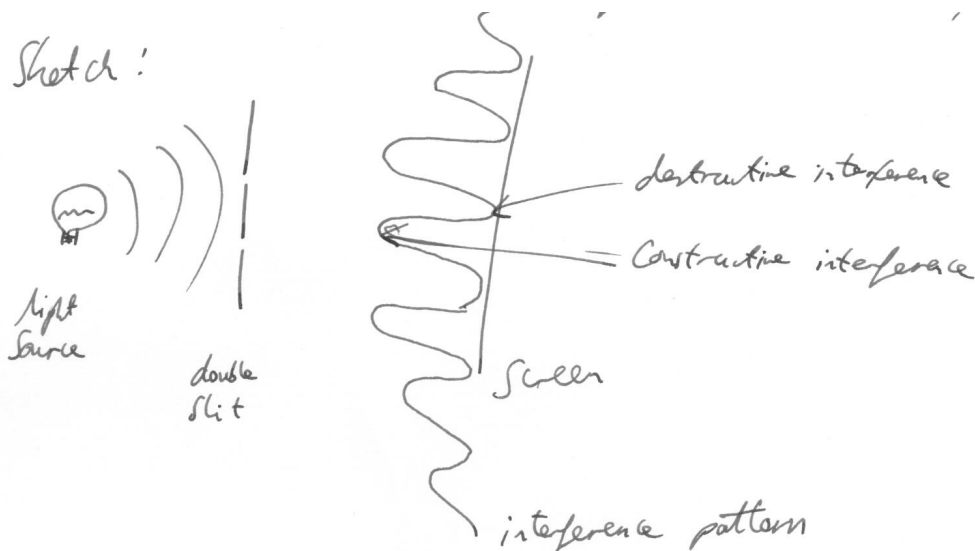


1.

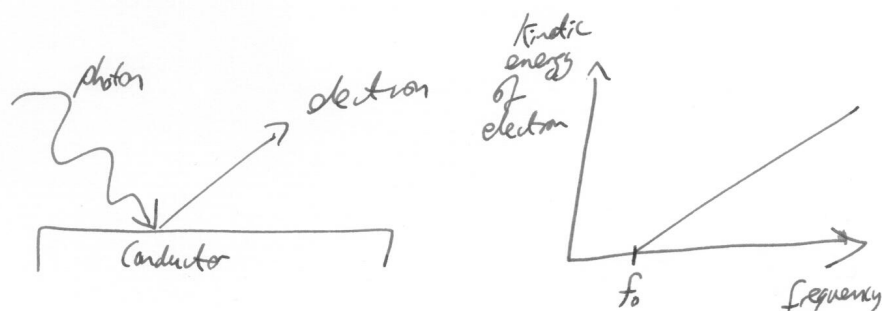
(a) The wave-particle duality is the concept that under certain circumstances, waves can display particle-like characteristics (e.g. light comes in discrete packets called photons), and particles can display wave-like characteristics such as interference and diffraction (e.g. electron diffraction). The particular choice as to whether to describe an object as a particle or a wave therefore depends on the context, and both should be seen as different aspects of the same thing.

From a practical standpoint, the wave-particle duality only becomes apparent when the object *or its surroundings* have dimensions comparable to its wavelength. deBroglie hypothesized that the wavelength of a particle would be given by the expression $\lambda = h/p$, where p is the momentum and h is Planck's constant. Likewise, the momentum of a wave is given by $p = h/\lambda = \hbar k$.

(b) The answer should include a description of wave-like characteristics: interference & diffraction.



particle-like behaviour: prime example is the photoelectric effect



The Kinetic Energy, $K.E.$ of the ejected electron = Energy of incident light – work function (ϕ). Remember, the work-function is the amount of energy required to release an electron from the material.

i.e. $K.E. = I - \phi$ where I is the light energy. It was initially thought, on the basis of classical electrodynamics that I would be the energy of the electromagnetic field, as dictated by the Poynting vector, and would be proportional to the light intensity. However, experiments showed two intriguing effects:

- (i) Changing the light intensity made no difference to the $K.E.$ of the ejected electrons, it only changed the *number* of them.
- (ii) Changing the colour of the light affected the $K.E.$ of the electrons, with a direct relationship between the light frequency and the $K.E.$

i.e. Einstein proposed that $I = hf$ where the constant of proportionality, h , is Planck's constant.

$$\Leftrightarrow K.E. = hf - \phi.$$

This means that light comes in packets or *quanta*, with an amount of energy equal to hf . These packets are called photons, and, as they are spatially localized, they can be considered as particles in certain situations.

