Physics 535 Project One: Hydrogen Molecule Energy Quantization

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April 1, 1999

Physics 535
for Professor D. Hobill

(a) After having adjusted the code for the Lennard-Jones potential to the Harmonic Oscillator potential and changing the values for V_0, x_{min}, and γ, we find that the resulting energy levels are

quantum number 0	energy -0.949930143
quantum number 1	energy -0.849931097
quantum number 2	energy -0.7499767542
quantum number 3	energy -0.6499843001
quantum number 4	energy -0.5499860048
quantum number 5	energy -0.4499878585
quantum number 6	energy -0.3499580920
quantum number 7	energy -0.2499840260
quantum number 8	energy -0.1499446332
quantum number 9	energy -0.0498689189

The code predicts ten energy levels with spacing of about 0.100.

(b) The Taylor Series expansion of the potential is

$$V(x) = V_0 + V'|_{x_{min}} + V''|_{x_{min}} \frac{(x - x_{min})^2}{2} + V'''|_{x_{min}} \frac{(x - x_{min})^3}{6} + \dots$$

Note that the second derivative term is zero at x_{min}. The force is the negative gradient of the potential:

$$F = -\nabla V(x) = -\nabla V_0 - \nabla \left[V'' \frac{(x - x_{min})^2}{2} \right] - \nabla \left[V''' \frac{(x - x_{min})^3}{6} \right] \quad (1)$$

The gradient of the constant V_0 is zero; we are left with the derivatives of the second and higher order terms. Note that the force is

$$F = -k(x - x_{min}) \quad (2)$$

Equating expressions (1) and (2) We have

$$-k(x - x_{min}) = -V''|_{x_{min}}(x - x_{min}) - \dots$$

$$\Rightarrow k \approx V''|_{x_{min}} \quad (3)$$

We have

$$V(x) = 4V_0\left[\left(\frac{a}{x}\right)^{12} - \left(\frac{a}{x}\right)^{6}\right].$$

The second derivative of this is

$$\frac{d^2V(x)}{dx^2} = 4V_0\left[156\frac{a^{12}}{x^{14}} - 142\frac{a^6}{x^8}\right]$$

evaluating this at $x_{min} = 2^{\frac{1}{6}}$ and substituing the result into equation (3), the spring constant is

$$k = 4V_0\left[\frac{156}{2^{\frac{14}{6}}a^2} - \frac{42}{2^{\frac{8}{6}}a^2}\right]$$

For a harmonic oscillator $omega = \sqrt{\frac{k}{m}}$, then,

$$\hbar\omega = \hbar\sqrt{\frac{k}{m}} = \hbar\sqrt{\frac{4V_0}{m}\left[\frac{156}{2^{\frac{14}{6}}a^2} - \frac{42}{2^{\frac{8}{6}}a^2}\right]} \to \left(\frac{\hbar\omega}{V_0}\right)^2 = \frac{4\hbar^2}{V_0ma^2}\left(\frac{156}{2^{\frac{14}{6}}} - \frac{42}{2^{\frac{8}{6}}}\right)$$

$$\to \left(\frac{\hbar\omega}{V_0}\right)^2 = \frac{8}{\gamma^2}\left(\frac{156}{2^{\frac{14}{6}}} - \frac{42}{2^{\frac{8}{6}}}\right) \to \frac{\hbar\omega}{V_0} \approx \frac{10.6918}{\gamma}$$

The actual spacings of the enegy levels for the harmonic ocsillator with $\gamma = 50$ is $\hbar\omega \approx 0.213836$. We do, in fact, find that the L-J spacings are more densely packed at higher energies because a wide well supports more bound states than a narrow well; the Lennard-Jones potential is wider at higher energies.

(c) In part (b) we established that

$$\frac{\hbar\omega}{V_0} \approx \frac{10.6918}{\gamma}$$

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Substituting $\gamma = 21.7$ and $V_0 = -4.747$ into this expression we have

$$\hbar\omega = 2.339eV$$

The computed vibrational excitations are inaacurate - the computed difference between the ground and first excited states is more than four times the observed values. The Lennard-Jones potential predicts only eight energy levels whereas 15 are observed. Consequently, we need a better approximaion to represent the potential for light atoms.

