The simple harmonic oscillator (SHO)

The basics:

This is a problem which we have encountered classically many times before; it comes about when a restoring force is proportional to the displacement, namely:

$$F(x) = -kx = m\frac{d^2x}{dt^2} \qquad (1)$$

If the force is conservative, we can always write

$$F(x) = -\frac{dV(x)}{dx} \quad \text{or} \quad V(x) = -\int F(x)dx$$

yielding

$$V(x) = \frac{1}{2}kx^2 \qquad (2)$$

The classical solutions are well known and result in constant frequency oscillations. The time dependence of the displacement is easily written as:

$$x(t) = A\cos\omega_0 t + B\sin\omega_0 t = C\cos(\omega_0 t + \varphi) \quad (3)$$

where $$\omega_0 = \sqrt{\frac{k}{m}} \quad (3a)$$

i.e. $k = m\omega_0^2$

This allows us to rewrite the potential as:

$$V(x) = \frac{1}{2}m\omega_0^2 x^2 \qquad (4)$$

Note:
The potential is time independent, allowing us to substitute into the TISE.
The potential is symmetrical, meaning we expect definite parity states.

Application of the TISE and the first two simplest states:

We can now fully write the TISE as:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega_0^2 x^2\psi(x) = E\psi(x) \qquad (5)$$

which can be rearranged as

$$\left(\frac{m\omega_0}{\hbar}\right)^2 x^2\psi(x) - \frac{2mE}{\hbar^2}\psi(x) = \frac{d^2\psi(x)}{dx^2}$$

Taking the limit for large x this approximates to

$$\frac{d^2\psi(x)}{dx^2} \approx \left(\frac{m\omega_0}{\hbar}\right)^2 x^2\psi(x) \qquad (6)$$

We shall use this limit for large x to guide us towards the solutions…

Consider a Gaussian or Normal distribution (a bell curve), which can be written as:

$$\psi(x) \propto e^{-\frac{ax^2}{2}}$$

differentiating twice with respect to x gives

$$\frac{d^2 e^{-\frac{ax^2}{2}}}{dx^2} = \left(a^2x^2 - a\right)e^{-\frac{ax^2}{2}}$$

again, taking the limit for large x gives

$$\frac{d^2 e^{-\frac{ax^2}{2}}}{dx^2} \approx a^2x^2e^{-\frac{ax^2}{2}} \qquad (7)$$

Comparing equations 6 and 7, immediately tells us that if we are to involve Gaussians in our solutions, then the following must be true:

$$a = \frac{m\omega_0}{\hbar} \qquad (8)$$

It transpires, indeed, that the general form of the wavefunctions for the SHO is a product of polynomial and a Gaussian:

$$\psi(x) = H(x)e^{-\frac{ax^2}{2}} \qquad \text{where} \quad H(x) \text{ is simply a polynomial in } x$$

We shall study the general solutions in some detail later, but first, we can actually solve for the two simplest states manually beginning with the trial solution:

$$\psi(x) = x^n e^{-\frac{ax^2}{2}} \qquad (9)$$

and substituting into the TISE, namely:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}m\omega_0^2x^2\psi(x)=E\psi(x)$$

We will require the second spatial derivative of our trial solution, namely:

$$\frac{d^2x^ne^{-\frac{ax^2}{2}}}{dx^2}=\left\{n(n-1)x^{n-2}-a(2n+1)x^n+a^2x^{n+2}\right\}e^{-\frac{ax^2}{2}}$$

which, when substituted into the TISE gives

$$Ex^ne^{-\frac{ax^2}{2}}=-\frac{\hbar^2}{2m}\left\{n(n-1)x^{n-2}-a(2n+1)x^n+a^2x^{n+2}\right\}e^{-\frac{ax^2}{2}}+\frac{1}{2}m\omega_0^2x^2x^ne^{-\frac{ax^2}{2}}$$

using equation 8 and after some manipulation this simplifies to

$$n(n-1)x^{n-2}-\frac{m\omega_0}{\hbar}(2n+1)x^n=-\frac{2mE}{\hbar^2}x^n$$

equating the coefficients of powers of x we obtain:

