2m\rho^2\dot\alpha\sin\theta\cos\theta\sin\beta\sin\gamma
\end{aligned}\right\} \tag{54}$$

The expression for T in terms of the generalized coordinates and generalized momenta is,

$$\begin{aligned}
T = {} & \frac{P_\rho^2}{2m} + \frac{P_\theta^2}{2I_2} + \frac{L_x^2}{2I_1} + \frac{L_y^2}{2I_2} + \frac{L_z^2}{2I_3} \\
& + \frac{\sin 2\theta}{2(I_1 - I_3)}\{\sin 2\theta\, L_y^2 - 2L_y p_\sigma - \csc 2\theta P_\sigma^2\}
\end{aligned} \tag{55}$$

or

$$\begin{aligned}
T = {} & \frac{p_\rho^2}{2m} + \frac{1}{2m\rho^2}\{p_\theta^2 + \sec^2\theta L_x^2 + \sec^2 2\theta L_y^2 \\
& + \csc^2\theta L_z^2 - 2\theta\sec 2\theta L_y p_\sigma \\
& + \sec^2 2\theta p_\sigma^2\}
\end{aligned} \tag{56}$$

From Eq. (56) for the kinetic energy, we obtain the equations of motion given by the Hamilton equations of motion,

$$\dot q_i = \frac{\partial H}{\partial p_i} \tag{57}$$

$$\dot p_i = -\frac{\partial H}{\partial q_i} \tag{58}$$

where, $q_i = q_i(\rho, \theta, \alpha, \beta, \gamma, \sigma)$ and

$$H = T + V(\rho, \theta, \sigma) \tag{59}$$

The equations of motion are

$$\left.\begin{aligned}
\dot{\rho} &= \frac{p_\rho}{m} \\
\dot{\theta} &= \frac{p_\theta}{I_2} \\
\dot{\alpha} &= -\frac{1}{I_2 \sin\beta}(\sec^2\theta \cos\gamma L_x - \sin\gamma \sec^2 2\theta L_y + \sin 2\theta \sec^2 2\theta \sin\gamma p_\sigma) \\
\dot{\beta} &= -\frac{1}{I_2}(-\sec^2\theta \sin\gamma L_x - \sec^2 2\theta \cos\gamma L_y + \sin 2\theta \sec^2 2\theta \cos\gamma\, p_\sigma) \\
\dot{\gamma} &= \frac{\cos\beta \sin\gamma}{I_2 \sin\beta}(\sec^2\theta \cos\gamma \csc\gamma L_x + \sec^2 2\theta L_y + \csc^2\theta \sin\beta \sec\beta \\
&\quad \times \csc\gamma L_z + \sin 2\theta \sec^2 2\theta p_\sigma)
\end{aligned}\right\} \tag{60}$$

$$\dot{\sigma} = \frac{I_2}{(I_1 - I_3)^2}(\sin 2\theta L_y - p_\sigma)$$

$$\left.\begin{aligned}
\dot{p}_\rho &= -\frac{2}{\rho}\left\{T - \frac{p_\rho^2}{2m}\right\} - \frac{\partial V}{\partial \rho} \\
\dot{p}_\theta &= \frac{1}{I_2}\left\{-\frac{\sin\theta}{\cos^3\theta}L_x^2 - \frac{1}{\cos^2 2\theta}L_y^2 + \frac{\cos\theta}{\sin^3\theta}L_z^2 + \frac{2L_y p_\sigma}{\cos^3 2\theta}(\sin^2 2\theta + 1)\right. \\
&\quad \left. - \frac{\sin 2\theta}{\cos^3 2\theta}P_\sigma^2\right\} - \frac{\partial V}{\partial \theta} \\
\dot{p}_\alpha &= 0 \\
\dot{p}_\beta &= -\frac{1}{I_2}\{(\cos\beta p_\alpha - p_\gamma)[\sec^2\theta \cos\gamma L_x + 2(\sin 2\theta p_\sigma - L_y) \\
&\quad \times \sec^2 2\theta \sin\gamma] \csc^2\beta\} \\
\dot{p}_\gamma &= -\frac{1}{I_2}\{(\sec^2\theta - \sec^2 2\theta)L_y + \sin 2\theta p_\sigma\} L_x \\
\dot{p} &= -\frac{\partial V}{\partial \sigma}
\end{aligned}\right\} \tag{61}$$

The equations of motion given by Eqs. (60) and (61) can be solved by numerical methods for a given realistic potential energy surface $V(\rho, \theta, \sigma)$.

