

4.36(2): The Anharmonic Oscillator

The energy levels of the anharmonic oscillator are:

$$E = \left(n + \frac{1}{2}\right) \hbar \omega - \left(n + \frac{1}{2}\right)^2 \hbar \omega x + \dots \quad (1)$$
$$= \hbar \omega \left(n + \frac{1}{2}\right) \left(1 - \left(n + \frac{1}{2}\right) x\right).$$

They can be described by the Morse potential:

$$U(r) = D_e \left(1 - \exp(-a(r - r_e))\right)^2 \quad (2)$$

where r_e is the equilibrium bond distance, and r is the separation between two atoms in a diatomic molecule.

Here:

$$x = \frac{\hbar a^2}{2\mu\omega} \quad (3)$$

where μ is the reduced mass, and where:

$$a = \left(\frac{k}{2D_e}\right)^{1/2} \quad (4)$$

the well parameter.

In eq. (4) D_e is the well depth relative to the dissociated atoms.

The Schrödinger equation can be solved exactly for the Morse potential (2), giving the energy levels:

$$E = \left(n + \frac{1}{2}\right) \hbar \omega - \left(n + \frac{1}{2}\right)^2 \hbar \omega x \quad (5)$$

In n theory the energy levels become:

$$E = \hbar \omega \left(n + \frac{1}{2}\right) \left(1 - \left(n + \frac{1}{2}\right) x\right) \left\langle m(r)^{1/2} \right\rangle \quad (6)$$

where:

$$\langle m(r) \rangle = \int \psi^* m(r) \psi dr \quad (7)$$

The wave functions of the harmonic oscillator can be calculated analytically for the atom surface potential:

$$U_1(r) = U(r) - D_e - (8)$$

$$= D_e \left(e^{-2a(r-r_e)} - 2e^{-a(r-r_e)} \right)$$

The Schrodinger equation is:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dr^2} + U_1 \psi = E \psi \quad (9)$$

The wave functions are given as follows:

$$\lambda := \frac{(2m D_e)^{1/2}}{a \hbar}, \quad (10)$$

$$z := 2\lambda \exp(-(r-r_e)) \quad (11)$$

$$N := \left(\frac{n! (2\lambda - 2n - 1)^{1/2}}{\Gamma(2\lambda - n)} \right) \quad (12)$$

where Γ is the gamma function. Then:

$$\psi = N z^{\lambda-n-1/2} e^{-z/2} L_n^{(2\lambda-2n-1)}(z) \quad (13)$$

where $L_n^{(d)}$ is a generalized Laguerre polynomial

$$L_n^{(d)}(z) = \frac{z^{-d} e^{-z}}{n!} \frac{d^n}{dz^n} (z^{n+d} e^{-z}) \quad - (14)$$

$$= \frac{\Gamma(d+n+1)}{n! \Gamma(d+1)} {}_1F_1(-n, d+1, z)$$

where ${}_1F_1$ is the Kummer confluent hypergeometric function. This can be calculated with a NAG routine.

In n theory these wave functions are modified w.r.t:

$$r \rightarrow \frac{r}{n(r)^{1/2}} \quad - (15)$$

and this is the effect of the vacuum. It would be interesting to graph this effect on the wave functions of the harmonic oscillator. Similarly it would be interesting to plot the effect of eq. (15) on the radial wave functions of the H atom, which are also related to the Laguerre polynomials.

Finally the energy levels from eq. (9) are given by:

$$\langle E \rangle = -\frac{\hbar^2}{2m} \int \psi^* \frac{\partial^2 \psi}{\partial r^2} d\tau + \int \psi^* U_1 \psi d\tau \quad - (16)$$

However it is much simpler to calculate the energy levels from eq. (1)