Vibration-rotation coupling in a Morse oscillator

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The Morse function is invaluable for describing the vibrational motion of diatomic molecules. The time independent Schrödinger equation can be solved in closed form for this potential only if molecular rotation is ignored or if the rotation is isolated from the vibrational motion by approximating it as a rigid rotor. To find the dependence of the energy eigenvalues on the vibrational and rotational state to a level of approximation that includes vibrational-rotational coupling, a higher level of approximation than the rigid rotor model is required. We present a method that can be understood by undergraduates, thus making the Morse potential a more useful example. The method yields results that are identical to those presented by Morse, but in a more elementary way. © *2007 American Association of Physics Teachers.*

I. INTRODUCTION

Despite the success of the Morse potential[1] as a potential energy function that adequately describes the vibrational motion of many diatomic molecules, it is rarely treated in introductory quantum mechanics courses as an example of a central potential. The reason is that, although the time independent Schrödinger equation can be solved in closed form for a rotationless motion, the inclusion of the centrifugal term renders the Schrödinger equation intractable. The Schrödinger equation for a rotationless molecule is essentially a one-dimensional problem. A first approximation that included molecular rotation is to treat the molecule as a rigid rotor, but this approximation is of only minor interest because it adds a term to the Hamiltonian that is independent of the vibrational motion. Therefore the energy eigenvalues are the same as those for the rotationless molecule, but with an added term that depends on only rotational parameters. Approximations beyond the rigid rotor model have been made,[2] including one by Morse himself,[1] but such approximations have limited pedagogical value.

In this paper we present a treatment of the three-dimensional problem including rotation that is accessible to students of introductory quantum mechanics. We obtain the same expressions for the energy eigenvalues as those obtained by Morse[1] using only elementary calculus. The results demonstrate the coupling between the vibrational and rotational degrees of freedom of the molecule. An approximation to the wave functions can also be obtained, but appears to be of limited interest.

II. BACKGROUND

The Morse potential for a diatomic molecule is given by

$$U(r) = D_e[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}], \qquad (1)$$

where r_e is the equilibrium internuclear separation and D_e, the well depth, is the dissociation energy of the molecule (ignoring the zero point vibrational energy); α is an adjustable shape parameter. The significance of these parameters is illustrated in Fig. 1.

Expanding Eq. (1) in a Taylor series about $r=r_e$ permits us to determine α in terms of D_e and the harmonic oscillator energy $\hbar\omega_0$, both of which can be determined experimentally. The determination of α can be done by equating the coefficient of the quadratic term in the expansion to the spring constant $\frac{1}{2}\mu\omega_0^2$, yielding

$$D_e\alpha^2 = \tfrac{1}{2}\mu\omega_0^2, \qquad (2)$$

where ω_0 is the frequency in the harmonic approximation and μ is the reduced mass of the nuclei.

If molecular rotation is (temporarily) ignored, then the Schrödinger equation with the potential energy given by Eq. (1) can be solved in closed form. The (vibrational) energy eigenvalues are[1]

$$E_n = -D_e + \left(n + \frac{1}{2}\right)\hbar\omega_0 - \left(\frac{1}{4D_e}\right)\left[\left(n + \frac{1}{2}\right)\hbar\omega_0\right]^2, \qquad (3)$$

where n is the vibrational quantum number. The rotational energy can be added to the vibrational energy assuming that the rotational motion occurs as a rigid rotor. However, the energy eigenvalues obtained in this way do not account for any coupling between rotational and vibrational motion. To account for this coupling the centrifugal term must be added to the Morse potential to form the effective potential U_{eff} given by

$$U_{\text{eff}}(r) = D_e[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}] + \frac{j(j+1)\hbar^2}{2\mu r^2}, \qquad (4)$$

