

Molecular Spinless Energies of the Morse Potential Energy Model

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We solve the Klein-Gordon equation with the Morse empirical potential energy model. The bound state energy equation has been obtained in terms of the supersymmetric shape invariance approach. The relativistic vibrational transition frequencies for the $X^1\Sigma^+$ state of ScI molecule have been computed by using the Morse potential model. The calculated relativistic vibrational transition frequencies are in good agreement with the experimental RKR values.

Key Words : Klein-Gordon equation, Morse potential model, Vibrational transition, ScI molecule

Introduction

There has been continuous interest in the analytical solutions of the Klein-Gordon equation with some typical diatomic molecule empirical potentials,¹⁻¹⁰ these potential models include the Morse potential,¹¹ Rosen-Morse potential,¹² Manning-Rosen potential,¹³ Pöschl-Teller potential,¹⁴ and Deng-Fan potential,¹⁵ etc. Diatomic potential energy functions have been applied in various issues, such as atom-atom collisions, molecular spectroscopy, molecular dynamics simulation, chemical reactivity, and transport properties for more complex systems.¹⁶ Alhaidari *et al.*¹⁷ pointed out that one can yield a nonrelativistic limit with a potential function $2V(r)$ from the Klein-Gordon equation with the equal scalar potential $S(r)$ and vector potential $V(r)$. In Ref.¹⁸ and¹⁹ the authors investigated relativistic energy equations of the improved Manning-Rosen potential²⁰ and improved Rosen-Morse potential,²¹ and calculated relativistic vibrational transition frequencies for the $a^3\Sigma_u^+$ state of $^7\text{Li}_2$ molecule and the $3^3\Sigma_g^+$ state of Cs_2 molecule.

In 1929, Morse¹¹ proposed the first three-parameter empirical potential energy function for diatomic molecules,

$$U_M(r) = D_e(1 - e^{-\alpha(r-r_e)})^2, \quad (1)$$

where D_e is the dissociation energy, r_e is the equilibrium bond length, and α denotes the range of the potential. The well-known Morse potential has been widely used in many fields, such as the diatomic vibrations,²² molecular simulations,²³⁻²⁵ etc. Based on the exact quantization rule for the nonrelativistic Schrödinger equation, Sun¹ proposed an exact quantization rule for the relativistic one-dimensional Klein-Gordon equation, and obtained the exact relativistic energies for the one-dimensional Morse potential. By using the asymptotic iteration method,²⁶ Bayrak *et al.*² investigated the bound state solutions of the Klein-Gordon equation for the equal scalar and vector Morse potentials. As far as we known, one has not reported predicting quantitatively the relativistic vibrational levels for real diatomic molecules in

terms of the Morse potential model.

In this work, we attempt to study the bound state solutions of the Klein-Gordon equation with the Morse potential energy model. The bound state energy equation is investigated by using the basic concept of the supersymmetric shape invariance approach. We also calculate the relativistic vibrational transition frequencies of the $X^1\Sigma^+$ state of ScI molecule and compare the present calculated values with the RKR experimental data.

Bound State Solutions

The Klein-Gordon equation with a scalar potential $S(r)$ and a vector potential $V(r)$ is given by

$$\begin{aligned} & \left[-\hbar^2 c^2 \nabla^2 + (Mc^2 - S(r))^2 \right] \Psi(r, \theta, \varphi) \\ & = [E - V(r)]^2 \Psi(r, \theta, \varphi), \end{aligned} \quad (2)$$

where ∇^2 is the Laplace operator, E is the relativistic energy of the quantum system, M is the rest mass of the quantum system, c is the speed of light, and $\hbar = h/2\pi$, h is the Planck constant. The rest mass M can be taken as the reduced mass μ for a diatomic molecule. We write the wave function as $\Psi = (r, \theta, \varphi) = (u_{v,J}(r)/r) Y_{j,m}(\theta, \varphi)$, where $Y_{j,m}(\theta, \varphi)$ is the spherical harmonic function. Substituting this form of the wave function into Eq. (2), we reduce the radial part of the Klein-Gordon equation,

