

1.3 Harmonic Oscillator

1. For the case of the harmonic oscillator, the potential energy is quadratic and hence the total Hamiltonian looks like:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad (1.3.1)$$

where k is the force constant for the Harmonic oscillator. (Note: the k here has nothing to do with momentum eigenvalues. It is just coincidental that we are using the same letter in the alphabet to describe these two unrelated items.) We will now look at the solution to this problem, since this forms the basis to a number of problems, for example the solution to vibrational motion in molecules and in infra-red spectroscopy. It also plays an important role in the quantum theory of solids, vibrational spectroscopy, etc.

2. The classical harmonic oscillator comprises a single mass attached to the end of a spring. When the spring is stretch the particle undergoes a simple harmonic motion. This is characterized by the particle moving from one end to the other and back and when there is no external disturbance this motion is perpetual. Furthermore all values of energy are possible, since the particle can vibrate about its equilibrium position with any amount of energy. (The energy determines how much the spring stretches.) It is possible for the particle to have zero energy (no motion). *There is no zero point energy in classical mechanics.* The simple pendulum is another example of the classical harmonic oscillator.
3. The quantum mechanical treatment of the harmonic oscillator leads to a different set of results. The particle can have zero point energy. The energy will be discrete. All this, as we can guess, will be enforced by the boundary conditions as we have seen before for PIB.
4. Plus, the zero point energy is something that reflects the Heisenberg uncertainty principle. Classically you can have the particle stationary at a given point. *But this amounts to knowing its position as well as velocity (or momentum), which is clearly in violation of the uncertainty principle.*
5. The harmonic oscillator energy eigenvalue problem (or the time-independent Schrödinger Equation) is:

$$\begin{aligned} H\psi &= E\psi \\ \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] \psi &= E\psi \\ \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left[E - \frac{1}{2} kx^2 \right] \psi &= 0 \\ \frac{d^2\psi}{dx^2} + [\lambda - \alpha^2 x^2] \psi &= 0 \end{aligned} \quad (1.3.2)$$

where we have substituted $\lambda = \frac{2mE}{\hbar^2}$ and $\alpha^2 = \frac{mk}{\hbar^2}$.

6. We will use an asymptotic analysis to solve this problem. [We will do something similar for the hydrogen atom later in the semester.]
7. For any fixed value of E , as $x \rightarrow \infty$, $\alpha^2 x^2 \gg \lambda$ and this leads to:

$$\frac{d^2\psi}{dx^2} = \alpha^2 x^2 \psi \quad (1.3.3)$$

For large x the solution to this equation is

$$\psi(x) = \exp\left[\pm\frac{\alpha}{2}x^2\right]. \quad (1.3.4)$$

This is true because:

$$\frac{d^2}{dx^2} \exp\left[\pm\frac{\alpha}{2}x^2\right] = \left[\alpha^2 x^2 \pm \alpha\right] \exp\left[\pm\frac{\alpha}{2}x^2\right] \quad (1.3.5)$$

and for large x the second term in the bracket is small as compared to the first term which helps us recover Eq. (1.3.3). Furthermore, as $x \rightarrow \infty$ only $\exp\left[-\frac{\alpha}{2}x^2\right]$ remains finite and $\exp\left[+\frac{\alpha}{2}x^2\right]$ becomes infinitely large. Hence, only $\exp\left[-\frac{\alpha}{2}x^2\right]$ is an acceptable solution.

