



Relativistic energies for diatomic molecule nucleus motions with the spin symmetry



Chun-Sheng Jia^{a,*}, Jian-Wei Dai^b, Lie-Hui Zhang^a, Jian-Yi Liu^a, Xiao-Long Peng^a

^a State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, People's Republic of China

^b School of Petroleum Engineering, Southwest Petroleum University, Chengdu 610500, People's Republic of China

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ABSTRACT

The analytical solutions of the Dirac equation with the spin symmetry for the improved Manning–Rosen potential energy model have been explored. We present the bound state energy equation and the corresponding upper and lower radial wave functions. The degeneracy between the two states of the spin doublet for the nucleus motions of the X¹Σ⁺ state of SiF⁺ molecule has been observed. When the vector potential is equal to the scalar potential, the relativistic effect of the nuclear motion leads to a little decrease in the vibrational energies, while to an increase in those if the vector potential is greater than the scalar potential.

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1. Introduction

To achieve very accurate rovibrational energy level structures of molecules by using the quantum mechanical methods, one must consider a variety of small physical effects arising from a fully relativistic treatment, non-Born–Oppenheimer approximation, and quantum electrodynamics [1]. By working on a relativistic description of the electronic motion and treating the nuclear motion within the framework of nonrelativistic quantum mechanics, some authors [2–5] carried out the all-electron Dirac–Coulomb calculations for bond lengths, dissociation energies, and harmonic vibration frequencies of dihalogens, hydrogen halides, interhalogens, and HX (X = Cl, Br and I) and IZ (Z = F, Cl and Br) diatomic molecules. The inclusion of relativity leads to a weakening of the bond, giving a decrease in the calculated harmonic frequencies and dissociation energies [2–5]. However, as far as we know, one has not reported the effects of the nuclear relativistic motion on the rovibrational energies for real diatomic molecules with the spin symmetry and pseudo-spin symmetry.

Within the framework of the Dirac equation, Ginocchio [6–8] found that the spin symmetry occurs when the difference potential between the vector potential $V(r)$ and scalar potential $S(r)$ is a constant (i.e., $V(r) - S(r) = \text{constant}$), and the pseudo-spin symmetry occurs when the sum potential of the vector potential $V(r)$

and scalar potential $S(r)$ is a constant (i.e., $V(r) + S(r) = \text{constant}$). The spin symmetry concept [9] is relevant for mesons [10]. The pseudo-spin symmetry concept [11] in nuclear theory refers to quasi-degeneracy of single-nucleon doublets and can be characterized with the non-relativistic quantum numbers. The spin symmetry is from the nuclear structure. By defining the reduced mass as $\mu = m_1 m_2 / (m_1 + m_2)$, where m_1 and m_2 are two nuclei masses of a diatomic molecule, Zhang et al. [12] incorporated the concepts of the spin symmetry and pseudo-spin symmetry to the diatomic molecular case, and represented the interaction potential of two nuclei by employing a diatomic molecule potential energy model. By using this scheme, some authors have investigated the spin symmetry and pseudo-spin symmetry solutions of the Dirac equations with some typical diatomic molecule potential models, such as the Kratzer potential [13], Morse potential [14], Pöschl–Teller potential [15–17], Rosen–Morse potential [18], and Manning–Rosen potential [19–22]. The Manning–Rosen potential has been used to describe the diatomic molecular vibrations [23–27]. By using the Pekeris-like approximation [28] to the centrifugal term and pseudo-centrifugal term, Wei and Dong [19,20] investigated approximately the bound state solutions of the Dirac equation with the original Manning–Rosen potential model under the conditions of the spin symmetry and pseudo-spin symmetry. In terms of the conventional Greene–Aldrich approximation scheme [29] to deal with the centrifugal term and pseudo-centrifugal term, Taşkin [21] studied approximately the analytical solutions of the Dirac equation for the Manning–Rosen potential with the

* Corresponding author. Fax: +86 28 8303 2901.

E-mail address: chshjia@263.net (C.-S. Jia).

spin-orbit coupling term. By using the improved Greene–Aldrich approximation scheme [30] to deal with the centrifugal term and pseudo-centrifugal term, Chen et al. [22] solved approximately the Dirac equation with the Manning–Rosen potential for the arbitrary spin-orbit quantum number. In these works, the authors did not reported quantitative tests on actual relativistic vibrational energies for real diatomic molecules.