5. PLOTS OF A POTENTIAL ENERGY SURFACE

In this section we show several plots of a potential energy surface for the water molecule (H_2O) in our system of hyperspherical coordinates. We

use atomic units (a.u.) and consider the hydrogen mass $m_H = 1837.416951$ a.u. and the oxygen mass $m_O = 29156.946713$ a.u.. The potential energy surface is given by

$$U(q_k) = E_e(q_k) + V_{nn}(q_k) \tag{62}$$

where $E_e(q_k)$ represents the electronic energy of the molecule, and $V_{nn}(q_k)$ is

$$V_{nn} = \sum_{k \le l}^{N} \frac{Z_k Z_l}{r_{kl}} \tag{63}$$

where Z_k is the nuclear charge and r_{kl} is the distance between two nuclei.

Figure 1 is the representation of $U(q_k)$ in relation to the θ and σ coordinates, where the ρ value is fixed. The two identical regions shown in the plot reflect the symmetry due to the presence of two identical hydrogen atoms in the system. The permutation symmetries are contained in the (θ, σ) plane.

Figure 2 is the representation of the $U(q_k)$ values as a function of ρ and σ (θ is fixed) coordinates; the range of variation of the hyperradius is con-

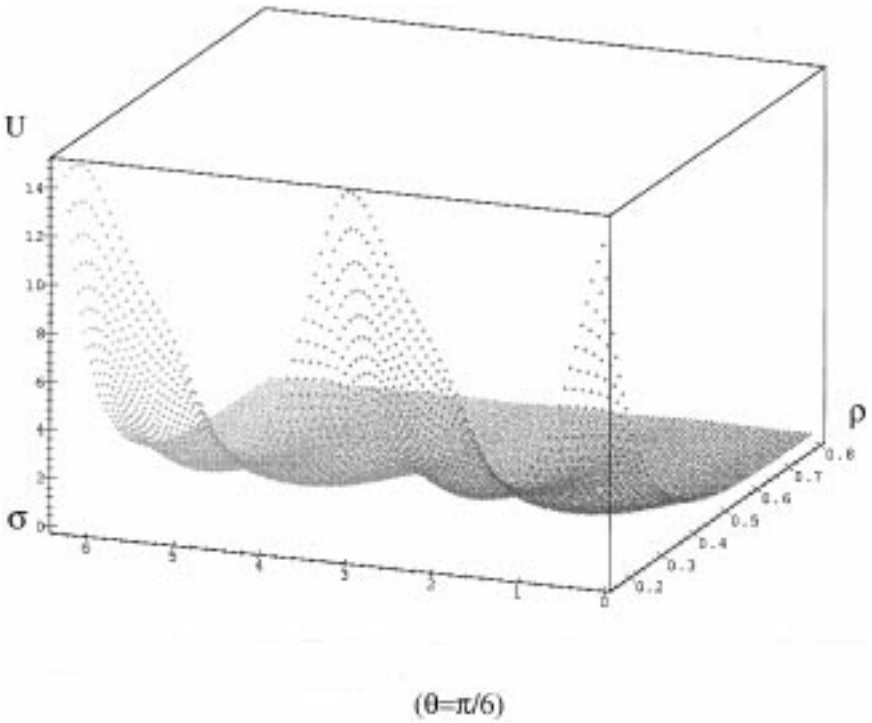

Fig. 1. The H_2O potential energy surface in relation to θ and σ. The hyperadius ρ is fixed at 0.01 bohr.