8. We propose the following solution to the Harmonic oscillator problem:

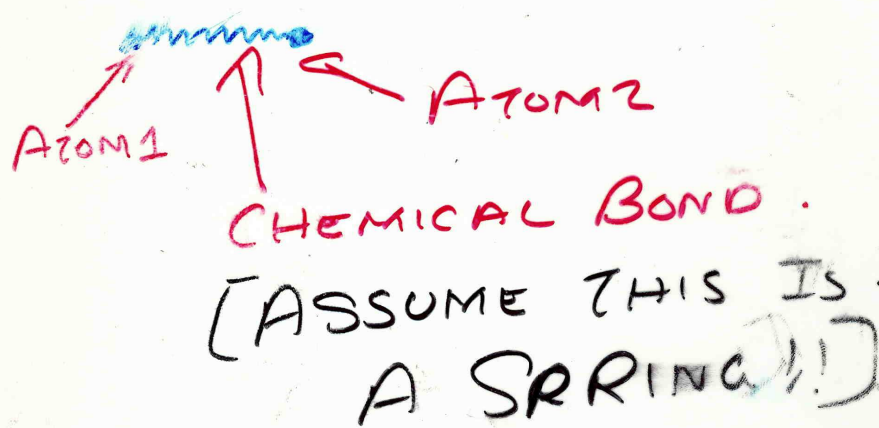
$$\psi(x) = \exp\left[-\frac{\alpha}{2}x^2\right] f(x). \quad (1.3.6)$$

We want to approximate $f(x)$ as a power series.

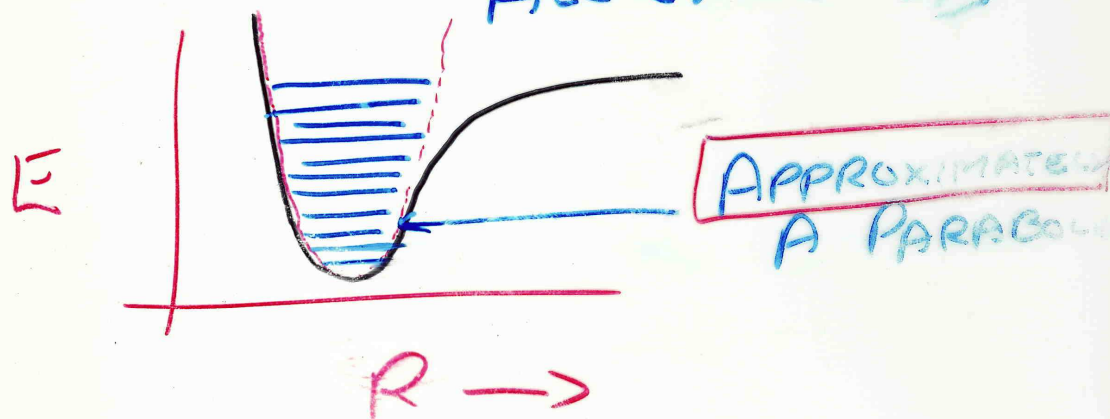
9. And when we substitute this into the differential equation we can get an equation that involves the coefficients of the power series used to approximate the function $f(x)$. And we can equate like powers of x^i for all values i . We end up with another *special function* as a solution to this equation. And this function is known as the Hermite polynomials!!
10. It is critical to go over this derivation for two reasons. (a) Buried in this derivation is a deep insight. In the final step of this derivation which leads to the Hermite polynomials, boundary conditions are again required to be enforced. Without the boundary conditions being enforced you don't get Hermite functions and you don't get discrete states!!. (a) We are all physical chemists and hence should have a certain degree of mathematical facility as part of our education (google/wikipedia notwithstanding).

HARMONIC OSCILLATOR

WHY?