In 1933, Manning and Rosen [23] proposed a potential function for diatomic molecules,

$$U_{MR}(r) = \frac{\hbar^2}{8\mu\pi^2 b^2} \left[\frac{\beta(\beta-1)e^{-2r/b}}{(1-e^{-r/b})^2} - \frac{Ae^{-r/b}}{1-e^{-r/b}} \right], \quad (1)$$

where β and A are two dimensionless parameters, parameter b is related to the range of the potential and has dimension of length. In 2012, Wang et al. [31] proposed a convenient form for the original expression (1) of the Manning–Rosen potential function,

$$U_{MR}(r) = D_e \left(1 - \frac{e^{\alpha r_e} - 1}{e^{\alpha r} - 1} \right)^2, \quad (2)$$

where $\alpha = 1/b$, D_e is the dissociation energy of a diatomic molecule, and r_e is the equilibrium bond length. Here, one term D_e has been added to the original Manning–Rosen potential energy function (1). This change only produces an energy of zero at the potential minimum, i.e. $U_{MR}(r_e) = 0$, and does not affect the physical properties of the Manning–Rosen potential. Potential (2) is the same as a simple diatomic molecular potential proposed by Deng and Fan [32] in 1957. It has been found that the Manning–Rosen potential, Schiöberg potential [33] and Deng–Fan potential are the same solvable empirical potential energy function for diatomic molecules [31]. With the help of the Deng–Fan potential, Rong et al. [34] investigated the F–H stretching motion in HF molecule. Nyeo and Yang [35] investigated the statistical mechanics of the quasi-one-dimensional system of DNA with the Deng–Fan potential for the interstrand hydrogen bonds of nucleotide pairs. By employing the Deng–Fan potential, Zhang et al. [36] calculated the rotational transitions for HF molecule. Recently, one of the present authors and collaborators [37–40] investigated the bound state solutions of the Klein–Gordon equation and the Schrödinger equation with the improved Manning–Rosen empirical potential energy model, and studied the vibrational energy spectra for the $a^3\Sigma_u^+$ state of ${}^7\text{Li}_2$ molecule. The improved Manning–Rosen potential model can well reproduce the experimental Rydberg–Klein–Rees (RKR) [41–43] potential curve for the $a^3\Sigma_u^+$ state of ${}^7\text{Li}_2$ molecule [44].

In this Letter, we attempt to study the bound state solutions of the Dirac equation with the improved Manning–Rosen potential model within the framework of the spin symmetry. In the presence of the inclusion of relativity, we investigate the discrepancies between the nonrelativistic and relativistic vibrational energies for the $X^1\Sigma^+$ state of SiF^+ ion molecule.

2. Dirac equation

In spherical coordinates, the Dirac equation with both scalar potential $S(r)$ and vector potential $V(r)$ is given by

$$\{\mathbf{c}\boldsymbol{\alpha} \cdot \mathbf{p} + \beta[Mc^2 + S(r)]\}\Psi(r, \theta, \varphi) = [E - V(r)]\Psi(r, \theta, \varphi), \quad (3)$$

where E is the relativistic energy of the quantum system, M is the mass of the system, c denotes the speed of light, $\hbar = h/2\pi$, h denotes the Planck constant, \mathbf{p} is the momentum operator, $\boldsymbol{\alpha}$ and β are the 4×4 Dirac matrices,

$$\mathbf{p} = -i\hbar\nabla, \quad \boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma}_i \\ \boldsymbol{\sigma}_i & 0 \end{bmatrix}, \quad \beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}, \quad (4)$$

where I denotes the 2×2 unit matrix, and $\boldsymbol{\sigma}_i$ are three-vector Pauli matrices, i.e.,