This directly led to the advent of quantum mechanics, as the wave-particle duality and the fact that light comes in discrete quanta came contrary to what classical mechanics or EM theory predicted. This was one of the first cases of the application of Planck's constant.

(c)

(i)

$$\text{Kinetic energy} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m\lambda^2}$$

We are assuming that $\lambda = 2\pi r$

$$\Rightarrow \text{Kinetic energy, } K.E. = \frac{\hbar^2}{2m \times (2\pi r)^2} = \frac{\hbar^2}{2mr^2}$$

$$\text{The potential energy, } P.E. = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$\Leftrightarrow \text{The total energy} = K.E. + P.E. = \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

(ii) The value of r at which the energy is a minimum is when $dE/dr = 0$

$$\Rightarrow -\frac{\hbar^2}{mr^3} + \frac{e^2}{2\pi\epsilon_0 r^2} = 0$$

$$\Rightarrow 2\pi\epsilon_0 r^2 \hbar^2 = mr^3 e^2$$

$$\Rightarrow r = \frac{2\pi\epsilon_0 \hbar^2}{me^2} = 23.9 \text{ pm.} \quad \text{This is the } \textit{Bohr radius}$$

(iii) The Bohr model of the Hydrogen atom is naïve, as it neglects the fact that an electron in such an orbit would emit radiation and quickly lose energy, leading to a collapse of the atom. A more detailed model, found by solving the Schrödinger equation for the Coulomb potential, finds the same value for r , but that the orbit is fuzzy and 3D. Discussion could also mention about fact that QM is probabilistic rather than deterministic.

Assessor's comments:

This question posed some difficulties for many of the candidates as it was a little more conceptually challenging than past questions. They were asked to determine the equilibrium size of the electron orbit in a hydrogen atom using Bohr's model, and most got the idea right, but only a few obtained the correct answer.

2

(a)

The potential energy of the system is V , where

$$V = 1/2 \kappa x^2 = 1/2 m \omega_c^2 x^2$$

Schrödinger's equation for this system is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \frac{1}{2} m \omega_c^2 x^2 \psi = \mathcal{E} \psi.$$

This problem can be simplified if we employ a change of variables from x to y , where $y = x \sqrt{m \omega_c / \hbar}$, and define $\alpha = 2E / \hbar \omega_c$

Schrödinger's equation is now:

$$\frac{d^2 \psi}{dy^2} + (\alpha - y^2) \psi = 0.$$

The solution of which is known to be $\psi(y) = F(y) e^{-y^2/2}$.

(To see where this comes from, look at the asymptotic solution when $y \gg a$, which is of the form $y = y^n \exp(-y^2/2)$.)

Substituting this form of $\psi(y)$ into the above equation, we find

$$F'' - 2yF' + (\alpha - 1)F = 0.$$

We should now assume a power series solution for $F(y)$;

$$F = \sum_{p=0}^{\infty} a_p y^p.$$

From which it can be seen that:

$$F' = \sum_{p=0}^{\infty} p a_p y^{p-1} \quad \text{and} \quad F'' = \sum_{p=0}^{\infty} p(p-1) a_p y^{p-2}.$$

An important point here is that y can never have a negative power, as that would lead to an infinity at $y = 0$ which would be unphysical (ψ must always be finite, as $|\psi(x)|^2$ represents the probability of the particle being located at position x). The first two terms of F'' therefore must equal 0, so we must put $p = p+2$ in the above expression for F'' .