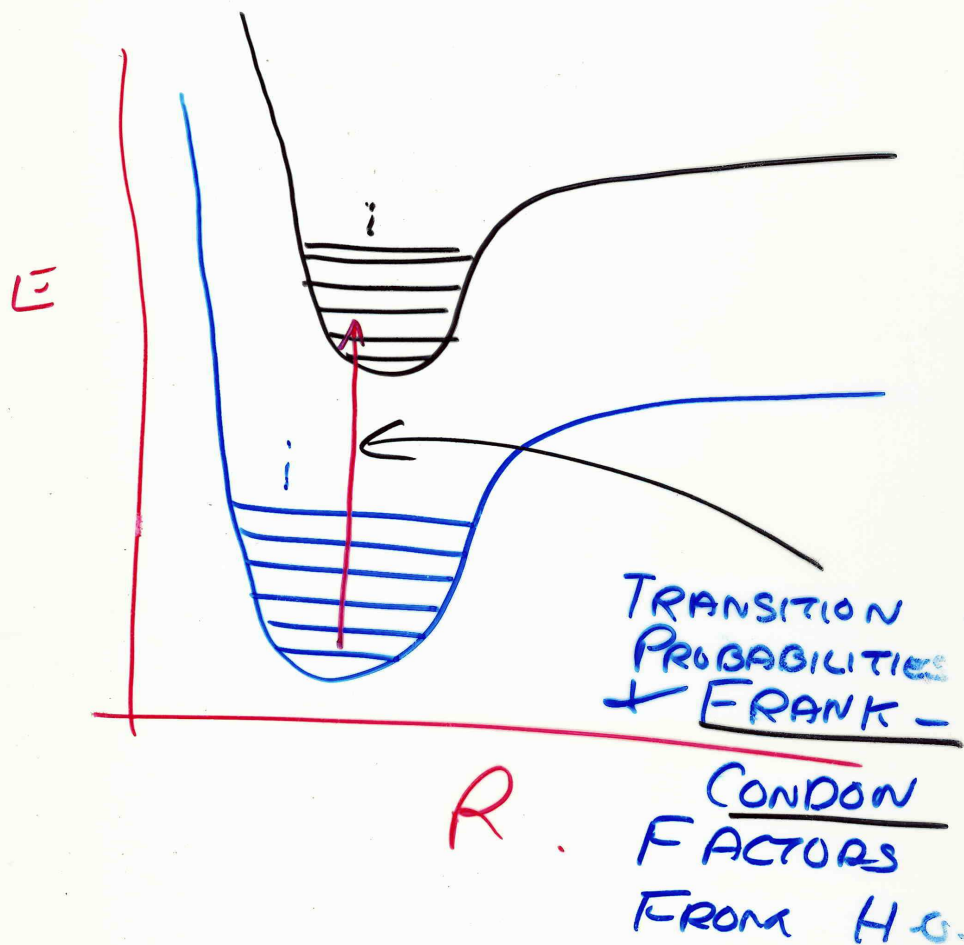


WORKS WELL IN MANY CASES [OF COURSE NOT ALL CASES!!]

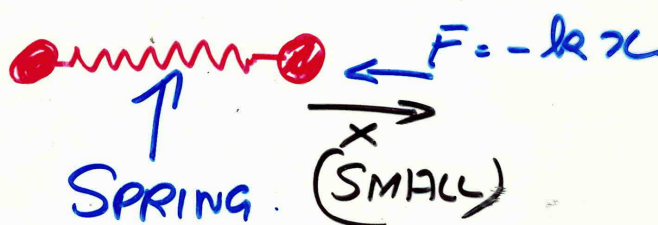


WE CAN DO A LOT.
WITH JUST H_0 !!

Eg.



THE STORY OF THE SPRING



$$F = -kx$$

[A RESTORING FORCE]

POTENTIAL ENERGY WHILE
IT OSCILLATES:

$$E = -\int F dx = \int +kx \cdot dx \\ = +\frac{1}{2} kx^2$$

8. So (as usual :-)) we write the solution to the Harmonic oscillator as:

$$\psi(x) = \exp\left[-\frac{\alpha}{2}x^2\right] f(x) \quad (13.6)$$

and again we want to approximate $f(x)$ as a power series (as we did earlier for the hydrogen atom).

9. And when substitute this into the differential equation we can get an equation that involves the coefficients of the power series used to approximate the function $f(x)$. And we can equate like powers of x^i for all values i . We end up with another *special function* as a solution to this equation. And this function is known as the Hermite polynomials!! I am gonna solve this on the board so you guys have an idea how one would solve such an equation.

$$\psi''(x) \cdot e^{-\alpha x^2} \left[f''(x) - 2\alpha x f'(x) + \alpha^2 x^2 f(x) - \alpha f(x) \right]$$

