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Rotation and vibration of diatomic molecule oscillator with hyperbolic potential function*

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The explicit expressions of energy eigenvalues and eigenfunctions of bound states for a three-dimensional diatomic molecule oscillator with a hyperbolic potential function are obtained approximately by means of the hypergeometric series method. Then for a one-dimensional system, the rigorous solutions of bound states are solved with a similar method. The eigenfunctions of a one-dimensional diatomic molecule oscillator, expressed in terms of the Jacobi polynomial, are employed as an orthonormal basis set, and the analytic expressions of matrix elements for position and momentum operators are given in a closed form.

Keywords: diatomic molecule, hyperbolic potential, matrix elements
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1. Introduction

Molecules are far more complex in structure than atoms, but they may be simplified by assuming the ratio of nuclear mass to electron mass to be large, which implies that the energy associated with the motion of the nuclei is much smaller than that associated with the motion of the electrons round the nuclei. This simplification is the basis of all molecular approximations. It is a good approximation to regard the nuclei as being fixed in calculating the electronic motion.[1]

The nuclei are assumed to have a stable equilibrium arrangement somewhere between a completely collapsed structure and a completely dispersed structure. The nuclear motions can then be classified into translations and rotations of the quasi-rigid equilibrium arrangement and internal vibrations of the nuclei about equilibrium; the translational motion does not give rise to non-classical features. We thus arrive at a classification of molecular energy levels and wavefunctions into electronic, vibrational, and rotational types. Bohn and Oppenheimer[2] have showed formally that the electronic part of the wavefunction does not change much as the nuclei move, so long as not too high vibrational and rotational modes are excited.

It is clear that two distinct problems arise in connection with molecular structure. One is to obtain electronic wavefunctions and potential energy function in nuclear coordinates. The other is to obtain the solution of the nuclear motion equation. The first problem can be solved analytically only in the simplest cases. And for solving the second problem, constructing a suitable potential function for diatomic molecules is very important.

For a diatomic molecule in general, if the nuclei have masses m_1 and m_2, and their relative position vector $\boldsymbol{r}$ has polar coordinates r, θ, φ, the equation for relative motion is

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi), \quad (1)$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, $V(r)$ is the potential function of the diatomic molecule. It has been found that the potential-energy function for the lowest electronic states of actual diatomic molecules can be represented by the Morse potential,[3] i.e.

$$V_{\mathrm{M}}(r) = D\{1 - \exp[-\alpha(r - r_0)]\}^2, \quad (2)$$

which contains three adjustable positive parameters: D, α, and r_0. It is clear that $V_{\mathrm{M}}(r)$ has a minimum

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value 0 at a point of $r = r_0$, and approaches D exponentially for large r. If $\frac{1}{\alpha}$ is somewhat smaller than the equilibrium distance r_0, $V_{\mathrm{M}}(r)$ becomes large (but not infinite) as r approaches zero. When the Morse potential is used as a potential function for the system of one-dimensional (1D) diatomic molecule, the Schrödinger equation is exactly solvable. The energy eigenvalues and eigenfunctions obtained from the equation are not only simple in form, but also practical in calculation.

Since the Morse potential function was introduced, numerous advances have been made in the field of diatomic molecules, and extensive uses of the potential function have been achieved.[1,4−8] At present the Morse potential is still one of potential functions used most in molecular physics and quantum chemistry.[9−11] However, for the Morse potential, if the distance between two atoms approaches zero, the interaction between the two atoms should approach infinity, because of the Coulomb repulsive action between the atomic nuclei, as well as the Coulomb and Pauli repulsive action among the electrons. It is obvious that, unlike the true interaction, the Morse potential is finite at $r = 0$, and cannot satisfy the boundary condition. Although the boundary condition seldom brings about a remarkable effect on bound states, it will give rise to some difficulty in solving the collision problems considered.