$$\begin{aligned} & \left[\hbar^2 c^2 \frac{d^2}{dr^2} + 2(\mu c^2 S(r) + E_{v,J} V(r)) + S^2(r) - V^2(r) \right. \\ & \left. + \frac{J(J+1)\hbar^2 c^2}{r^2} \right] u_{v,J}(r) = (E_{v,J}^2 - \mu^2 c^4) u_{v,J}(r), \end{aligned} \quad (3)$$

where v and J denotes the vibrational and rotational quantum numbers, respectively. In the presence of the equal scalar and vector potentials, $S(r) = V(r)$, Eq. (3) turns to the following form

$$\left[-\hbar^2 c^2 \frac{d^2}{dr^2} + 2(\mu c^2 + E_{v,J})V(r) + \frac{J(J+1)\hbar^2 c^2}{r^2} \right] u_{v,J}(r) = (E_{v,J}^2 - \mu^2 c^4) u_{v,J}(r). \quad (4)$$

In the nonrelativistic limit, Eq. (4) produces the Schrödinger equation with the potential $2V(r)$. In the case of the nonrelativistic limit, we employ the scheme proposed by Alhaidari *et al.*¹⁷ to make the interaction potential as $V(r)$, not $2V(r)$. We write Eq. (4) in the form

$$\left[-\hbar^2 c^2 \frac{d^2}{dr^2} + 2\left(\mu c^2 \frac{S(r)}{2} + E_{v,J} \frac{V(r)}{2} \right) + \left(\frac{S(r)}{2} \right)^2 - \left(\frac{V(r)}{2} \right)^2 + \frac{J(J+1)\hbar^2 c^2}{r^2} \right] u_{v,J}(r) = (E_{v,J}^2 - \mu^2 c^4) u_{v,J}(r). \quad (5)$$

Taking the scalar and vector potentials as the equal Morse potential, $S(r) = V(r) = U_M(r)$, we produce the following second-order Schrödinger-like equation,

$$\left[\hbar^2 c^2 \frac{d^2}{dr^2} + (\mu c^2 + E_{v,J}) D_e (1 - e^{-\alpha(r-r_e)})^2 + \frac{J(J+1)\hbar^2 c^2}{r^2} \right] u_{v,J}(r) = (E_{v,J}^2 - \mu^2 c^4) u_{v,J}(r). \quad (6)$$

This equation is exactly solvable for the case of $J=0$. However, Eq. (6) is only approximately solvable when the centrifugal term is included ($J \neq 0$). We take the Pekeris approximation scheme to deal with the centrifugal term.²⁷ Taking the coordinate transformation of $x = (r-r_e)/r_e$, the centrifugal potential is expanded in a series around $x=0$,

$$U_{CP}(r) = \frac{J(J+1)\hbar^2 c^2}{r^2} = \frac{J(J+1)\hbar^2 c^2}{r_e^2} \frac{1}{(1+x)^2} = \gamma(1-2x+3x^2+\dots), \quad (7)$$

where $\gamma = (J(J+1)\hbar^2 c^2)/r_e^2$. The centrifugal potential $U_{CP}(r)$ is replaced by the following form of

$$U_{CP}(r) = \gamma(d_0 + d_1 e^{-\alpha r} + d_2 e^{-2\alpha r}), \quad (8)$$

where d_0 , d_1 , and d_2 are the coefficients. Employing the coordinate transformation $x = (r-r_e)/r_e$, we expand expression (8) in a series around $x=0$,

$$U_{CP}(r) = \gamma(d_0 + d_1 e^{-\alpha r_e} + d_2 e^{-2\alpha r_e}) - \gamma \alpha r_e e^{-\alpha r_e} (d_1 + 2d_2 e^{-\alpha r_e}) x + \gamma \alpha^2 r_e^2 e^{-\alpha r_e} (d_1/2 + 2d_2 e^{-\alpha r_e}) x^2 + \dots \quad (9)$$