$$\boldsymbol{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (5)$$

where $i = \sqrt{-1}$. In the presence of a spherical field, the Dirac Hamiltonian commutes with the total angular momentum operator \mathbf{J} and the spin-orbit coupling operator $K = -\beta(\boldsymbol{\sigma} \cdot \mathbf{L} + 1)$, where \mathbf{L} is the orbital angular momentum. The eigenvalues of K are $\kappa = J > 0$ and $\kappa = -(J+1) < 0$ for unaligned spin ($j = J - 1/2$) and aligned spin ($j = J + 1/2$), respectively, where κ denotes the spin-orbit quantum number, j denotes total angular momentum quantum number, and J denotes rotational quantum number for a diatomic molecule system. One can take (H, K, J^2, J_z) as the complete set of the conservative quantities, and classify the spinor wave functions according to the spin-orbit quantum number κ and vibrational quantum number v in the following forms,

$$\Psi_{v\kappa} = \frac{1}{r} \begin{bmatrix} F_{v\kappa}(r) Y_{jm}^J(\theta, \varphi) \\ iG_{v\kappa}(r) Y_{jm}^{\bar{J}}(\theta, \varphi) \end{bmatrix}, \quad (6)$$

where the upper and lower components $F_{v\kappa}(r)$ and $G_{v\kappa}(r)$ of the Dirac spinor are real square-integral functions, $Y_{jm}^J(\theta, \varphi)$ and $Y_{jm}^{\bar{J}}(\theta, \varphi)$ are the spherical harmonic functions, and m is the projection of the total angular momentum on the third axis.

For a diatomic system, the rest mass M can be regarded as the reduced mass μ of the diatomic molecule. Substituting Eq. (6) into Eq. (3) leads us to obtain two coupled differential equations for the upper and lower spinor components $F_{v\kappa}(r)$ and $G_{v\kappa}(r)$ as follows:

$$\begin{aligned} & \left(\frac{d}{dr} + \frac{\kappa}{r} \right) F_{v\kappa}(r) \\ &= \frac{1}{\hbar^2 c^2} [\mu c^2 + E_{v\kappa} - (V(r) - S(r))] G_{v\kappa}(r), \end{aligned} \quad (7)$$

$$\begin{aligned} & \left(\frac{d}{dr} - \frac{\kappa}{r} \right) G_{v\kappa}(r) \\ &= \frac{1}{\hbar^2 c^2} [\mu c^2 - E_{v\kappa} + (V(r) + S(r))] F_{v\kappa}(r). \end{aligned} \quad (8)$$

Under the condition of the spin symmetry, i.e., the difference potential $\Delta(r) = V(r) - S(r) = C_s = \text{constant}$, we can eliminate the lower component $G_{v\kappa}(r)$ and obtain a second-order differential equation satisfied by the upper component $F_{v\kappa}(r)$ from Eqs. (7) and (8),

$$\begin{aligned} & \left(-\hbar^2 c^2 \frac{d^2}{dr^2} + \frac{\kappa(\kappa+1)\hbar^2 c^2}{r^2} \right. \\ & \quad \left. + (\mu c^2 + E_{v\kappa} - C_s)(V(r) + S(r)) \right) F_{v\kappa}(r) \\ &= (E_{v\kappa}^2 - \mu^2 c^4 + C_s(\mu c^2 - E_{v\kappa})) F_{v\kappa}(r). \end{aligned} \quad (9)$$

The lower component $G_{v\kappa}(r)$ is obtained from Eq. (7),

$$G_{v\kappa}(r) = \frac{\hbar^2 c^2}{\mu c^2 + E_{v\kappa} - C_s} \left(\frac{d}{dr} + \frac{\kappa}{r} \right) F_{v\kappa}(r). \quad (10)$$

We consider the bound state solutions that demand the upper and lower spinor components $F_{v\kappa}(r)$ and $G_{v\kappa}(r)$ satisfy the regularity conditions: $F_{n\kappa}(0) = G_{n\kappa}(0) = 0$ and $F_{n\kappa}(\infty) = G_{n\kappa}(\infty) = 0$.

Under the condition of the exact spin symmetry, i.e., $C_s = 0$, $V(r) + S(r) = 2V(r)$, Eq. (9) becomes the following form

$$\begin{aligned} & \left(-\hbar^2 c^2 \frac{d^2}{dr^2} + \frac{\kappa(\kappa+1)\hbar^2 c^2}{r^2} + 2(\mu c^2 + E_{v\kappa})V(r) \right) F_{v\kappa}(r) \\ &= (E_{v\kappa}^2 - \mu^2 c^4) F_{v\kappa}(r). \end{aligned} \quad (11)$$

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