Another problem for the Morse potential is its inaccuracy, which is due to the replacement of the Van der Waals term by an exponential. This makes the value of the Morse potential smaller than that from the experiments in a region of large r. Therefore efforts have been made to try to improve it; at the same time, some new potential functions are also suggested.[1,5,12−19]

In 1986, Schiöberg[20] suggested a hyperbolic potential function,

$$V_{\mathrm{H}}(r) = D\left[1 - \sigma \coth(\alpha r)\right]^2, \tag{3}$$

where D, α, and σ are the adjustable positive parameters. This potential function can improve the accuracy of Morse potential to some extent. Being similar to the Morse potential, $V_{\mathrm{H}}(r)$ has a minimum value 0 at the point of

$$r = r_0 = \frac{1}{\alpha}\mathrm{arctanh}\sigma, \tag{4}$$

and approaches D exponentially for large r. Unlike the Morse potential, the hyperbolic potential function approaches infinity at the point of $r = 0$. In the region of large r, the hyperbolic potential is closer to reality than the Morse potential for some diatomic molecules. It is evident that the hyperbolic potential $V_{\mathrm{H}}(r)$ is more accurate in a way than the Morse potential.

In the present paper, we give approximate energy eigenvalues and eigenfunctions for a three-dimensional (3D) system, and rigorous solutions as well as matrix elements of position and momentum operators for a 1D system. We solve approximately the stationary state Schrödinger equation for a 3D diatomic molecule oscillator with a hyperbolic potential function by means of the hypergeometric series method in Section 2. In Section 3, we also obtain rigorous energy eigenvalues and eigenfunctions for the 1D system using a similar method. We then employ the wavefunction, expressed in terms of the Jacobi polynomial, as an orthogonal basis set to obtain analytic expressions of matrix elements of the position and momentum operators.

2. Approximate energy eigenvalues and eigenfunctions

If the potential function $V(r)$ is replaced by $V_{\mathrm{H}}(r)$ in Eq.(1), the stationary state Schrödinger equation for a 3D diatomic molecule oscillator with a hyperbolic potential function is obtained as

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V_{\mathrm{H}}(r)\right]\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi). \tag{5}$$

As a wave equation with a spherically symmetric potential, Eq.(5) can be separated in spherical coordinates to give

$$\Psi(r,\theta,\varphi) = \frac{\Phi(r)}{r}Y_{lm}(\theta,\varphi), \tag{6}$$

where $Y_{lm}(\theta,\varphi)$ is a spherical harmonic function with angular momentum quantum numbers being l and m. We can then obtain the radial equation

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\Phi(r)}{\mathrm{d}r^2} + \left[V_{\mathrm{H}}(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}\right]\Phi(r) = E\Phi(r), \tag{7}$$

by substituting Eq.(6) into Eq.(5).

Equation (7) is the wave equation for 1D motion of a particle of mass μ in a potential $V_{\mathrm{H}}(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}$, with the boundary condition where $\Phi(r)$ vanishes at the points of $r = 0$ and $r \to \infty$. If l is not too large, we are primarily interested in vibrations of

small amplitude about the minimum. We can then introduce the following approximation:

$$\frac{l(l+1)}{r^2} \approx \frac{l(l+1)}{r_0^2}\left\{C_0 + C_1\frac{\exp(-2\alpha r)}{1-\exp(-2\alpha r)} + C_2\left[\frac{\exp(-2\alpha r)}{1-\exp(-2\alpha r)}\right]^2\right\}, \quad (8)$$

where

$$C_0 = 1 - \left[\frac{1-\exp(-2\alpha r_0)}{2\alpha r_0}\right]^2 \times \left[\frac{8\alpha r_0}{1-\exp(-2\alpha r_0)} - 3 - 2\alpha r_0\right], \quad (9)$$

$$C_1 = 2\left[\exp(2\alpha r_0) - 1\right]\left\{3\left[\frac{1-\exp(-2\alpha r_0)}{2\alpha r_0}\right] - (3+2\alpha r_0)\left[\frac{1-\exp(-2\alpha r_0)}{2\alpha r_0}\right]\right\}, \quad (10)$$