Taking up to the second-order degrees in the series expressions (7) and (9), and comparing equal powers of Eq. (7) and (9), we yield the following expressions for the coefficients d_0 , d_1 , and d_2 ,

$$d_0 = 1 - \frac{3}{\alpha r_e} + \frac{3}{\alpha^2 r_e^2}, \quad (10)$$

$$d_1 = 2e^{\alpha r_e} \left(\frac{2}{\alpha r_e} - \frac{3}{\alpha^2 r_e^2} \right), \quad (11)$$

$$d_2 = e^{2\alpha r_e} \left(\frac{3}{\alpha^2 r_e^2} - \frac{1}{\alpha r_e} \right). \quad (12)$$

Substituting expression (8) into Eq. (6) gives the following equation

$$\left[-\frac{d^2}{dr^2} + \frac{\gamma d_1 - 2(\mu c^2 - E_{v,J}) D_e e^{\alpha r_e}}{\hbar^2 c^2} e^{-\alpha r} + \frac{\gamma d_2 + (\mu c^2 + E_{v,J}) D_e e^{2\alpha r_e}}{\hbar^2 c^2} e^{-2\alpha r} \right] u_{v,J}(r) = \tilde{E}_{v,J} u_{v,J}(r). \quad (13)$$

where $\tilde{E}_{v,J}$ is defined as

$$\tilde{E}_{v,J} = \frac{1}{\hbar^2 c^2} [E_{v,J}^2 - \mu^2 c^4 - (\mu c^2 + E_{v,J}) D_e - \gamma d_0]. \quad (14)$$

We apply the supersymmetric shape invariance approach to solve Eq. (13).²⁸⁻³⁰ The ground-state wave function $u_{0,J}(r)$ is expressed as

$$u_{0,J}(r) = \exp(-\int W(r) dr), \quad (15)$$

where $W(r)$ is called a superpotential in supersymmetric quantum mechanics.²⁸ Substituting expression (15) into Eq. (13) leads us to obtain the following relation satisfied by the superpotential $W(r)$,

$$W^2(r) - \frac{dW(r)}{dr} = \frac{\gamma d_1 - 2(\mu c^2 + E_{v,J}) D_e e^{\alpha r_e}}{\hbar^2 c^2} e^{-\alpha r} + \frac{\gamma d_2 + (\mu c^2 + E_{v,J}) D_e e^{2\alpha r_e}}{\hbar^2 c^2} e^{-2\alpha r} - \tilde{E}_{0,J}, \quad (16)$$

where $\tilde{E}_{0,J}$ is the ground-state energy. Letting the superpotential $W(r)$ as

$$W(r) = A e^{-\alpha r} + B, \quad (17)$$

where A and B are two constants. Substituting this expression into expression (16) leads us to rewrite the ground-state wave function $u_{0,J}(r)$ as

$$u_{0,J}(r) = e^{-Br} e^{\frac{A}{\alpha} e^{-\alpha r}}. \quad (18)$$

We consider the bound state solutions, which demand the wave function $u_{v,J}(r)$ to satisfy the boundary conditions: $u_{v,J}(\infty) = 0$ and $u_{v,J}(0)$ is limentary. These regularity conditions demand $A > 0$ and $B > 0$.

Using expression (17) of superpotential $W(r)$, we can construct a pair of supersymmetric partner potentials $U_-(r)$ and $U_+(r)$,

$$U_-(r) = W^2(r) - \frac{dW(r)}{dr} = B^2 + (2AB + \alpha A) e^{-\alpha r} + A^2 e^{-2\alpha r}, \quad (19)$$

$$U_+(r) = W^2(r) + \frac{dW(r)}{dr} = B^2 + (2AB - \alpha A) e^{-\alpha r} + A^2 e^{-2\alpha r}. \quad (20)$$

From expressions (19) and (20), we can have the following relationship

$$U_+(r, a_0) = U_-(r, a_1) + R(a_1), \quad (21)$$

where $a_0 = B$, a_1 is a function of a_0 , i.e., $a_1 = h(a_0) = a - \alpha$, and the remainder $R(a_1)$ is independent of r , $R(a_1) = a_0^2 - a_1^2$. Relation (21) shows that the partner potentials $U_-(r)$ and $U_+(r)$ are the shape-invariant potentials. Their energy spectra can be determined with the shape invariance approach.²⁹ The energy spectra of the potential $U_-(r)$ are given by