Substituting for F , F' and F'' into Schrödinger's equation leads to the following:

$$\sum_{p=0}^{\infty} [(p+2)(p+1)a_{p+2} - (2p+1-\alpha)a_p] y^p = 0.$$

For a non-trivial solution, the coefficient of each power of y must vanish, leading to the following recursion relationship:

$$\frac{a_{p+2}}{a_p} = \frac{(2p+1-\alpha)}{[(p+1)(p+2)]}.$$

However, the resulting power series tends to infinity with increasing y (the limit of a_{p+2}/a_p tends to $1/p$, the sum of which is infinity), so we must truncate the power series.

The solution can be re-written as two power series, each containing either all even or odd powers of y . Using the recursion relation above, all coefficients can be expressed in terms of either a_0 or a_1 . Then we need to choose some value for p , say, n , such that $2p+1-\alpha=0$. That power series will end there, and we need to neglect the other power series.

Both of these conditions lead to the following:

$$\begin{aligned} \alpha &= 2n+1 \text{ for } n = 0, 1, 2, \dots \\ a_1 &= 0 \text{ for } n \text{ even, } a_0 = 0 \text{ for } n \text{ odd} \end{aligned}$$

From our definition of $\alpha = 2E/\hbar\omega_c$ we have for the energy eigenstates of the quantum simple harmonic oscillator:

$$E_n = (n+1/2)\hbar\omega_c.$$

That is, discrete, equally spaced energy levels, with a ground state, or *zero-point energy*, of $(1/2)\hbar\omega_c$. Each energy level corresponds to a phonon mode. What is the consequence of the zero-point Energy? It means that according to quantum mechanics, a harmonic oscillator can never be completely at rest, because then we would know its momentum (zero) and position precisely, which goes against Heisenberg's Uncertainty principle. In practice it means that even at absolute zero, the atoms in a material will still be jiggling around by a very small amount.

- (b)
 (i) Normalising, we find that the first three wave functions are

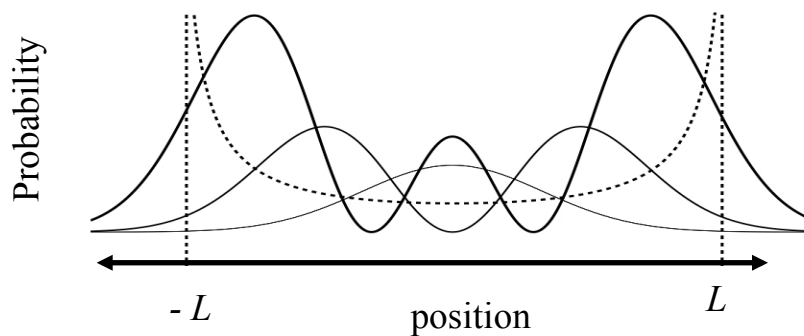
$$\psi_0(x) = \frac{m\omega_c}{4\pi\hbar} e^{-\frac{m\omega_c}{\hbar}x^2}$$

$$\psi_1(x) = \frac{3m\omega_c}{4\pi^2\hbar} x e^{-\frac{m\omega_c}{\hbar}x^2}$$

$$\psi_2(x) = \frac{m\omega_c}{16\pi\hbar} \left(\frac{2m\omega_c}{\hbar} x^2 - 1 \right) e^{-\frac{m\omega_c}{\hbar}x^2}$$

In the ground state, the most probable position is in the centre, whereas for higher levels, the probability oscillates quickly.

- (i) & (ii):



The differences between the classical and quantum harmonic oscillator are that for the ground state, the classical oscillator is most likely to be found at the extremes, whereas the quantum oscillator is most likely to be found at the centre. Also, the quantum oscillator has a finite probability of being found beyond the classical extremes of motion.

