QUANTUM MECHANICS A (SPA-5319)

The Quantum Harmonic Oscillator (QHO)

The simple harmonic oscillator is a system we have encountered classically many times before; it comes about when a restoring force is proportional to the displacement, namely:

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

If the force is conservative, we can always write

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

yielding

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

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

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

where $\omega_0 = \sqrt{\frac{k}{m}}$, or equivalently $k = m\omega_0^2$. This allows us to rewrite the potential as:

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

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

Application of the TISE and the first two simplest states:

We can now fully write the TISE as:

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

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

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

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

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

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

$$a = \frac{m\omega_0}{\hbar} \tag{8}$$

Indeed, it transpires that the general form of the wavefunctions for the QHO is a product of polynomial and a Gaussian:

$$\psi(x) = H(x)e^{-\frac{ax^2}{2}},$$

where $H(x)$ is a simple 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.

We will begin with the trial solution:

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

and substitute it into the TISE, $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}m\omega_0^2x^2\psi(x)=E\psi(x)$. 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 $n=1$ are solutions (good, we have the two first states). We also have

$$\frac{\omega_0}{\hbar}(2n+1) = \frac{2E}{\hbar^2}\,,$$

therefore

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

giving $E_0 = \frac{1}{2}\hbar\omega_0$ and $E_1 = \frac{3}{2}\hbar\omega_0$. In fact, the following expression happens to be true for all eigenstates (all values of *n*):

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

(this will not proven here, but there exist elegant operator methods - involving energy raising and lowering operators –that can be used to 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:

$$\psi_0(x) = N_0 e^{-\frac{ax^2}{2}} \qquad \text{and} \qquad E_0 = \frac{1}{2}\hbar\omega_0 \qquad \text{for } n = 0$$

and

$$\psi_1(x) = N_1 x e^{-\frac{ax^2}{2}} \qquad \text{and} \qquad E_1 = \frac{3}{2}\hbar\omega_0 \qquad \text{for } n = 1$$

The full wavefunctions are therefore $\Psi_0(x,t) = N_0 e^{-\frac{ax^2}{2}} e^{-\frac{iE_0 t}{\hbar}}$ and $\Psi_1(x,t) = N_1 x e^{-\frac{ax^2}{2}} e^{-\frac{iE_1 t}{\hbar}}$.

One important result is that the energy levels for a QHO 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).

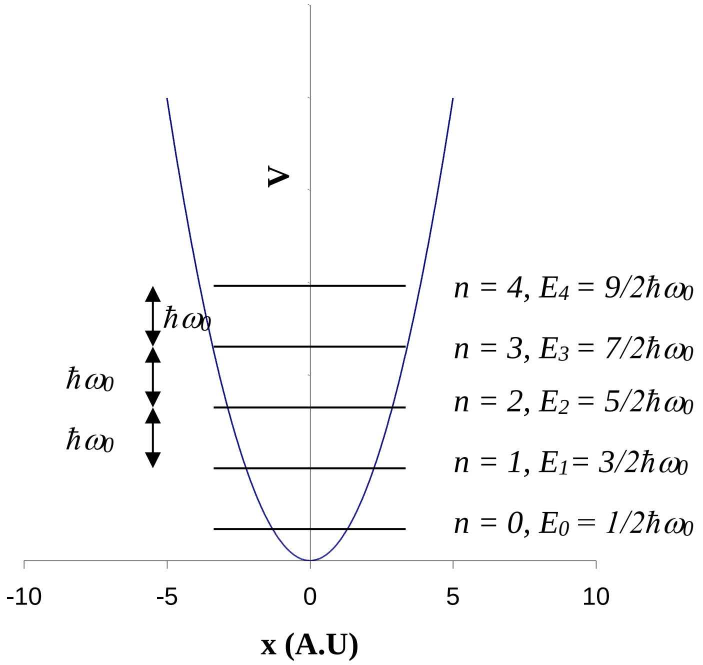

Figure 1: *SHO energy levels superimposed on a sketch of the potential.*

A general expression for the Eigenstates: As we previously commented, the general form of the wavefunctions of the QHO 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 by:

$$\psi_n(x) = A_n H_n(\xi) e^{-\frac{ax^2}{2}} \tag{11}$$

where $a = \frac{m\omega_0}{\hbar}$. In this form A_n is a normalization constant and $H_n(\xi)$ is a Hermite polynomial.