As above, the effective spring constant is the second derivative of the potential evaluated at x_{min}. The Morse potential is

$$V(x) = V_0[(1 - e^{-\beta(x-x_{min}}) - 1]$$

The second derivative of this is

$$V''(x) = V_0(-2\beta^2 e^{-\beta(x-x_{min})} + 4\beta^2 e^{-2\beta(x-x_{min})})$$

at x_{min} the second derivative is

$$V'' = 2V_0\beta^2$$

and similarly, equating this to k we can write

$$\hbar\sqrt{\frac{k}{m}} = \hbar\sqrt{\frac{2V_0\beta^2}{m}} = 0.515 \rightarrow \beta^2 = \frac{0.515^2 m}{2V_0\hbar^2}$$

From the expression for γ we can find m:

$$\gamma^2 = \frac{2ma^2V_0}{\hbar^2} \rightarrow m = \frac{hbar^2\gamma^2}{2a^2V_0}$$

and

$$a = \frac{x_{min}}{2^{\frac{1}{6}}}$$

Then $\beta = 1.78$. However, $\beta = 1.78$ predicts 26 energy levels. With $\beta = 3.089$ The energy levels predicted by the Morse potential are

quantum number 0	-4.448436260
quantum number 1	-3.881000757
quantum number 2	-3.352219105
quantum number 3	-2.862445116
quantum number 4	-2.410917521
quantum number 5	-1.998231649
quantum number 6	-1.624146819
quantum number 7	-1.288831592
quantum number 8	-0.9922282696
quantum number 9	-0.7345134020
quantum number 10	-0.5153195262
quantum number 11	-0.3352240324
quantum number 12	-0.1932878941
quantum number 13	-0.09032508731
quantum number 14	-0.02602777810

Below is a plot of the Morse and Lennard-Jones potentials:

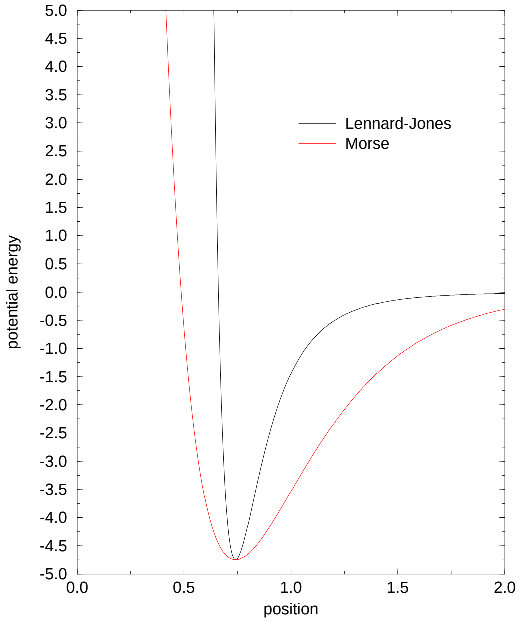

Figure 1: The Morse and Lennard-Jones Potentials

The Morse potential provides a better estimate of the number of energy levels because it is wider than the Lennard-Jones Potential.

(d) The second derivative of the potential is

$$V_0''(x) = V_0\left(\frac{2}{x_{min}^2}\right) = k$$

and as above,

$$\hbar\omega = \hbar\sqrt{\frac{k}{m}} = \hbar\sqrt{\frac{2V_0}{mx_{min}^2}}$$

and the expression for m is

$$m = \frac{\hbar^2\gamma^2}{2V_0}\left(\frac{2^{\frac{1}{6}}}{x_{min}}\right)^2$$

Consequently

$$\hbar\omega = \frac{2V_0}{2^{\frac{1}{6}}\gamma} = 0.3900$$

This potential provides a decent approximation of the Hydrogen molecule noting that the actual spacing is 0.515. Below is a list of the the vibrational energy levels of the harmonic potential for the Hydrogen Molecule:

quantum no. = 0	energy = -4.611605167
quantum no. = 1	energy = -4.340820312
quantum no. = 2	energy = -4.070034981
quantum no. = 3	energy = -3.799288034
quantum no. = 4	energy = -3.528569221
quantum no. = 5	energy = -3.257653952
quantum no. = 6	energy = -2.986943483
quantum no. = 7	energy = -2.716237068
quantum no. = 8	energy = -2.445398569
quantum no. = 9	energy = -2.174735785
quantum no. = 10	energy = -1.903930187
quantum no. = 11	energy = -1.633069515
quantum no. = 12	energy = -1.362293243
quantum no. = 13	energy = -1.091475606
quantum no. = 14	energy = -0.8208422065
quantum no. = 15	energy = -0.5500326157
quantum no. = 16	energy = -0.2791704535
quantum no. = 17	energy = -0.8661840111E-02