Eg. (13.2): $f''(x) - 2\alpha x f'(x) + \alpha^2 x^2 f(x) - \alpha f(x) = 0$

$$\therefore f''(x) - 2\alpha x f'(x) + (\alpha - \alpha^2 x^2) f(x) = 0$$

$\gamma = \sqrt{2\alpha}; \quad f(x) \equiv H(\gamma)$

$$\frac{d^2 H}{d\gamma^2} = \alpha \frac{d^2 H}{dx^2}$$

$$\frac{d^2 H}{d\gamma^2} - 2\gamma \frac{dH}{d\gamma} + (\alpha - 1)H = 0$$

$$f''(x) - 2\alpha x f'(x) + (\epsilon - \alpha) f(x) = 0 \rightarrow \textcircled{A}$$

$$f(x) = \sum_{i=0}^{\infty} a_i x^i$$

$$f'(x) = \sum_{i=1}^{\infty} a_i i x^{i-1}$$

$$f''(x) = \sum_{i=2}^{\infty} a_i i(i-1) x^{i-2}$$

Using these in Eq. \textcircled{A} :

$$\left[\sum_{i=2}^{\infty} a_i i(i-1) x^{i-2} \right] - 2\alpha \left[\sum_{i=1}^{\infty} a_i i x^i \right] + (\epsilon - \alpha) \left[\sum_{i=0}^{\infty} a_i x^i \right] = 0$$

$$\Rightarrow \left[\sum_{k=0}^{\infty} a_{k+2} (k+2)(k+1) x^k \right] =$$

$$2\alpha \left[\sum_{k=1}^{\infty} a_k k x^k \right] + (\epsilon - \alpha) \left[\sum_{k=0}^{\infty} a_k x^k \right] = 0$$

$$\begin{aligned} \Rightarrow x^0 [a_2 \cdot 2 + (\lambda - \alpha) a_0] + \\ x^1 [a_3 (3)(2) - 2\alpha a_1 + (\lambda - \alpha) a_1] + \\ x^2 [a_4 (4)(3) - 2\alpha a_2(2) + (\lambda - \alpha) a_2] + \\ x^3 [a_5 (5)(4) - 2\alpha a_3(3) + (\lambda - \alpha) a_3] + \\ \dots = 0 \quad \rightarrow \textcircled{B} \end{aligned}$$

This is basically:

$$C_0 x^0 + C_1 x^1 + C_2 x^2 + \dots = 0.$$

And for the left side to be equal to zero,

$$C_0 = C_1 = C_2 = \dots = C_i = 0.$$

$$\Rightarrow a_2 = -\frac{a_0 (\lambda - \alpha)}{2}$$

$$a_{k+2} = -\frac{a_k [(\lambda - \alpha) - 2k]}{2}$$

This is because Eq. (B) can also be written as:

$$x^0 [2a_2 + (A-d)a_0] + \sum_{k=1}^{\infty} x^k [a_{k+2} (k+2)(k+1) - \cancel{a_k} (2dk - (A-d))] = 0.$$

Now as $k \rightarrow \infty$.

$$a_{k+2} \approx \frac{2kd}{k^2} a_k = \frac{2d}{k} a_k$$

\Rightarrow Eq (B) as $k \rightarrow \infty$.

$$\sum_k \frac{d^k}{(k!)^2} x^k \approx e^{+dx^2}.$$

That diverges as $x \rightarrow \infty$

So the series:

$$f(r) = \sum_{i=0}^{l_{max}} a_i r^i$$

Has to be TRUNCATED.

Say; for $k = l_{max}$

$$(l - \alpha) - 2\alpha l_{max} = 0.$$

all ' a_k ' for $k > l_{max}$
 $a_k = 0.$

THE SERIES TRUNCATES

↓

$$l - \alpha - 2\alpha l_{max} = 0.$$

$$\Rightarrow l - \alpha [2l_{max} + 1] = 0 \quad \rightarrow \text{C}$$

AFTER, Eq. (13.2) kLE SAID:

$$\lambda \alpha = \frac{2mE}{\hbar^2}$$

$$\alpha^2 = \frac{mk}{\hbar^2}$$

$$\Rightarrow \frac{\lambda}{\alpha} = \frac{2mE}{\hbar^2} \frac{\hbar}{\sqrt{mk}}$$

$$k = m\omega^2$$

$$\Rightarrow \frac{\lambda}{\alpha} = \frac{2mE}{\hbar m\omega} = \frac{2E}{\hbar\omega}$$

Using this in Eq. (C)

$$\left(\frac{\lambda}{\alpha}\right) - (2I_{\text{max}} + 1) = 0$$

$$\Rightarrow \frac{2E}{\hbar\omega} = 2I_{\max} + 1$$

$$\Rightarrow E = \frac{\hbar\omega}{2} [2I_{\max} + 1].$$

OR .