$n(n-1)=0$, therefore $n=0$ and $n=1$ (good, we have the two first states)

and

$\frac{\omega_0}{\hbar}(2n+1)=\frac{2E}{\hbar^2}$, therefore $E_n=\hbar\omega_0\left(n+\frac{1}{2}\right)$, giving $E_0=\frac{1}{2}\hbar\omega_0$ and $E_1=\frac{3}{2}\hbar\omega_0$

infact, the expression:

$$E_n=\hbar\omega_0\left(n+\frac{1}{2}\right)\text{ where }n=0,1,2,3\ldots(10)$$

happens to be true for all eigenstates (all values of n) although we haven't proven it here.

There exist elegant operator methods, involving energy raising and lowering operators, which prove the general case. You will encounter these in QMB, but for the time being please accept equation 10 as read.

Let us now return to two first eigenstates we have solved for and write them explicitly:

$$\psi_0(x)=N_0e^{-\frac{ax^2}{2}}\text{ for }n=0,\ E_0=\frac{1}{2}\hbar\omega_0\text{ and therefore }\Psi_0(x,t)=N_0e^{-\frac{ax^2}{2}}e^{-\frac{iE_0t}{\hbar}}$$

and

$$\psi_1(x)=N_1xe^{-\frac{ax^2}{2}}\text{ for }n=1,\ E_1=\frac{3}{2}\hbar\omega_0\text{ and therefore }\Psi_1(x,t)=N_1xe^{-\frac{ax^2}{2}}e^{-\frac{iE_1t}{\hbar}}$$

One important result is that the energy levels for a SHO are all equally spaced, with spacing $\hbar\omega_0$, and that once again in quantum mechanics, the ground state energy is non zero (these results are summarized in figure 1).

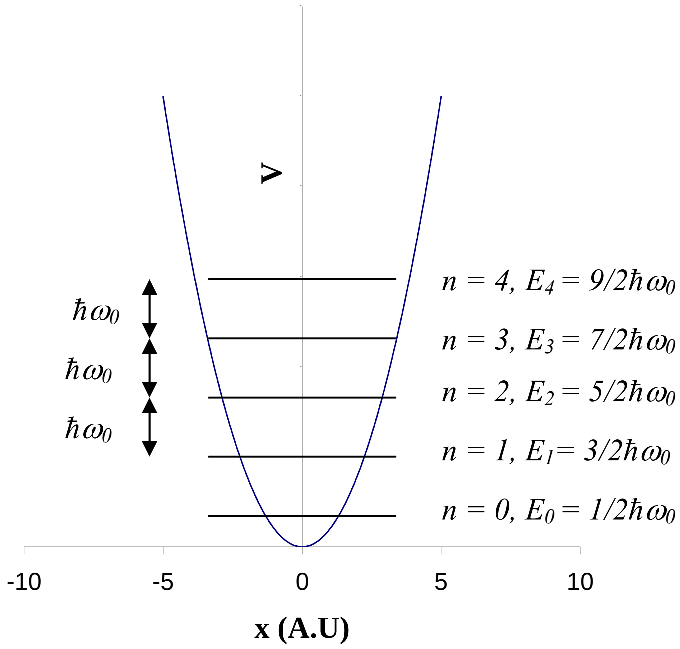

Figure 1: SHO energy levels superimposed on a sketch of the potential.

A general expression for the Eigenstates:

As we previously commented, the general form of the wavefunctions of the SHO will involve the product of a polynomial and a Gaussian; it is now time to study these in more detail. A general expression for the wavefunction $\psi_n(x)$ is given in equation 11:

$$\psi_n(x) = A_n H_n(\xi) e^{-\frac{ax^2}{2}} \qquad (11) \qquad \text{with} \qquad a = \frac{m\omega_0}{\hbar}$$

In this form A_n is a normalization constant and $H_n(\xi)$ is a Hermite polynomial. The Hermite polynomial is defined in terms of the dimensionless parameter, ξ, which is proportional to x, infact it is given by: $\xi = \sqrt{a}x$, and the first few Hermite polynomials are listed in table I