The Hermite polynomials are defined in terms of the dimensionless parameter, ξ, which is proportional to x. In fact, 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 follows:

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

A note on the classical turning points: A classical harmonic oscillator 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 harmonic oscillator of energy E_n, the turning point x_0 will be a function of E_n. This means we can write it more fully as $x_{0,n}$. By equating the energy to the potential (equation 4) we can show that:

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

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.

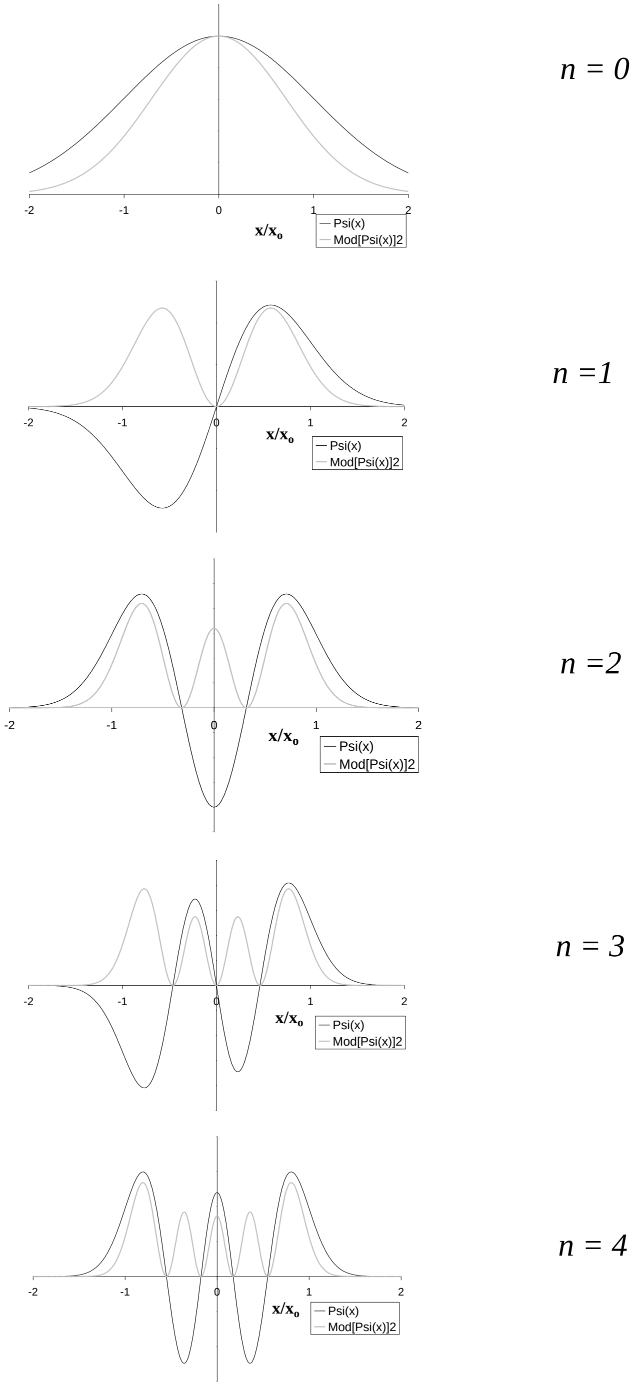

Figure 2: *The first five wavefunctions and probability densities for the QHO, with the spatial coordinate plotted in units of the classical turning point* x_0*. The wavefunctions alternate pleasingly between positive and negative parity. Note:* ***all*** *probability densities are non-zero beyond the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

An Application - Energy levels of diatomic molecules: We can use our results for the quantum mechanical QHO 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.

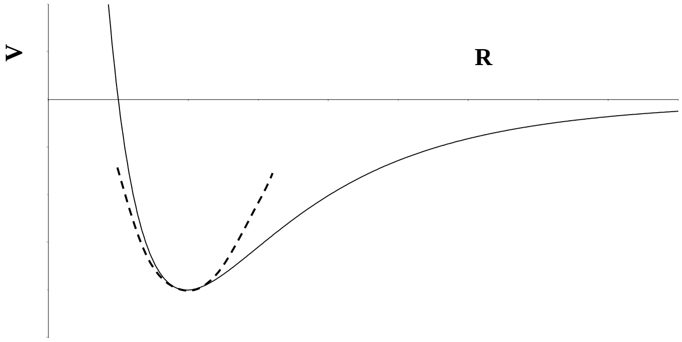

Figure 3: *A parabolic or harmonic approximation near the equilibrium separation of an actual interatomic potential.*

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:

$$\frac{1}{M^*} = \frac{1}{M_a} + \frac{1}{M_b} \tag{14}$$

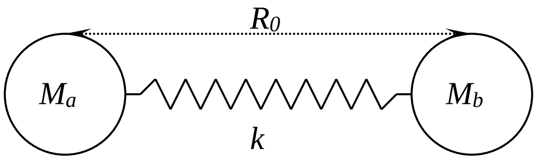

Figure 4: *A cartoon of a diatomic molecule.*

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 module (and also in QMB!). We can express the energy levels in terms of 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 levels for diatomic molecules, including all additional levels, as shown in figure 5.

