

Diatomic Molecules Effective Potential for an Harmonic Oscillator Model

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Abstract

A model anharmonic potential was considered and was used in the Schrödinger time independent wave equation to describe a carbon monoxide molecule. Central difference scheme was used in approximating the derivative term in the Schrödinger equation leading to a tri-diagonal band system of equation. The method of LU-decomposition of Gaussian – elimination with back substitution was used to solve the system because it cannot be solved analytically. The effective potentials for large show no unique turning point but as the value of decreases, the effective potential shows unique turning point which suggest an approach to equilibrium point.

Keywords: Anharmonic, Model, Potential, Schrödinger, Carbon monoxide, Effective potential.

1.0 Introduction

Anharmonic potential has always been an exciting and interesting field due to its broad application in molecular vibrations and useful in science [1]. Numerous numerical methods including renormalized strong-coupling expansion, perturbation expansion, the hill determinant method, and the algebraic method, have been proposed to investigation these anharmonic potentials [2].

One model of molecular dynamics using the anharmonic oscillator[3] employed the non-linear coupling of six separate anharmonic oscillators. The anharmonicity in the reference potential H_0 , arises from the use of Morse-potential rather than a linear potential and it is a super position in the mass scaled coordinates, of the form

$$H_0 = \sum_{\alpha=1}^6 \left[\frac{p_{\alpha}^2}{2} + D(1 - e^{-a_{\alpha}Q_{\alpha}})^2 \right] \quad (1)$$

where $Q_{\alpha} = r - r_e$, r is the distance between atoms, r_e is the equilibrium bond distance and a_{α} controls the width of the potential

The energy of the reference Hamiltonian is given by [3]

$$E_{\alpha} = \hbar W_{\alpha} \left[\frac{1}{2} + V_{\alpha} \left(1 - \frac{V_{\alpha}^{max}}{2V_{\alpha}} \right) \right] \quad (2)$$

Where E_{α} is the energy of the oscillator, V_{α} is the quantum number oscillator, V_{α}^{max} is the maximum number of quanta associated with a bound state of energy and W_{α} is the harmonic frequencies.

To improve the theory of molecular vibrations the anharmonic oscillators such as Morse and Mie-type potentials (Kratzer potential and its generalization) can be used to solve exactly the Schrodinger equation (SE) and provide more reliable model for diatomic molecules [4].

Souza et al, (2006) used the pseudo harmonic oscillator potential

$$V(r) = D_0 \left(\frac{r}{r_0} - \frac{r_0}{r} \right)^2, \quad (3)$$

to model the molecular vibration of linear molecules. Because the potential is almost harmonic, by careful transformation, the resulting Schrödinger equation can be solved by kummer confluent functions as the Eigen functions.

Our potential model is similar but different in form from the pseudo harmonic oscillator in that it is fully anharmonic.

$$V(r) = \frac{D}{2} \left(\frac{r}{r_0} \right)^2 + \alpha \left(\frac{r}{r_0} \right)^4 \quad (4)$$

The first term is the usual harmonic oscillator while the anharmonicity is contained in the second term. In practical terms, the first term maintains the bonding while the second term creates room for the dissociation of the atoms depending on the strength of .

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D is the bond dissociation enthalpy [KJmol⁻¹] at 298K for carbon monoxide and is equal to 1076 KJmol⁻¹, α is a parameter related to the dissociation energy and r₀ is the molecular spacing between the nuclide of the atoms.

2.0 Methodology

Our potential model is given by (4).

The classical Hamiltonian is given as

$$H = \frac{p^2}{2\mu} + V(r) \tag{5}$$

Where $\frac{p^2}{2\mu}$ the Kinetic energy and V(r) is is Potential energy.