- (c) Assume that all the potential energy is converted to kinetic energy. Therefore, the ground state energy of $\frac{1}{2} \hbar \omega_c = \frac{p^2}{2m}$ where $\omega_c = \sqrt{\frac{k}{m}}$

$$\Rightarrow p = \sqrt{m\hbar\omega_c}$$

We will assume that $\Delta p = p$

$$\text{Therefore, } \Delta p \Delta x = \frac{\hbar}{2} \Rightarrow \Delta x = \frac{\hbar}{2\Delta p} \sim \frac{\hbar}{2p} = \frac{\hbar}{2\sqrt{m\hbar\omega_c}}$$

$$\text{Now, } \omega_c = \sqrt{\frac{300}{1.67 \times 10^{-27}}} = 4.2 \times 10^{14} \text{ rad/s}$$

$$\Rightarrow \Delta x = \frac{\hbar}{2\sqrt{m\hbar\omega_c}} = 6 \text{ pm}$$

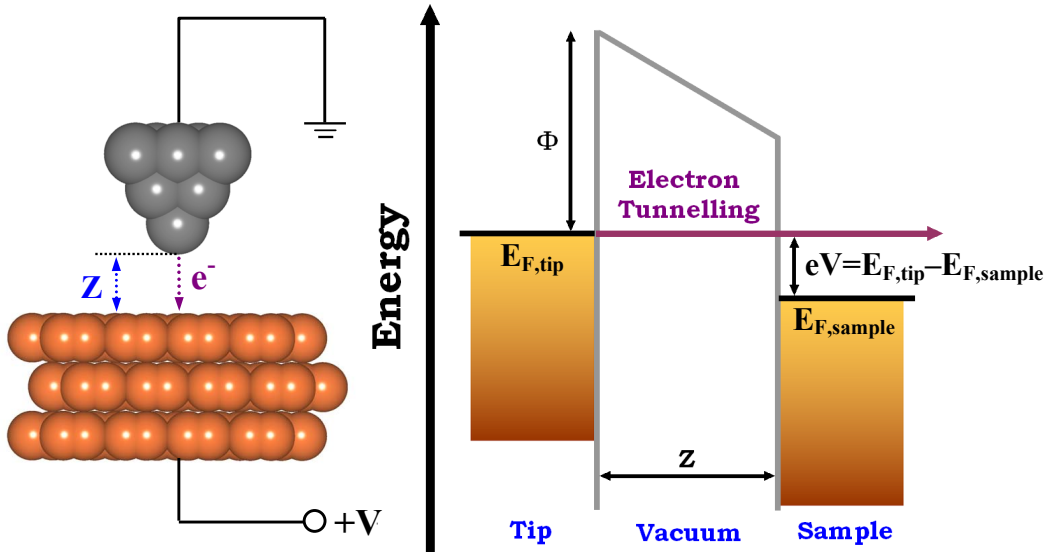
Assessor's comments:

This question was reasonably well answered. Everybody who attempted it obtained the correct energy levels and were able to plot the probability density, but only 1 candidate normalized the wavefunctions correctly. A few people applied the uncertainty principle correctly and were able to determine the positional uncertainty of a Hydrogen atom.

3

(a)

An example of electron tunneling across a gap:



Here, an electron with total energy E_{FL} encounters a barrier of height ϕ , where $\phi > E_{FL}$.

Within the barrier, the electron is described by the wavenumber k , where

$$k = \sqrt{\frac{2m(E_{FL} - \phi)}{\hbar^2}}$$

However, as the electron's total energy is less than the barrier height, k is complex.

Remember, the kinetic energy of the particle is $\frac{\hbar^2 k^2}{2m}$, so if k is complex then the kinetic energy will be negative, which does not make physical sense, so is contrary to classical mechanics, which predicts that the electron simply cannot pass the barrier.

Examples of tunneling:

- (i) Across the gate oxide in a FET
- (ii) In the STM
- (iii) In Photosynthesis
- (iv) In Alpha-decay

(b)

(i) A conventional diode has a doping density of around 10^{22} dopant atoms / m^3 . In contrast, a resonant tunneling diode has a doping density of up to 10^{25} dopant atoms / m^3 . This causes the depletion region to be *very* thin, of the order 10 nm.