$$\begin{aligned} \tilde{E}_{0,J}^{(-)} &= 0, \\ \tilde{E}_{\nu,J}^{(-)} &= \sum_{k=1}^{\nu} R(a_k) = R(a_1) + R(a_2) + \dots + R(a_{\nu}) \\ &= (a_0^2 - a_1^2) + (a_1^2 - a_2^2) + \dots + (a_{\nu-1}^2 - a_{\nu}^2), \quad (22) \\ &= a_0^2 - a_{\nu}^2 = B^2 - (B - \nu\alpha)^2 \end{aligned}$$

where the quantum number $\nu = 0, 1, 2, \dots$

By comparing Eq. (19) with Eq. (16), we obtain the following three relationships

$$B^2 = -\tilde{E}_{0,J}, \quad (23)$$

$$2AB + \alpha A = \frac{\gamma d_1 - 2(\mu c^2 + E_{\nu,J})D_e e^{a r_e}}{\hbar^2 c^2}, \quad (24)$$

$$A^2 = \frac{\gamma d_2 + 2(\mu c^2 + E_{\nu,J})D_e e^{2a r_e}}{\hbar^2 c^2}. \quad (25)$$

Solving Eqs. (24) and (25), we have

$$A = \frac{\sqrt{\gamma d_2 + 2(\mu c^2 + E_{\nu,J})D_e e^{2a r_e}}}{\hbar^2 c^2}, \quad (26)$$

$$B = \frac{\gamma d_1 - 2(\mu c^2 + E_{\nu,J})D_e e^{a r_e}}{\hbar^2 c^2} \frac{1}{2A} - \frac{\alpha}{2}. \quad (27)$$

From Eqs. (13), (16) and (19), we obtain the following relationship for $\tilde{E}_{\nu,J}$,

$$\tilde{E}_{\nu,J} = \tilde{E}_{\nu,J}^{(-)} - \tilde{E}_{0,J}. \quad (28)$$

With the help of Eqs. (22) and (23), we arrive at the following expression for $\tilde{E}_{\nu,J}$,

$$\tilde{E}_{\nu,J} = -(B - \nu\alpha)^2. \quad (29)$$

Substituting expression (27) into expression (29) and using expression (26), we find the relativistic rotation-vibrational energy equation for the diatomic molecule in the presence of equal scalar and vector Morse potential energy models,

$$\begin{aligned} E_{\nu,J}^2 - \mu^2 c^4 &= (\mu c^2 + E_{\nu,J})D_e + \gamma d_0 \\ &\quad - \left(\frac{\gamma d_1 - 2(\mu c^2 + E_{\nu,J})D_e e^{a r_e}}{2\sqrt{\gamma d_2 + 2(\mu c^2 + E_{\nu,J})D_e e^{2a r_e}}} - \left(\nu + \frac{1}{2} \right) \hbar c \alpha \right)^2. \quad (30) \end{aligned}$$

When $J = 0$, $\gamma = 0$, we obtain the relativistic vibrational energy equation for the diatomic molecule with equal scalar and vector Morse potentials,

$$E_{\nu,J}^2 - \mu^2 c^4 = \left(2 \left(\nu + \frac{1}{2} \right) \hbar c \alpha \sqrt{(\mu c^2 + E_{\nu,J})D_e} - \left(\nu + \frac{1}{2} \right) \hbar^2 c^2 \alpha^2 \right). \quad (31)$$

Employing the superpotential $W(r)$ given in expression (17) and the ground-state wave function $u_{0,J}(r)$ given in expression (18), we can calculate the excited state wave functions by using the explicit recursion operator approach.^{31,32}

Discussions

The force constant k_e is defined as the second derivatives of the potential energy function $U(r)$ for a diatomic molecule, $k_e = (d^2 U(r))/dr^2|_{r=r_e}$. From this definition and the relation $k_e = 4\pi^2 \mu c^2 \omega_e^2$, we have the expression satisfied by the potential parameter α appearing in the Morse potential (1),

$$\alpha = \pi c \omega_e \sqrt{\frac{2\mu}{D_e}}, \quad (32)$$

where ω_e is the equilibrium harmonic vibrational frequency.