The time independent Schrödinger equation is given by

$$\left\{ \frac{-\hbar^2}{2\mu} \nabla^2 + V(r) \right\} \Psi(r, \theta, \varphi) = E\Psi(r, \theta, \varphi) \tag{6}$$

Defining $\Psi(r, \theta, \varphi) = \frac{1}{r} R(r)Y(\theta, \varphi)$ we have

$$\frac{d^2R}{dr^2} - \frac{L(L+1)R}{r^2} + \frac{2\mu(E-V(r))}{\hbar^2} = 0 \tag{7}$$

Let $\frac{r}{r_0} = \bar{r}$

$$\tag{8}$$

The model potential now becomes

$$V(r) = \frac{D}{2} \bar{r}^{-2} + \Gamma \bar{r}^{-4} \tag{9}$$

Substituting equation (9) into (7) we have

$$\frac{d^2R(\bar{r})}{d\bar{r}^2} - \frac{L(L+1)R(\bar{r})}{\bar{r}^2} + \frac{2\mu r_0^2}{\hbar^2} \left(E - \frac{D\bar{r}^2}{2} - \alpha\bar{r}^4 \right) R(\bar{r}) = 0 \tag{10}$$

Let $\beta_1 = L(L+1)$ and $\beta_2 = \frac{2\mu r_0^2}{\hbar^2}$

We have

$$\frac{d^2R(\bar{r})}{d\bar{r}^2} + \left(-\frac{\beta_1}{\bar{r}^2} + \beta_2 E - \frac{\beta_2 D\bar{r}^2}{2} - \beta_2 \alpha\bar{r}^4 \right) R(\bar{r}) = 0 \tag{11}$$

Using central difference to solve the above equation we have

$$\frac{d^2R(\bar{r})}{d\bar{r}^2} = \frac{R_{n+1} - 2R_n + R_{n-1}}{H^2} \tag{12}$$

$$\frac{R_{n+1} - 2R_n + R_{n-1}}{H^2} + \left(-\frac{\beta_1}{\bar{r}^2} + \beta_2 E - \frac{\beta_2 D\bar{r}^2}{2} - \beta_2 \alpha\bar{r}^4 \right) R_n = 0 \tag{13}$$

$$R_{n+1} + R_{n-1} + \left(-2 - \frac{\beta_1 H^2}{\bar{r}^2} + \beta_2 E H^2 - \frac{\beta_2 D\bar{r}^2 H^2}{2} - \beta_2 \alpha\bar{r}^4 H^2 \right) R_n = 0 \tag{14}$$

Let

$$\gamma_n = \left(-2 - \frac{\beta_1 H^2}{\bar{r}^2} + \beta_2 E H^2 - \frac{\beta_2 D\bar{r}^2 H^2}{2} - \beta_2 \alpha\bar{r}^4 H^2 \right) \tag{15}$$

$$R_{n+1} - \gamma_n R_n + R_{n-1} = 0 \tag{19}$$

Equation (19) is the system of band equation and is solved using Gaussian elimination method with back and forward substitution to obtain the effective potential.

AR=B

Constants for carbon monoxide

Our guest energy is given by $E = \hbar\omega (n + 10000)$. The guest energy was chosen arbitrarily to ensure numerical stability.

The guest energy E for n=0

$$E = 1000 \omega = 1.05 \times 10^{34} \times 4.9200093 \times 10^8 = 5.166 \times 10^{-20} J$$

The reduced mass of carbon monoxide is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$= \frac{12 \times 16}{12 + 16}$$

$$\mu = \frac{28 \times 6.02 \times 10^{25}}{28 + 16} = 1.1390602g$$

$$\text{Nuclide separation } r_0 = 112.81 \times 10^{-12} m$$

$$\beta_2 = \frac{2\mu r_0^2}{\hbar^2} = 2.6296217 \times 10^5$$

$$D = 1.787375415 \times 10^{-18} J \text{ (The bond dissociation enthalpic for C-O)}$$

3.0 Results and Discussion

The effective potential is given by

$$V_{eff} = -\frac{L(L+1)}{r^2} + V(\bar{r})$$

Fig. 1 shows the graph of the effective potential for $L = 0 = L = 0$, the effective potential is essentially that of simple harmonic oscillator. This is parabola, symmetric about $\bar{r} = 0$ axis. Classically, there is a unique turning point ($\bar{r} = 0$) about which periodic motion occurs.