(ii) At a given energy, E_n , the current, i_n is proportional to the transmission probability, T_n at that energy. We can write this as

$$i_n \propto T_n$$

When a voltage bias is applied, it opens up multiple energy channels, so the total current, $I = \sum i_n \propto \sum T_n$

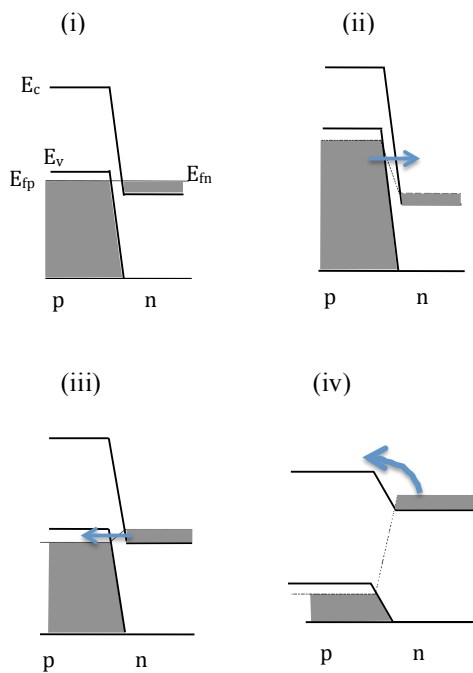
However, these channels are very close together in energy, so we can replace the summation with an integral, so the overall current becomes:

$$I \propto \int_0^{eV} T_n dE$$

Now, the current depends on the density of electronic states on both sides, denoted by ρ_l and ρ_r .

i.e. $I \propto \int_0^{eV} \rho_l \rho_r T_n dE$

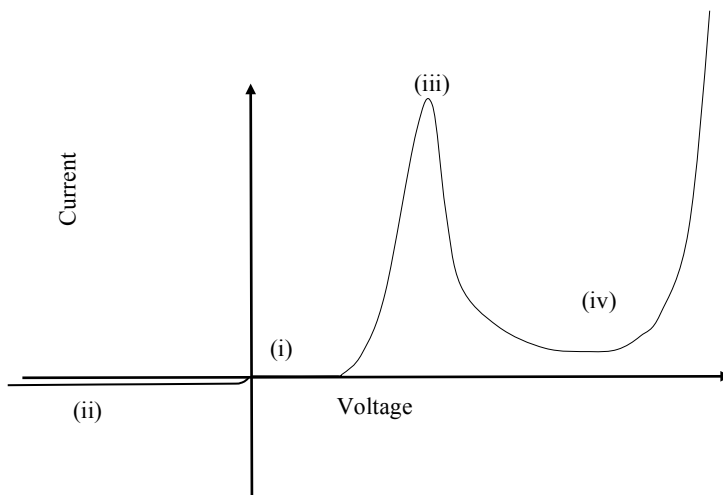
(c)



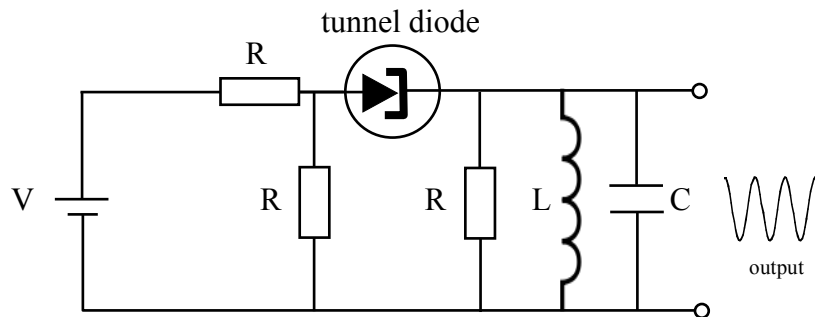
In Fig. (a), i.e. under zero applied bias: there is no net current flow, as the electron current from the conduction band of the n-type into the valence band of the p-type is balanced by the electron current from the valence band of the p-type in to the conduction band of the n-type. In Fig. (b), under reverse bias conditions, the bands on the p-type side are raised relative to the n-type side, and electrons can flow from p to n, tunneling across the depletion region. The width of this region will increase as the voltage is increased, so little current will actually flow. In Fig. (c), which is under a low forward bias, the electron-filled states in the n-type conduction band overlap with the holes in the p-type valence band and a significant current can tunnel across the depletion region, similar to Regime B in Fig. (b). In Fig. (d), as the forward bias is increased, the degree of overlap between the n-type conduction band electrons and the