Table I: The first few Hermite polynomials

$H_0(\xi) = 1$
$H_1(\xi) = 2\xi$
$H_2(\xi) = 4\xi^2 - 2$
$H_3(\xi) = 8\xi^3 - 12\xi$
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$

Note that in each case n relates directly to the highest power of ξ (or x). The normalization constant, A_n, can be written for all n as shown in equation 12.

$$A_n = \left(\frac{a}{\pi}\right)^{\frac{1}{4}} \left(\frac{1}{2^n n!}\right)^{\frac{1}{2}} \qquad (12)$$

A note on the classical turning points:

A classical SHO will have well defined turning points or limits which define the amplitude of the resulting oscillations. These can be easily found by considering that the oscillator will be instantaneously at rest at the turning points, meaning that all the oscillator energy is in the form of potential energy. For a SHO of energy E_n, the turning point, x_0, will depend on this energy so can be written more fully as $x_{0,n}$. By equating the energy to the potential (equation 4) we can show that:

$$x_{0,n} = \pm\sqrt{\frac{2E_n}{m\omega_0^2}} \qquad (13)$$

As can be seen in figure 2 where the first few wavefunctions are plotted, this is another occasion in quantum mechanics where a non zero wavefunction (and therefore non zero probability) exists of finding the system in a classically forbidden region.