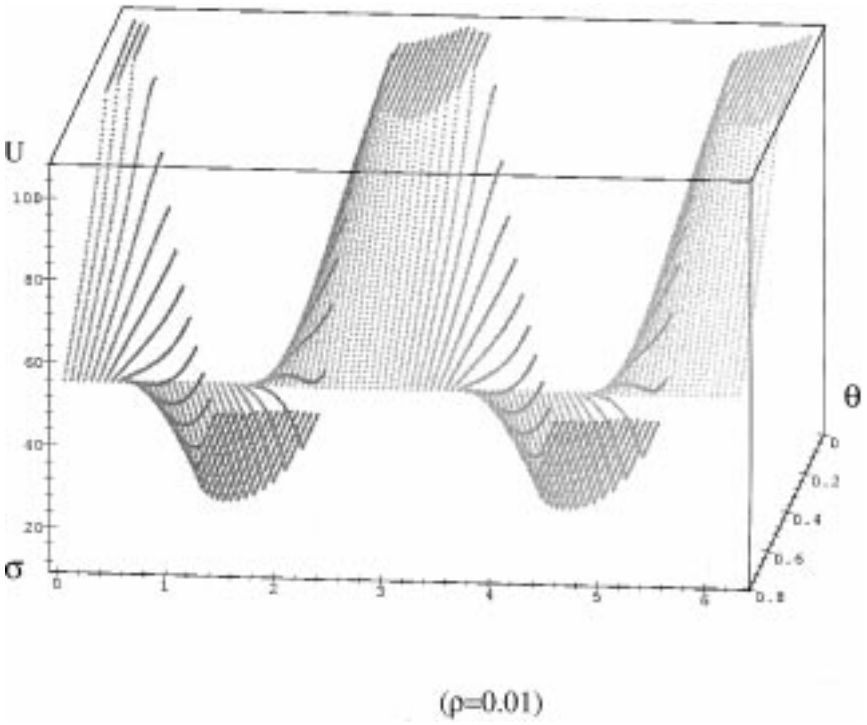

Fig. 2. The H_2O potential energy surface in relation to ρ and σ. The hyperangle θ is fixed at $\pi/6$.

strained to $0 \leq \rho \leq 1$. We notice that for $\rho \to 0$, the potential rises rapidly due to the repulsion of the nuclei when they are close toghether.

Figure 3 plots the potential energy surface in relation to ρ and θ with σ fixed at $3\pi/2$. We can see the behavior of $U(q_k)$ in the dissociation region.

Figure 4 is a plot of $U(q_k)$ in relation to ρ with $\sigma = \pi/4$ and $\theta = \pi/4$. The range of ρ is $0 \leq \rho \leq 2.5$. The plot is similar to that of a diatomic molecule.

6. CONCLUSIONS

In this paper we defined a novel system of hyperspherical coordinates for three body systems and treated in detail the quantum mechanics and the classical mechanics of such systems.

The quantum mechanical Hamiltonian is simple and easy to implement for numerical calculations. Although some classical equations of motion are indeed very simple, the relative complexity of many others demands the use of numerical methods for their solution when applied to particular cases. In