When the anharmonicity parameter $\alpha = 10 \times 10^{-13}$, the effective potential is as shown in fig. 2. Here, there is no unique turning point. There is infinite number of points at which $\frac{dv}{dr} = 0$, as such there is no single equilibrium point about which to expect periodic motion which was also discuss by [6]. Quantum mechanically, this may be an approximation to a molecular bond close to dissociation representing a vanishing bound system.

As the anharmonicity parameter decreases, $\alpha = 10 \times 10^{-14}$ (Fig. 3), the effective potential, though similar to that of $\alpha = 10 \times 10^{-13}$, is less turning point, suggesting approach to existence of unique equilibrium point.

For $\alpha = 10 \times 10^{-17}$ (Fig. 4, Fig. 5 and Fig. 6) the harmonicity strength is so weak to alter the effective potential from that of harmonic oscillator. The result is that for these values of α , the harmonic oscillator potential is restored with unique turning point.

Molecular spectra or effective potential can be used to understand the motion of electrons in molecules, and also the vibration and rotation of the nuclei as we have seen in the above result.

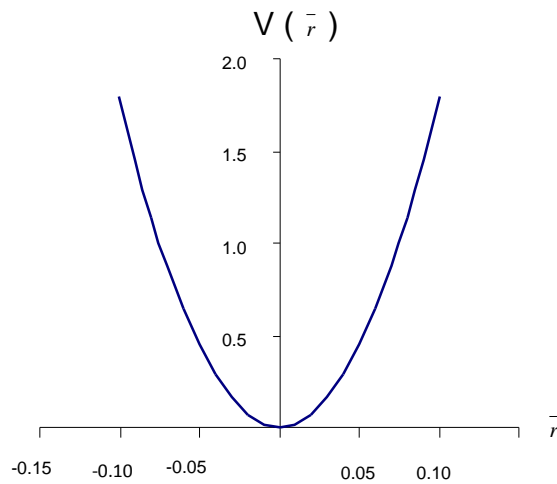


Fig 1: Harmonic Oscillator Effective Potential

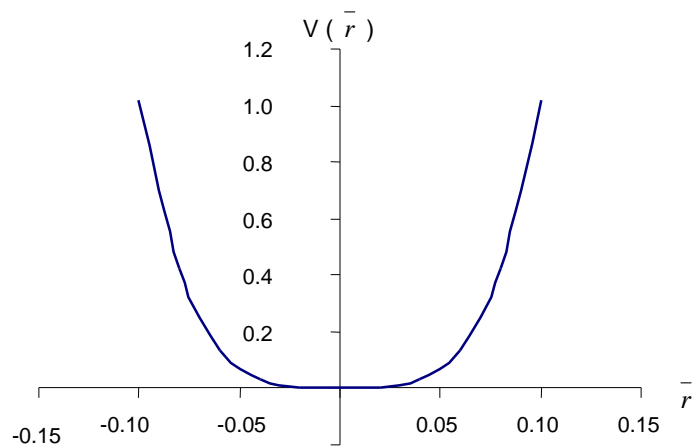


Fig 2: Effective potential for model potential $\alpha = 10 \times 10^{-13}$,

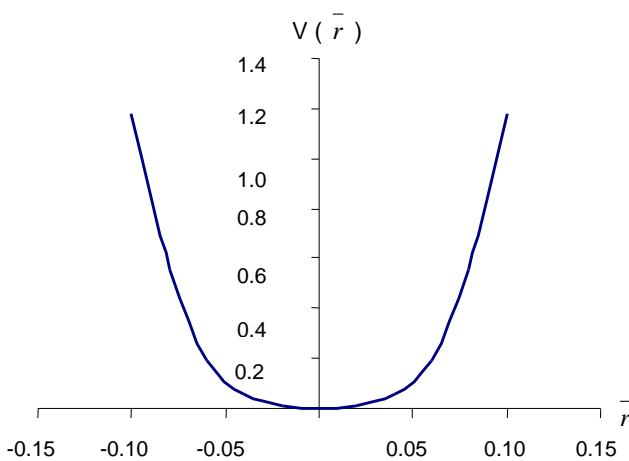


Fig 3: Effective potential for model potential $\alpha = 10 \times 10^{-14}$

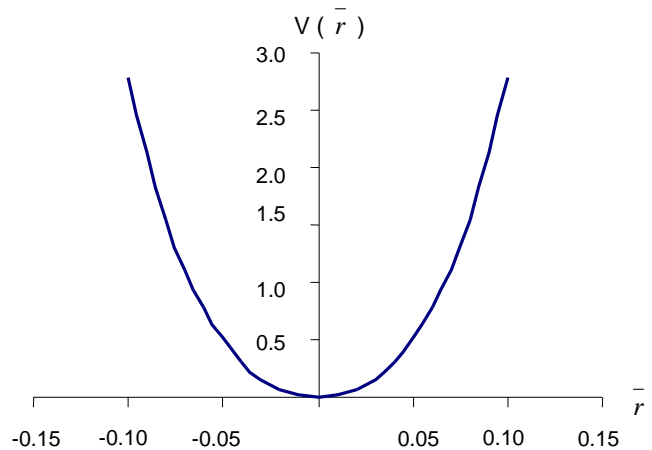


Fig 4: Effective potential for model potential $\alpha = 10 \times 10^{-15}$

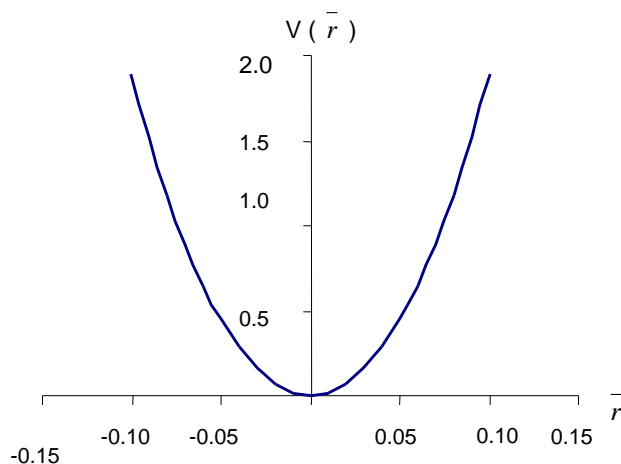


Fig 5: Effective potential for model potential $= 10 \times 10^{-16}$

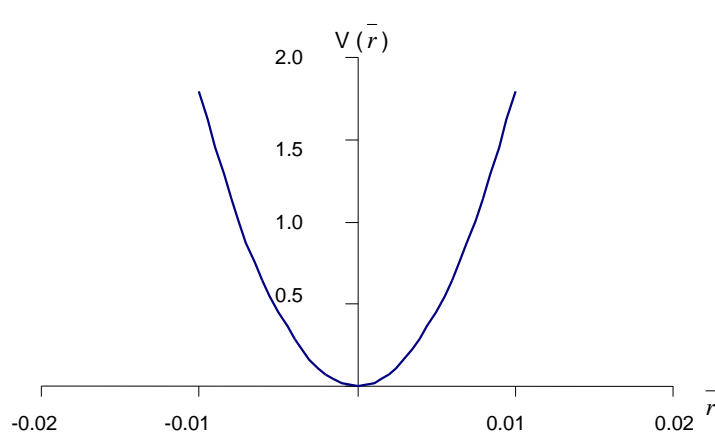


Fig 6: Effective potential for model potential $= 10 \times 10^{-17}$

4.0 Conclusion

Anharmonic potential was applied to carbon monoxide, and the effective potentials obtained show the impact of anharmonicity as we kept varying the values. As the value of the anharmonicity decreases, the effective potential tends to approach an equilibrium point. The anharmonic potential of our type can also be applied to different diatomic molecules.

5.0 References

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