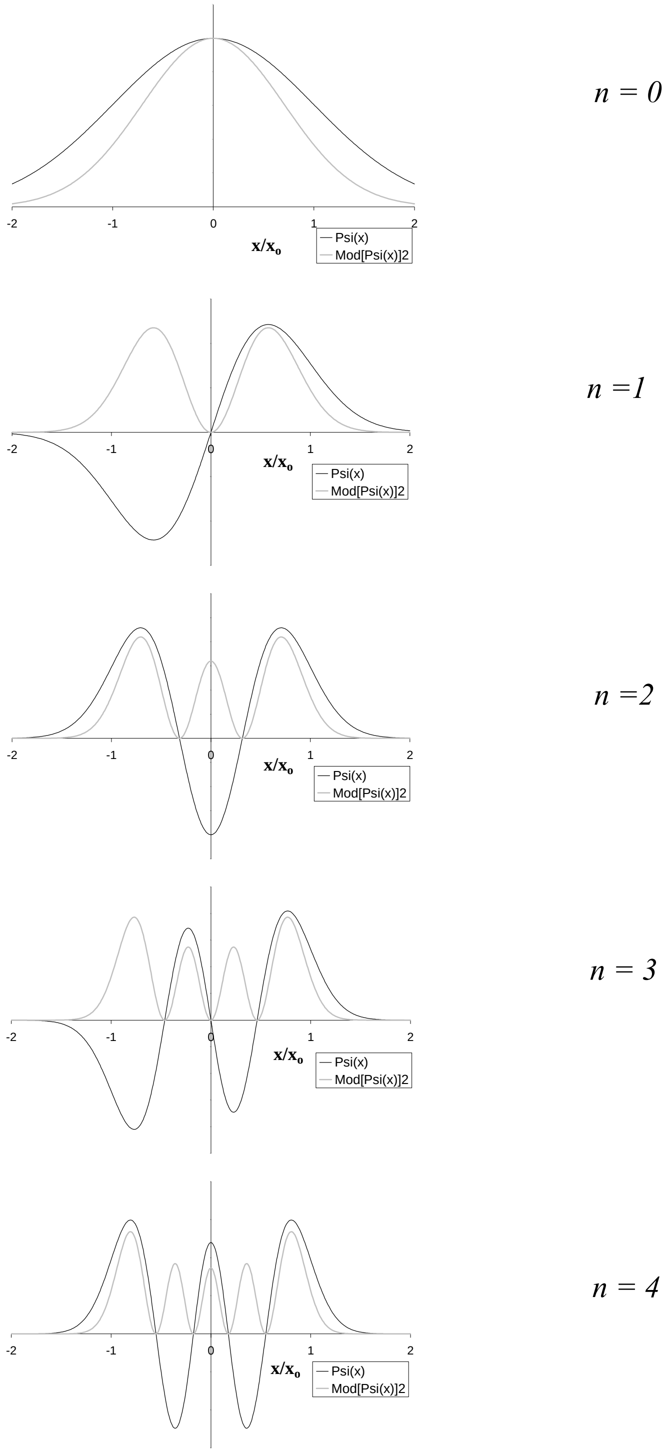

Figure 2: The first five wavefunctions and probability densities for the SHO, with the spatial coordinate plotted in units of the classical turning point x_0. The wavefunctions alternate pleasingly between positive and negative parity. Note: all probability densities are non zero beyond the classical turning points ($x/x_0 = \pm 1$)!

An Application - Energy levels of diatomic molecules:

We can use our results for the quantum mechanical SHO to analyse the energy levels of simple molecules. Although the actual interatomic potential between the constituents of a diatomic molecule is not a simple parabola, we can apply a parabolic (or harmonic) approximation, so long as the displacements from the equilibrium separation are not too great, as shown in figure 3.

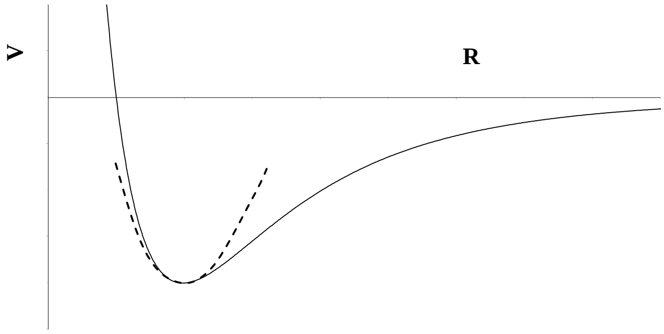

Figure 3: A parabolic or harmonic approximation near the equilibrium separation of an actual interatomic potential.

Using the harmonic approximation we can begin to build a model for diatomic molecules and investigate their vibrational, as well as other, energy levels.

A cartoon of a diatomic molecule is shown in figure 4; it consists of two atoms, mass M_a and M_b, held together by bonds of effective spring constant k, a distance R_0 apart. This arrangement will oscillate with frequency ω_0 given by:

$$\omega_0 = \sqrt{\frac{k}{M^*}}$$

which looks like equation 3a, except we are using M^* , the effective mass for the system, which can be easily calculated using:

$$\frac{1}{M^*} = \frac{1}{M_a} + \frac{1}{M_b} \qquad (14)$$

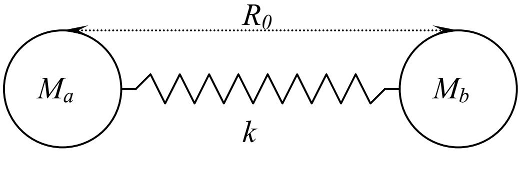

Figure 4: A cartoon of a diatomic molecule.

The energy of a diatomic molecule can be changed in several ways; there are electronic excitations (and we can denote these by the principal quantum number, $n = 1,2\ldots$)as well as vibrational excitations (which we will denote by a vibrational quantum number, $v = 0,1,2,3\ldots$) and finally rotational excitations (denoted by a rotational quantum number, $j = 0,1,2,3\ldots$, you will encounter these in detail later in this course, also in QMB!). We have made a small change to our notation so far, by using v instead of n for vibrations, so that equation 10 becomes:

$$E_n = \hbar\omega_0\left(v + \frac{1}{2}\right)$$

It is now time for us to look at the full energy-internuclear separation for diatomic molecules, including all additional levels… as shown in figure 5.