where j is the rotational quantum number. Figure 2 shows a plot of $U_{\text{eff}}(r)$ for $j=0$ and $j\neq 0$. As the angular momentum increases, the well depth decreases and the equilibrium internuclear separation increases. Clearly, the vibrational spacing will be different for each value of the rotational quantum number j. Therefore, the energy eigenvalues obtained by solution of the Schrödinger equation with $U_{\text{eff}}(r)$ will include coupling between the vibrational and rotational degrees of
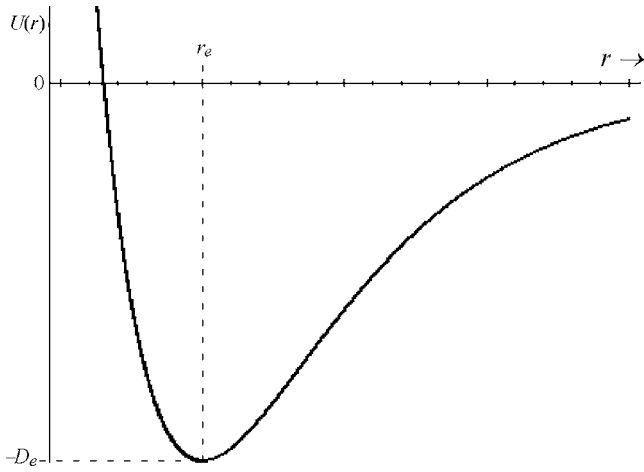
Fig. 1. The Morse potential, Eq. (1), showing the significance of the parameters D_e and r_e.
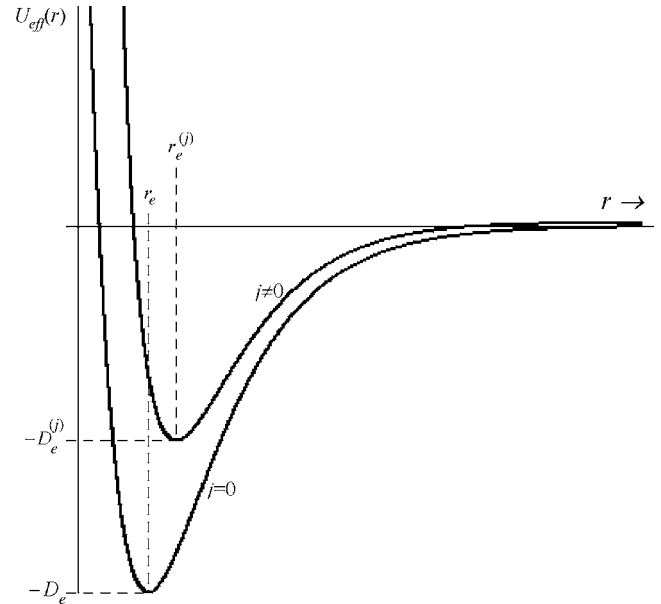

Fig. 2. The effective potential for the Morse potential illustrating the increase in the internuclear separation and the decrease in the dissociation energy.

freedom. Making the usual substitution in the radial Schrödinger equation

$$u(r) = rR(r), \tag{5}$$

where $R(r)$ is the radial part of the wave function, we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + \left[D_e[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}] + \frac{j(j+1)\hbar^2}{2mr^2} \right]u(r)$$

$$= Eu(r). \tag{6}$$

Equation (6) cannot be solved in closed form for $j \neq 0$ so an approximation, preferably one that provides physical insight, must be employed.

Because the deviations of the coordinate r from the internuclear separation r_e are small, the substitution

$$x = \frac{r - r_e}{r_e} \tag{7}$$

is made. This substitution converts the effective potential in Eq. (4) to

$$U_{\text{eff}}(x) = D_e[e^{-2\alpha r_e x} - 2e^{-\alpha r_e x}] + B\frac{1}{(1+x)^2}, \tag{8}$$

where the rotational energy B is given by

$$B = \frac{j(j+1)\hbar^2}{2\mu r_e^2}. \tag{9}$$

Note that $[j(j+1)\hbar^2 B]$ is the rigid rotor energy so that using the rigid rotor model to describe the rotational motion corresponds to $x=0$. In this approximation, rotation is accounted for by adding $[j(j+1)\hbar^2 B]$ to the energy eigenvalues given in Eq. (3).

The rotational energy B is much smaller than D_e, and, for small values of j, $\hbar\omega_0$ as well. The relation between these constants can be obtained by noting that the parameter $\alpha \sim 1/r_e$ in Eq. (2), which we rearrange to obtain

$$\frac{2\hbar^2}{\mu r_e^2} \approx \left(\frac{\hbar\omega_0}{D_e} \right)\hbar\omega_0. \tag{10}$$

The left-hand side of Eq. (10) is essentially B for small values of j. The vibrational spacing $\sim\hbar\omega_0$ is much smaller than

the depth of the well D_e into which the vibrational levels fit. There are typically 20–30 vibrational levels in a well that describes a diatomic molecule. Hence, according to Eq. (10), $B \ll \hbar\omega_0$. We may solve Eq. (2) for μr_e^2 using the approximation that $\alpha \sim 1/r_e$ and obtain

$$\mu r_e^2 = \frac{2D_e}{\omega_0^2}, \tag{11}$$

which, when substituted in Eq. (9), gives

$$\frac{B}{D_e} \approx \left[\frac{j(j+1)}{4} \right]\left(\frac{\hbar\omega_0}{D_e} \right)^2 \ll 1. \tag{12}$$

Equations (10) and (12) show that $B \ll \hbar\omega_0 \ll D_e$. Therefore, for each value of n there is a set of j-states (starting with $j=0$) that describe rotation.