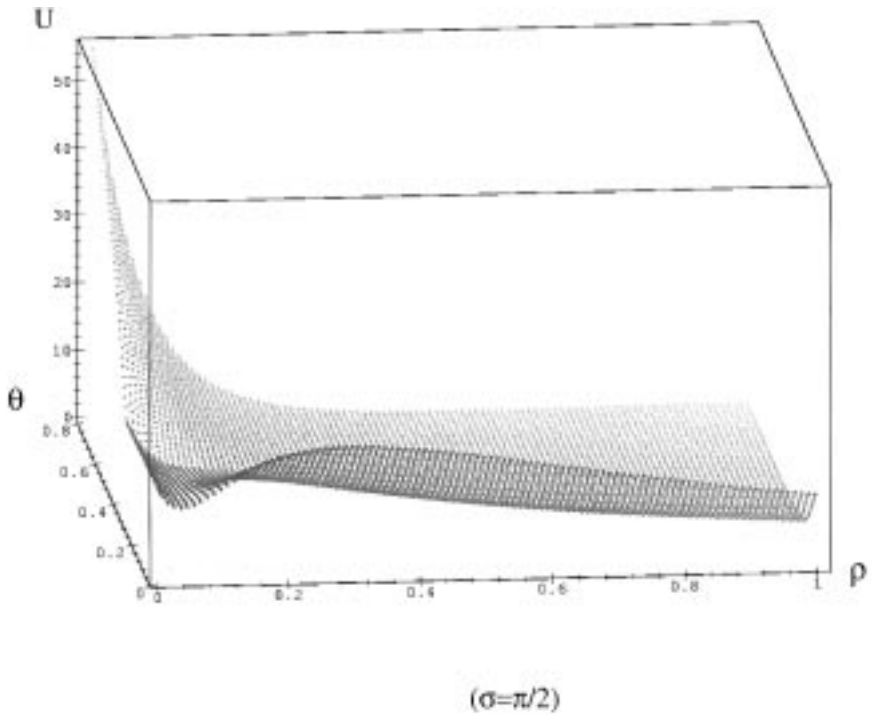

Fig. 3. The H_2O potential energy surface as a function of ρ and θ with σ fixed at $3\pi/2$.

these coordinates, the motion of a three-particle system in space is equivalent to the motion of one particle in a six-dimensional space.

We also stress that the method of orthogonal transformation, using matrix algebra, is efficient for passing from Cartesian coordinates to hyperspherical coordinates.

Equations (22)–(24) are general expressions for the distances between the nuclei for any three-atom molecule in terms of the internal coordinates ρ, θ, and σ.

The results obtained show that the hyperspherical coordinate system used is very convenient: it allows a simplification of the expressions, and it also leads naturally to a separation of the coordinates into two groups.

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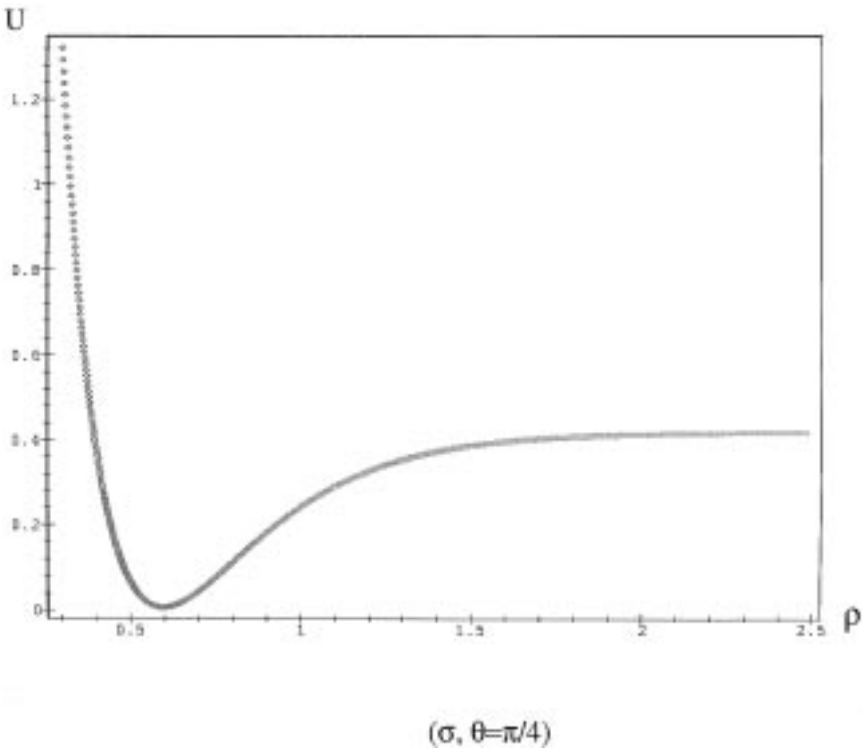

Fig. 4. The H_2O potential energy surface as a function of the hyperadius ρ with both σ and θ fixed at $\pi/4$.

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