$$C_2 = \left[\exp(2\alpha r_0) - 1\right]^2\left[\frac{1-\exp(-2\alpha r_0)}{2\alpha r_0}\right]^2 \times \left[3 + 2\alpha r_0 - \frac{4\alpha r_0}{1-\exp(-2\alpha r_0)}\right], \quad (11)$$

and higher-order terms are neglected. In fact, Eq.(8) is the approximate expansion of the centrifugal potential $\frac{l(l+1)}{r^2}$ nearby $r = r_0$, the minimum point of $V_{\mathrm{H}}(r)$.

Inserting Eqs.(3) and (9) into Eq.(8) and letting

$$z = \exp(-2\alpha r) \quad (12)$$

yields the following equation:

$$z^2\frac{\mathrm{d}^2\Phi(z)}{\mathrm{d}z^2} + z\frac{\mathrm{d}\Phi(z)}{\mathrm{d}z} - \left[K^2 + Q\frac{z}{1-z} + \left(S^2 - \frac{1}{4}\right)\left(\frac{z}{1-z}\right)^2\right]\Phi(z) = 0, \quad (13)$$

where $\Phi(z) = \Phi(r)$, and

$$K = \sqrt{\frac{\mu D}{2\alpha^2\hbar^2}(1-\sigma)^2 + \frac{l(l+1)}{4\alpha^2 r_0^2}C_0 - \frac{\mu E}{2\alpha^2\hbar^2}}, \quad (14)$$

$$Q = -\frac{2\mu D}{\alpha^2\hbar^2}\sigma(1-\sigma) + \frac{l(l+1)}{4\alpha^2 r_0^2}C_1, \quad (15)$$

$$S = \sqrt{\frac{2\mu D}{\alpha^2\hbar^2}\sigma^2 + \frac{l(l+1)}{4\alpha^2 r_0^2}C_2 + \frac{1}{4}}. \quad (16)$$

Here we select a trial solution

$$\Phi(z) = z^K(1-z)^{S+\frac{1}{2}}\Omega(z), \quad (17)$$

and insert it into Eq.(13), and we have

$$z(1-z)^2\frac{\mathrm{d}^2\Omega(z)}{\mathrm{d}z^2} + \left[(2K+1) - 2(K+1+S)z\right]\frac{\mathrm{d}\Omega(z)}{\mathrm{d}z} - \left[(2K+1)\left(S+\frac{1}{2}\right) + Q\right]\Omega(z) = 0. \quad (18)$$

Equation (18) is a hypergeometric equation of variable z. The solutions of the equation can be expressed as

$$\Omega_1(z) = F(a,b,c;z) \quad (19)$$

and

$$\Omega_2(z) = z^{-2K}F(a-c+1, b-c+1, 2-c; z), \quad (20)$$

where $F(a,b,c;z)$ is a hypergeometric function, and

$$a = K + S + \frac{1}{2} - \sqrt{K^2 + S^2 - Q - \frac{1}{4}}, \quad (21)$$

$$b = K + S + \frac{1}{2} + \sqrt{K^2 + S^2 - Q - \frac{1}{4}}, \quad (22)$$

$$c = 2K + 1. \quad (23)$$

Considering the boundary condition where the wavefunction is finite as $r \to \infty$, we must give up $\Omega_2(z)$, and select $\Omega_1(z)$ as the solution of Eq.(18). On the other hand, it is found that it is necessary to obtain a polynomial solution in order to satisfy another boundary condition where the wavefunction is finite as $r = 0$, i.e.

$$a = -n, \quad n = 0, 1, 2, \cdots, \leq \sqrt{S^2 - Q - \frac{1}{4}} - S - \frac{1}{2}. \quad (24)$$

Hence, we can obtain solutions of Eq.(19) satisfying the boundary conditions, i. e.

$$\Omega(z) = F(-n, b, c; z), \quad (25)$$

where $F(-n,b,c;z)$ is in fact the nth degree Jacobi polynomial, i.e.