The approximations of Morse[1] and Pekeris[2] were made by expanding each of the three terms in the effective potential about $x=0$ (equivalent to expanding about $r=r_e$). They then truncated the expansion and retained only the low order terms such that the form of the resultant expression would be the same as the expansion for a rotationless Morse function, but with new parameters $D_e^{(j)}$ and $r_e^{(j)}$, both of which depend on B and thus j. We may write

$$U_{\text{eff}}(r) \approx D_e^{(j)}[e^{-2\alpha(r-r_e^{(j)})} - 2e^{-\alpha(r-r_e^{(j)})}]. \tag{13}$$

The original D_e is then replaced by $D_e^{(j)}$ in the expression for the energy eigenvalues of the rotationless Morse potential, Eq. (3), to give a new set of energy eigenvalues E_{nj} that include the effects of both vibration and rotation.

III. PROPOSED METHOD

Our approach is simple and to the same level of approximation as that employed by Morse.[1] We therefore arrive at

the same expression for the energy eigenvalues E_{nj}. We first find the minimum in the effective potential curve for $j \neq 0$ by differentiating $U_{\text{eff}}(r)$ and setting the result equal to zero. This procedure yields the "new" equilibrium internuclear separation $r_e^{(j)}$, which we then use to find the new $D_e^{(j)}$. We make the substitution $D_e \to D_e^{(j)}$ in Eq. (3) and obtain the energy eigenvalues E_{nj}.

We set the derivative of the effective potential in Eq. (8) equal to zero to obtain $r_e^{(j)}$ from $x_e^{(j)}$, which, in accord with Eq. (7), is defined to be

$$x_e^{(j)} = \frac{r_e^{(j)} - r_e}{r_e}. \tag{14}$$

The result is the transcendental equation

$$\frac{dU_{\text{eff}}(x)}{dx} = 0$$

$$= (-2\alpha D_e)[e^{-2\alpha r_e x_e^{(j)}} - e^{-\alpha r_e x_e^{(j)}}] - 2B\frac{1}{(1+x_e^{(j)})^3}. \tag{15}$$

Approximations must be made to solve for $x_e^{(j)}$. If we expand the exponentials and the binomial $(1+x_e^{(j)})^{-3}$ in Eq. (15), we obtain

$$(-2\alpha r_e D_e)\left[-(\alpha r_e x_e^{(j)}) + \tfrac{3}{2}(\alpha r_e x_e^{(j)})^2\right]$$
$$- 2B + 6Bx_e^{(j)} - 12B[x_e^{(j)2}] = 0. \tag{16}$$

We drop terms higher than the first power in $x_e^{(j)}$ and find

$$x_e^{(j)} \simeq \left(\frac{1}{\alpha r_e}\right)^2\left(\frac{B}{D_e}\right), \tag{17}$$

so that the new equilibrium internuclear separation is

$$r_e^{(j)} = r_e\left(1 + \frac{B}{\alpha^2 r_e^2 D_e}\right), \tag{18}$$

which, as expected, is greater than r_e. We find the new dissociation energy $D_e^{(j)}$, $U_{\text{eff}}(r=r_e^{(j)})$ by substituting Eq. (17) into Eq. (8) and expanding each of the three terms, retaining terms up to second order in $x_e^{(j)}$ to arrive at

$$-D_e^{(j)} \simeq D_e[-1 + (\alpha r_e x_e^{(j)})^2] + B[1 - 2x_e^{(j)} + 3(x_e^{(j)})^2] \tag{19}$$

$$= -D_e + B\left[1 - \frac{1}{\alpha^2 r_e^2}\left(\frac{B}{D_e}\right)\right]. \tag{20}$$

We see that the minimum value of the Morse potential for $j \neq 0$ has been raised by $B(1-B/\alpha^2 r_e^2 D_e)$. Because $\alpha^2 r_e^2 \approx 1$ and $B/D_e \ll 1$, the well is raised by an amount less than B, the rigid rotor energy.