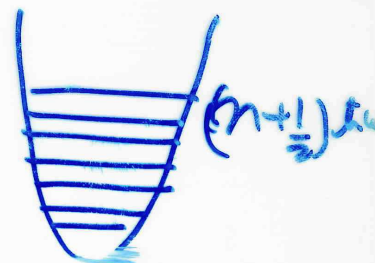
$$E_m = \frac{\hbar\omega}{2} [2m + 1] = (m + \frac{1}{2})\hbar\omega$$

[SINCE 'I_{MAX}' IS AN INTEGER WE JUST CALLED IN 'm'].

QUANTIZED STATES:

AGAIN! ENFORCED BY.

B.C.S (BOUNDARY COND.).



SO WE HAVE THE
H.O. ENERGY
LEVELS.

$$\psi_m(x) = e^{-\alpha x^2/2} \sum_{n=0}^m a_n x^n.$$

$\{a_n\}$ are given by Eq.

$$a_{m+2} = - \frac{a_m [(2-\alpha) - 2\alpha m]}{(m+2)(m+1)}$$

(RECURSION RELATION)

TRADITIONALLY WHAT'S DONE
IS :

$$x \rightarrow \frac{r}{\sqrt{\alpha}} \quad \text{HERMITE POLYNOMIALS}$$

$$\psi_m(x) = e^{-r^2/2} \cdot H_m(r)$$

ANOTHER IMPORTANT.
RELATION THAT APPEARS
DUE TO THE RECURSION
RELATION :

FOR ODD EIGENSTATES!

$$m = 1, 3, 5, \dots \quad [E_m = (m + \frac{1}{2})\hbar\omega]$$

ONLY ODD POLYNOMIALS.

$$H_m(x) = -H_m(-x)$$

(ODD SYMMETRY UNDER
INVERSION)

FOR EVEN 'm': EVEN POLYNOMIALS

$$H_m(x) = +H_m(-x). \quad [\text{EVEN SYMMETRY}]$$

10. The $n = 0$ state is a Gaussian (proportional to $\exp[-(\alpha/2)x^2]$) and the wavefunction and the probability density look as follows:

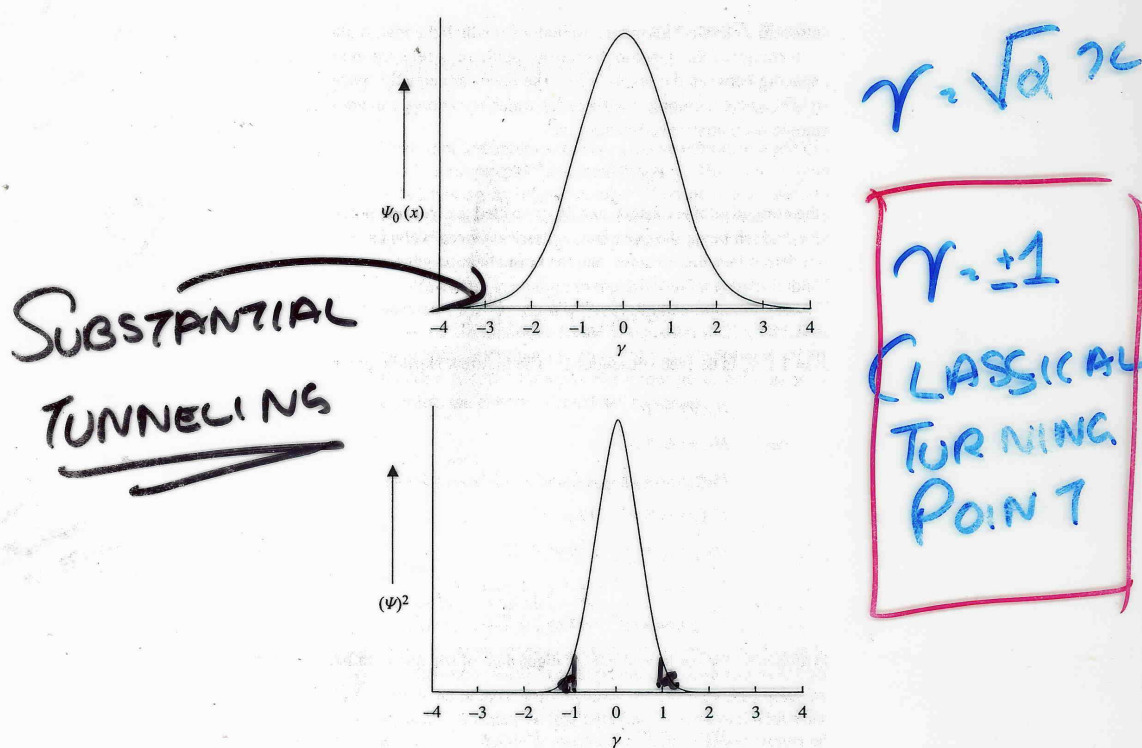


Figure 16: $n = 0$ wavefunction and probability for the harmonic oscillator. The x-axis is γ .

11. The $n = 0$ state is a Gaussian (proportional to $\exp[-(\alpha/2)x^2]$) and the wavefunction and the probability density look as follows:

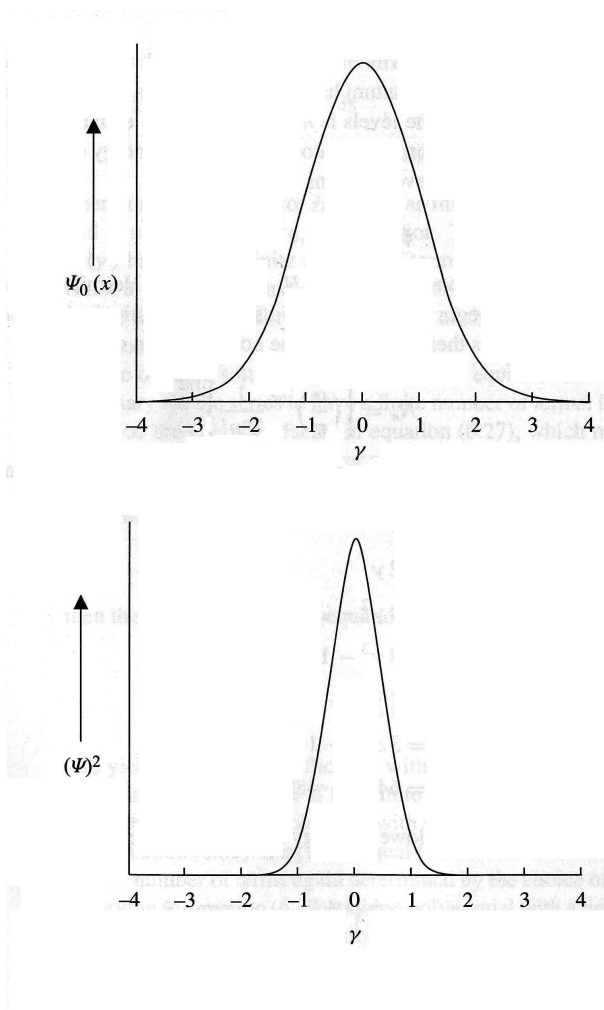


Figure 2: $n = 0$ wavefunction and probability for the harmonic oscillator. The x-axis is γ .

12. Consider the point where the total energy is equal to the potential energy:

$$\frac{1}{2}h\nu = \frac{1}{2}kx^2 = \frac{1}{2}h\nu\gamma^2 \quad (1.3.7)$$

Note now that what this expression means is the total energy is equal to the potential energy. This could only happen at the “turning point” of the *classical* oscillator. Hence the classical turning point for the ground state oscillator is at $\gamma = \pm 1$. But from the above figure we see that the ground state wavefunction of the quantum harmonic oscillator is *not* zero at this point. Hence there is substantial tunneling!! In fact 0.16 of the probability exists beyond the classical turning point.