$$F(-n,b,c;z) = \sum_{j=0}^{n}\frac{(-n)_j(b)_j}{j!(c)_j}z^j \quad (26)$$

and

$$(b)_j = b(b+1)(b+2)\cdots(b+j-1). \quad (27)$$

The energy eigenvalues can then be given by Eqs.(22) and (25) as follows:

$$E_n = D(1-\sigma)^2 + \frac{l(l+1)\hbar^2}{2\mu r_0^2}C_0 - \frac{\alpha^2\hbar^2}{2\mu} \times \left[\frac{S^2 - Q - \frac{1}{4} - \left(S+n+\frac{1}{2}\right)^2}{S+n+\frac{1}{2}}\right]^2, \quad (28)$$

and the corresponding eigenfunctions can be obtained as follows:

$$\Psi_n(r,\theta,\varphi) = \frac{1}{r} z^{K_n} (1-z)^{S+\frac{1}{2}} F(-n,b,c;z) Y_{lm}(\theta,\varphi), \quad (29)$$

where

$$K_n = \sqrt{\frac{\mu D}{2\alpha^2\hbar^2}(1-\sigma)^2 + \frac{l(l+1)}{4\alpha^2 r_0^2} C_0 - \frac{\mu E_n}{2\alpha^2\hbar^2}}. \quad (30)$$

3. Rigorous solutions and matrix elements for 1D system

The motion of a diatomic molecule oscillator with a 1D hyperbolic potential function can be described by the following stationary state Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V_{\mathrm{H}}(x)\right]\psi(x) = \varepsilon\psi(x), \quad (31)$$

where

$$V_{\mathrm{H}}(x) = D[1-\sigma\coth(\alpha x)]^2. \quad (32)$$

By comparing with Eq.(7), we can easily obtain rigorous energy eigenvalues from Eq.(28), i.e.

$$\varepsilon_n = D(1-\sigma)^2 - \frac{\alpha^2\hbar^2}{2\mu} \times \left[\frac{s^2 - q - \frac{1}{4} - \left(s+n+\frac{1}{2}\right)^2}{s+n+\frac{1}{2}}\right]^2, \quad (33)$$

and corresponding eigenfunctions from Eqs.(17) and (25), i.e.

$$\psi_n(x) = N_n y^{k_n} (1-y)^{s+\frac{1}{2}} F(-n,\beta,\gamma;y), \quad (34)$$

where $n = 0,1,2,\cdots,\leq \sqrt{s^2-q-\frac{1}{4}} - s - \frac{1}{2}$, N_n are normalization constants, and

$$y = \exp(-2\alpha x), \quad (35)$$

$$\beta = k + s + \frac{1}{2} + \sqrt{k^2 + s^2 - q - \frac{1}{4}}, \quad (36)$$

$$\gamma = 2k+1, \quad (37)$$

$$q = -\frac{2\mu D}{\alpha^2\hbar^2}\sigma(1-\sigma), \quad (38)$$

$$s = \sqrt{\frac{2\mu D}{\alpha^2\hbar^2}\sigma^2 + \frac{1}{4}}. \quad (39)$$

$$k_n = \sqrt{\frac{\mu D}{2\alpha^2\hbar^2}(1-\sigma)^2 - \frac{\mu\varepsilon_n}{2\alpha^2\hbar^2}}. \quad (40)$$

Here it should be noted that the eigenfunctions (34) can be normalized, the normalization constants are

$$N_n = \left[\frac{2\alpha(\gamma-1)(\gamma)_n \Gamma(\beta+\gamma+1)}{n!(\beta-\gamma+n+1)(\beta)_n \Gamma(\gamma)\Gamma(\beta-\gamma+1)}\right]^{1/2}. \quad (41)$$

As is well-known, the quantum-dynamical variables do not obey the commutative law of multiplication. It is convenient to represent such noncommutative dynamical variables, which are called operators, as matrices. Matrix theory provides a very flexible representation scheme, since there exist an arbitrarily large number of ways of choosing rows and columns of a matrix, all of which are of equal validity.