We consider the $X^1\Sigma^+$ state of ScI molecule. Taking the experimental values of D_e , r_e , and ω_e as inputs, we can determine the value of the potential parameters α in terms of expression (32), $\alpha = 1.28094315 \times 10^8 \text{ cm}^{-1}$. The molecular constants of the $X^1\Sigma^+$ state of ScI molecule are taken from the literature³³: $D_e = 2.858 \text{ eV}$, $r_e = 2.6078 \text{ \AA}$, and $\omega_e = 277.18 \text{ cm}^{-1}$. A successful potential energy function should reproduce the experimental potential curve as determined by the Rydberg-Klein-Rees (RKR) method.³⁴⁻³⁶ The experimental RKR data points reported by Reddy *et al.*³³ for the $X^1\Sigma^+$ state of ScI molecule are depicted in Figure 1, which also contains the potential energy curve reproduced by the Morse potential model. The average absolute deviation of the Morse potential for the $X^1\Sigma^+$ state of ScI molecule from the RKR potential reported by Reddy *et al.*³³ is 0.0344% of

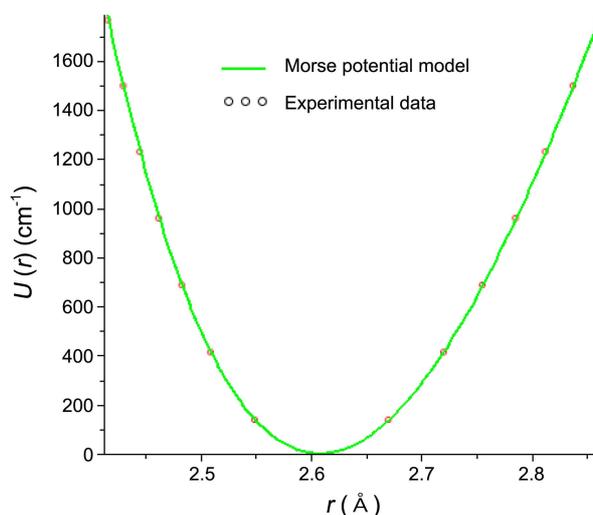


Figure 1. (Color online) RKR data points and the Morse potential energy model for the $X^1\Sigma^+$ state of ScI molecule.

Table 1. A comparison of the calculated relativistic vibrational transition frequencies and experimental RKR values for the $X^1\Sigma^+$ state of ScI molecule (in units of cm^{-1})

| $\nu (\rightarrow \nu-1)$ | RKR value | Present calculation |
|---------------------------|-----------|---------------------|
| 1 | 275.6 | 275.513 |
| 2 | 273.8 | 273.847 |
| 3 | 272.2 | 272.181 |
| 4 | 270.5 | 270.514 |
| 5 | 268.9 | 268.848 |
| 6 | 267.2 | 267.181 |

D_e . This average absolute deviation satisfies the Lippincott criterion, *i.e.*, an average absolute deviation of less than 1% of the dissociation energy D_e .³⁷ The average deviation is defined as

$$\sigma_{\text{av}} = 100 \frac{\sum (|U_{\text{exp}}(r) - U_{\text{calc}}(r)|)}{N_p D_e}, \quad (33)$$

where N_p is the number of experimental data points, $U_{\text{exp}}(r)$ and $U_{\text{calc}}(r)$ are the experimentally determined potential and the empirical potential, respectively. This accuracy indicator has been used in a large body of literature on assessing the accuracy of an empirical potential model.^{38,39}

By applying energy eigenvalue Eq. (31), we can calculate relativistic vibrational transition frequencies for the $X^1\Sigma^+$ state of ScI molecule. The present calculated values are given in Table 1, in which we also list the RKR values taken from the literature.³³ It is clear that the relativistic vibrational transition frequencies obtained by using the Morse potential mode are good agreement with the RKR data.

Conclusions

In this work, we have studied the bound state solutions of the Klein-Gordon equation with the Morse potential energy model. The energy eigenvalue equation has been obtained in terms of the supersymmetric shape invariance approach. We calculate the relativistic vibrational transition frequencies for the $X^1\Sigma^+$ state of ScI molecule. The relativistic vibrational transition frequencies predicted with the Morse potential model are good agreement with the experimental RKR values.

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