13. Another striking feature from Fig. 2 is that the probability is a maximum at $\gamma = 0$. We should compare this with the classical harmonic oscillator. In the classical case the velocity is maximum at $\gamma = 0$. And in fact the velocity is zero at the edges, which is why it turns back towards the equilibrium point. Since the classical harmonic oscillator moves very fast at the equilibrium point and very slow at the classical turning point, we would conclude that the classical harmonic oscillator spends the least bit of time at the equilibrium point and the maximum at the turning point. Hence the likelihood of finding the classical particle is maximum at the edges (or the turning point) and is minimum at the equilibrium point. This is exactly contradictory to what we have for the quantum harmonic oscillator ground state as seen in Fig. 2.

14. In Fig. 3 a few higher harmonic oscillator wavefunctions are presented and in Fig. 4 the probability density for the $n = 10$ state is presented.

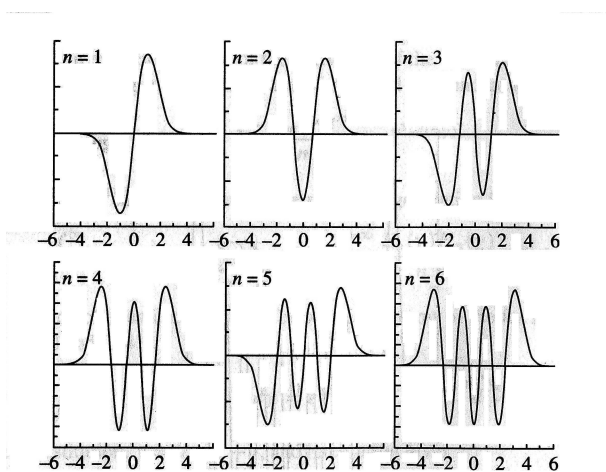
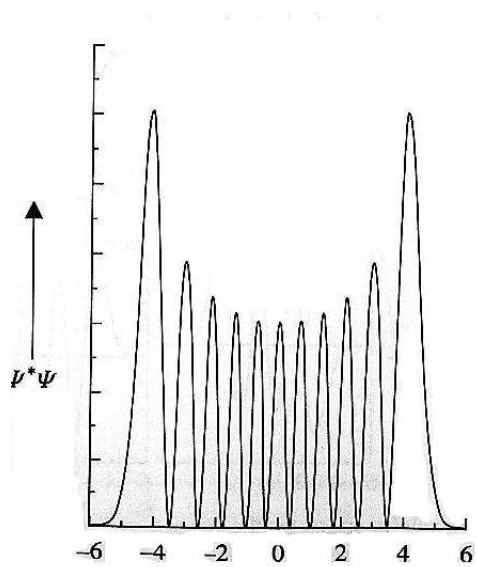


Figure 3: The harmonic $n = 1$ through $n = 6$ states. Note each state has $n - 1$ nodes. The x-axis is γ .

15. From both of these figures the probability along the edges increases and the state becomes more and more “classical-like” for large n . But is this really true?

Figure 4: Probability of the $n = 10$ state.

16. In fact the quantum description of a macroscopic harmonic oscillator is exactly equivalent to a classical description. Let's see if this makes sense. Consider a 1 gram mass connected to a spring that is initially displaced an amount equal to 1 cm. Let the frequency of oscillation be 1 Hz. This implies the force constant, $k = 4\pi^2 g/s^2$. At the classical turning point, $x = 1\text{ cm}$ and the total energy is equal to the potential energy $\frac{1}{2}kx^2 = 2\pi^2 gcm^2/s^2$. Now if we were to treat the exact same system quantum mechanically then we would have $(n + \frac{1}{2}) h\nu = \frac{1}{2}kx^2 = 2\pi^2 gcm^2/s^2$, which gives approximately $n = 10^{27}$!! This means the classical system corresponds to the quantum system at this very large quantum number. But the quantum system has $(10^{27} - 1)$ nodes with an average separation of 10^{-27} cm very much smaller than what we can measure. Hence the quantum density also looks smooth and is indistinguishable from the classical density!!
17. This last argument very nicely demonstrates the Bohr correspondence for the harmonic oscillator.