The effective potential may now be approximated by making the substitutions $r_e \to r_e^{(j)}$ and $D_e \to D_e^{(j)}$ into the rotationless Morse function, Eq. (1). The energy eigenvalues that include the effects of rotation are obtained by making the
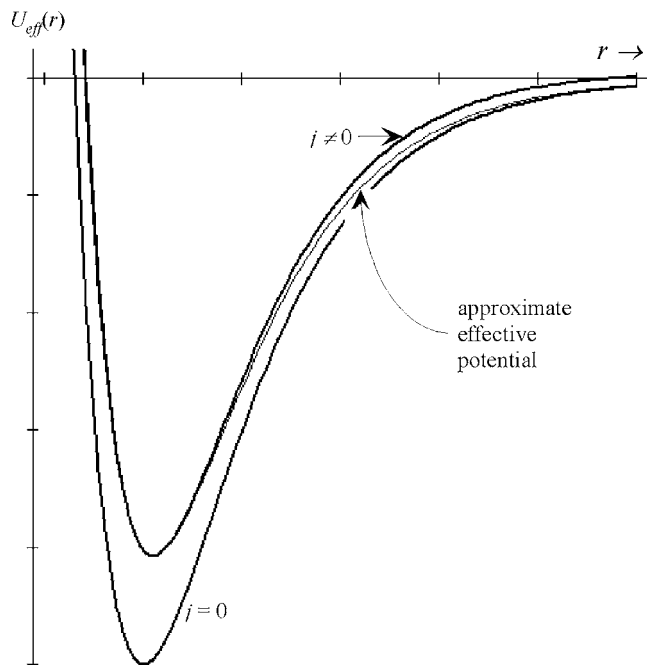

Fig. 3. The effective Morse potential for $j=0$ (for reference) and $j=12$ (heavy lines). The remaining curve was obtained by letting $r_e \to r_e^{(j)}$ and $D_e \to D_e^{(j)}$ as discussed in the text. The high rotational quantum number $j=12$ was chosen to emphasize the difference between the exact effective potential and the approximate one.

substitution $D_e \to D_e^{(j)}$ from Eq. (20) into Eq. (3). The result is

$$E_{nj} = -D_e + \left(n + \frac{1}{2}\right)\hbar\omega_0\left[1 - \frac{1}{4D_e}\left(n+\frac{1}{2}\right)\hbar\omega_0\right] \tag{21}$$

$$- \left(\frac{j(j+1)\hbar^2}{4\mu r_e^2 D_e}\right)\left(n+\frac{1}{2}\right)\hbar\omega_0$$

$$- \frac{j(j+1)\hbar^2}{2\mu r_e^2}\left[1 - \frac{j(j+1)\hbar^2}{\mu^2 r_e^4 \omega_0^2}\right]. \tag{22}$$

The coupling between vibration and rotation is represented by the cross term proportional to $[j(j+1)(n+\tfrac{1}{2})]$, which contains both the vibrational and rotational quantum numbers.

We may gauge the efficacy of this approximation by comparing the exact effective potential for a given value of j with that obtained from the approximation. Figure 3 shows a plot of $U_{\text{eff}}(r)$ for the relatively high value $j=16$, which was chosen to accentuate the difference between the approximated $U_{\text{eff}}(r)$ and the actual potential. Smaller values of j yielded nearly indistinguishable curves. The plot for $j=0$ is included in Fig. 3 for reference.

We emphasize that the method presented here is equivalent to that given by Morse,[1] who obtained the same approximate expressions for $r_e^{(j)}$ and $D_e^{(j)}$ as those derived here. The difference is that Morse expanded the effective potential in a Taylor series and, after making the small x approximation, grouped the expansion into a Morse-like potential with adjustable constants that depend on j. In contrast, we used elementary calculus to find the approximation to $r_e^{(j)}$ by differentiating and setting the derivative of $U_{\text{eff}}(x)$ equal to zero after expanding terms in the derivative. We use this value of

$r_e^{(j)}$ to obtain $D_e^{(j)}$, which was then used in a rotationless Morse function that approximates the effective potential. The level of approximation is the same in the two cases.

The method presented here should make it feasible to include the three-dimensional Morse potential with the usual potentials studied in an introductory quantum mechanics course. If studied in this way, the Morse potential provides a clear example of the coupling between two degrees of freedom, vibration and rotation.

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PHYSICS RESEARCH AND EDUCATION: COMPUTATION AND COMPUTER-BASED INSTRUCTION AMERICAN JOURNAL OF PHYSICS THEME ISSUE

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