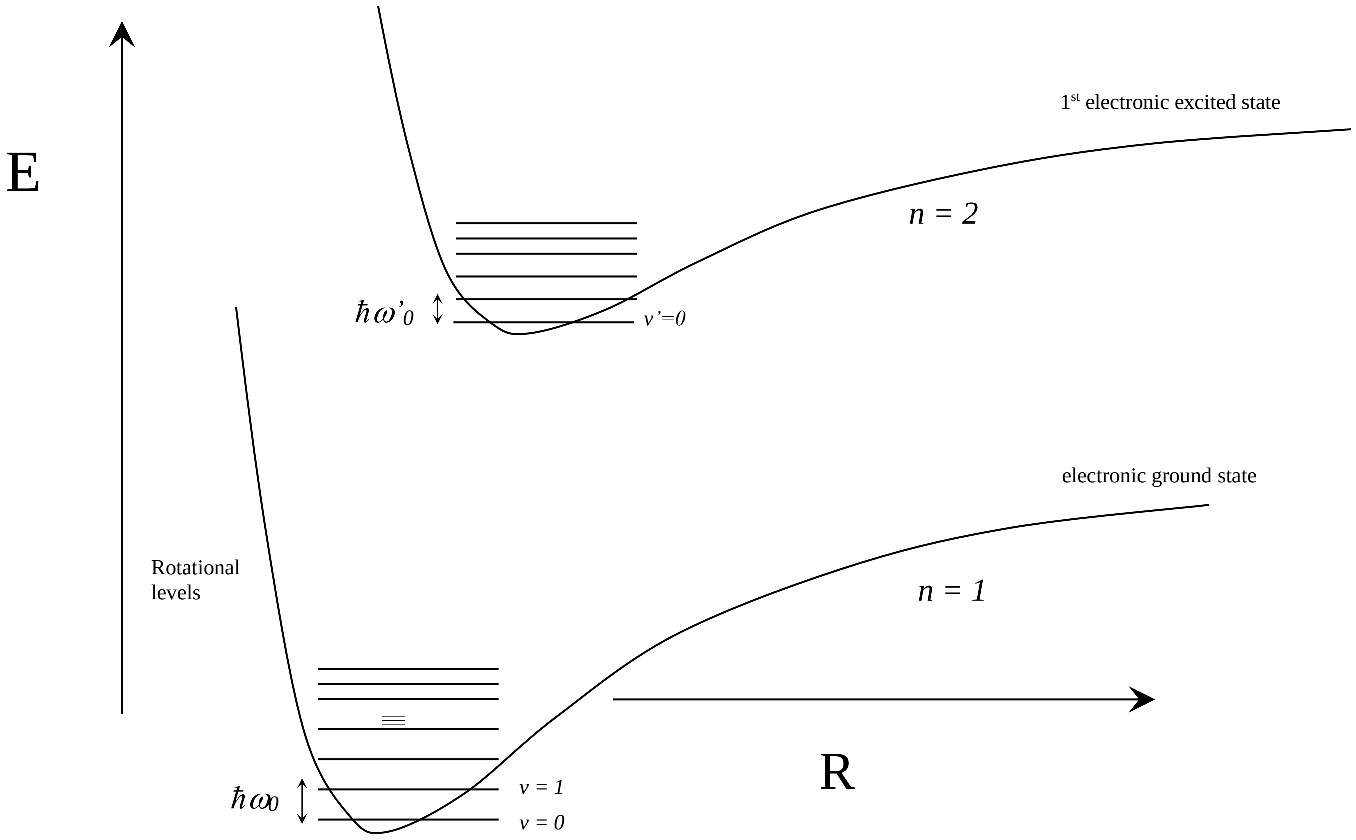

Figure 5: *energy internuclear separation diagram for the ground and first electronic excited state of a diatomic molecule.*

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, while vibrational excitations are typically tenths of *eV* in size and require infra-red photon energies, and whereas the rotational excitations are hundredths of *eV* or smaller and correspond to microwave photon energies.