Diagonal matrix elements of an operator that is in a diagonal form are just eigenvalues of the operator. If the operator is not in a diagonal form, the diagonal matrix elements are expectation values of operators for states that are normalized, and off-diagonal matrix elements are related to probabilities for transitions between pairs of states.

The eigenfunctions of a 1D diatomic molecule with the hyperbolical potential functions, expressed in terms of the Jacobi polynomial, can be employed as an orthonormal basis set in the theory of rotation and vibration for the polyatomic molecules. Therefore, the analytic expressions for matrix elements of common operators can be calculated in a closed form.[21]

From Eq.(35) the position operator can be written as

$$\hat{x} = -\frac{1}{2\alpha}\ln y. \quad (42)$$

We can also obtain the following relationship:

$$\hat{x} = -\frac{1}{2\alpha}\frac{\partial}{\partial\lambda} y^\lambda\Big|_{\lambda=0}, \quad (43)$$

if we use the method introduced by Sage.[22] Generally we have

$$\hat{x}^l = \left(-\frac{1}{2\alpha}\right)^l \frac{\partial^l}{\partial\lambda^l} y^\lambda\Big|_{\lambda=0}, \quad l = 1,2,3,\cdots. \quad (44)$$

We then obtain the matrix elements of position operator

$$\langle m|\hat{x}^l|n\rangle = \left(-\frac{1}{2\alpha}\right)^l \frac{\partial^l}{\partial\lambda^l}\langle m|y^\lambda|n\rangle\Big|_{\lambda=0}, \quad (45)$$

where

$$\langle m|\, y^l\, |n\rangle = \int_0^\infty \psi_m(x)\, y^\lambda \psi_n(x)\mathrm{d}x$$
$$= \frac{N_m N_n}{2\alpha} \sum_{i=0}^{m}\sum_{j=0}^{n} \frac{(-m)_i\,(-n)_j\,(\beta)_i\,(\beta)_j\,\Gamma\left[\beta - \frac{1}{2}(m+n) - 2S + i + j + \lambda - 1\right]\Gamma(2S+2)}{i!j!\,(\beta - m - 2S)_i\,(\beta - n - 2S)_j\,\Gamma\left[\beta - \frac{1}{2}(m+n) + i + j + \lambda + 1\right]}, \quad (46)$$

by means of Eq.(26) and the properties of B-function.[23]

In the way similar to Eq.(42), the momentum operator can be expressed as

$$\hat{p} = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x} = 2\alpha\mathrm{i}\hbar y\frac{\mathrm{d}}{\mathrm{d}y}. \quad (47)$$

Then we can obtain the matrix element of momentum operator

$$\langle m|\, \hat{p}\, |n\rangle = 2\alpha\mathrm{i}\hbar\, \langle m|\, y\frac{\mathrm{d}}{\mathrm{d}y}\, |n\rangle, \quad (48)$$

where

$$\langle m|\, y\frac{\mathrm{d}}{\mathrm{d}y}\, |n\rangle$$
$$= \int_0^\infty \psi_m(x)\, y\frac{\mathrm{d}}{\mathrm{d}y}\psi_n(x)\mathrm{d}x$$
$$= \frac{N_m N_n}{8\alpha} \sum_{i=0}^{m}\sum_{j=0}^{n} \frac{(n - m + 2j - 2i)\,(-m)_i\,(-n)_j\,(\beta)_i\,(\beta)_j\,\Gamma\left[\beta - \frac{1}{2}(m+n) - 2S + i + j - 1\right]\Gamma(2S+2)}{i!j!\,(\beta - m - 2S)_i\,(\beta - n - 2S)_j\,\Gamma\left[\beta - \frac{1}{2}(m+n) + i + j + 1\right]}, \quad (49)$$

which is similar to the calculation of position matrix elements.

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