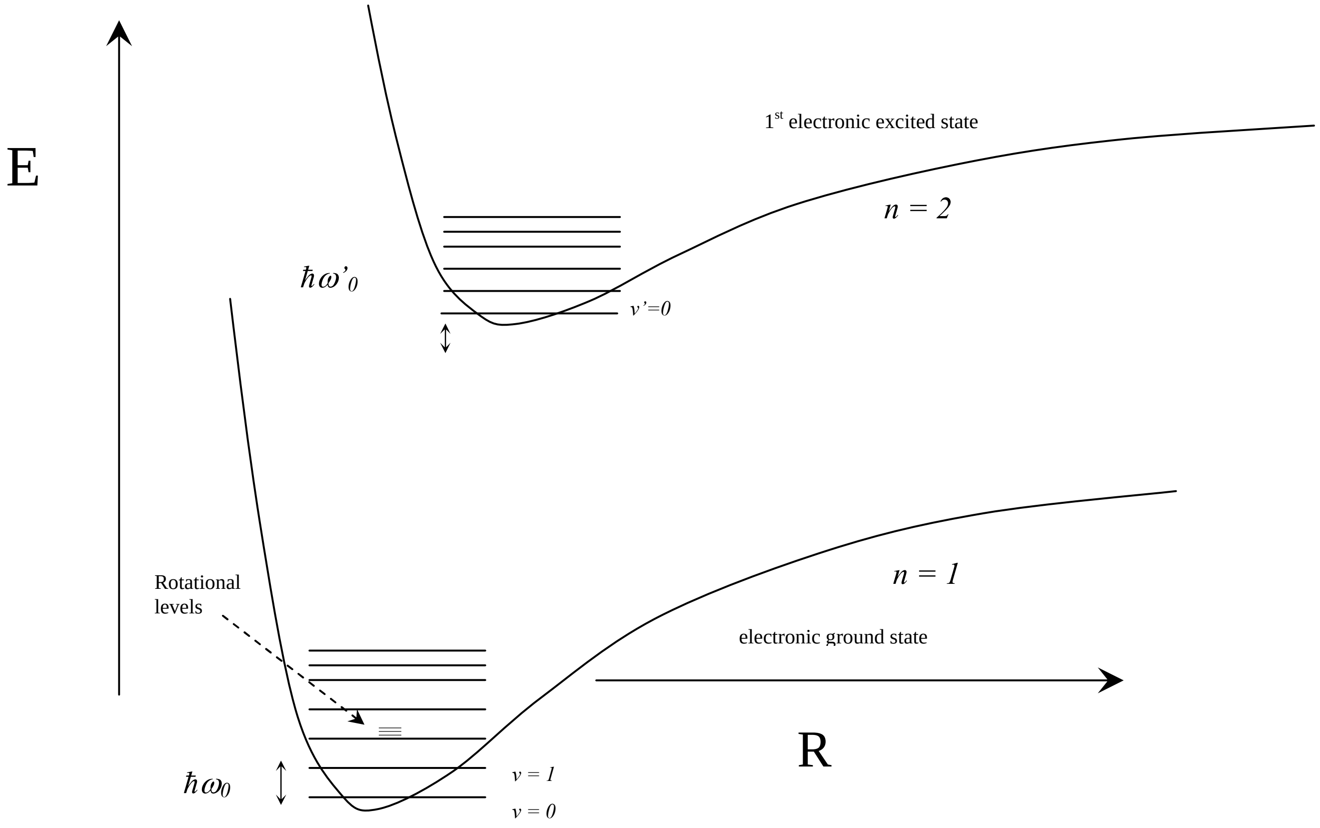

Figure 5: energy internuclear separation diagram for the ground and first electronic excited state of a diatomic molecule.

Figure 5 merits some comments; we notice that the vibrational energy levels start off equally spaced, but at higher energies deviate from the harmonic approximation. We also notice that the vibrational energy quanta are not the same in the electronic ground state as in the first electronic excited state (the effective spring constant of the bonds is different when the electrons are excited). The rotational energy levels are extremely closely spaced, and are present on all levels (shown just on one in the diagram, for clarity). It is also worth considering the relative sizes of the energies required to affect excitations. Electronic excitations are typically eV sized and would require ultra-violet or visible photon energies, vibrational excitations are typically tenths of eV in size and require infra-red photon energies, whereas the rotational excitations are hundredths of eV or smaller and correspond to microwave photon energies.