p-type valence band holes decreases, as more of them start to overlap with the band gap within the p-type. This has the effect of reducing the current across the depletion region as there are fewer states for the n-type electrons to tunnel into. In Fig. (e), similar to Regime (c) in Fig. (b), the current drops to its minimum value, as there is no longer any overlap between the conduction band electrons in the n-type and holes in the p-type: there are no available states for the electrons to tunnel into. The only current that can flow at this point is a small inelastic tunnel current and a small thermal diffusion current. In Fig. (f), when the applied forward bias is large enough, the height of the potential barrier between the n and p-type is low enough for a thermal diffusion current to flow over the barrier, and this becomes the dominant means of current flow.

(d)



(e) Resonant tunneling diodes initially gained a lot in interest for their potential application in oscillator circuits, particularly ones operating at high (Microwave) frequencies. The reason for this can be seen by considering the simplest possible oscillator : an LC circuit (i.e. an inductor in parallel with a capacitor). Due to the phase difference of 180 degrees between the voltage dropped across each of these, energy is effectively continually transferred from one component to the other — the circuit is an oscillator. Once the oscillations begin, if we remove the voltage driving source, the oscillations would continue indefinitely in the absence of any resistance within the circuit. However, all circuits have some resistance, so real oscillator circuits have a finite Q-factor. In principle, if we could add a negative resistance into the circuit to counteract the stray resistance of the components, we could greatly increase the circuit's Q-factor. This is done by adding a resonant tunneling diode into the LC circuit, and ensuring that it is operating in the middle of its NDR region. This is illustrated below. In recent years, the tunnel diode has been replaced by digital components which are more reliable and which have significantly better performance.



Typical circuit utilising a tunnel diode. The voltage source V is used to set the diode operating in the NDR region, and to start the oscillation. It also provides the energy to sustain the oscillation of the circuit. The oscillation frequency is $\left(\frac{1}{2\pi\sqrt{LC}}\right)$.

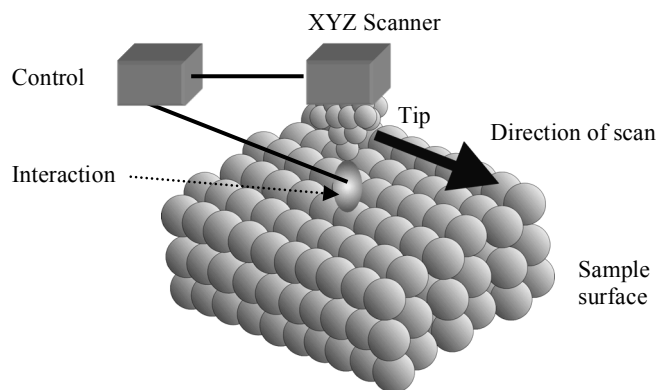
Assessor's comments:

This was very well answered in general. Almost all candidates drew the correct band structure of the resonant tunneling diode and understood its operation. A number of candidates over-complicated part b(ii), and attempted to calculate the transmission probability for a tunneling barrier, even though that is not what was asked for.

4.

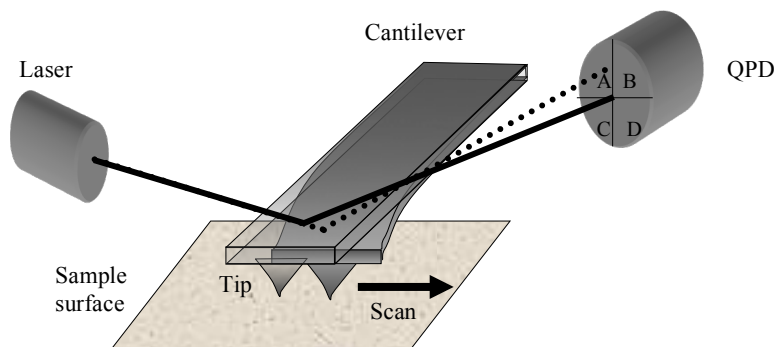
(a)

The basic principle behind the operation of all SPMs is that a sharp probe tip is scanned in close proximity to a sample surface, whilst some interaction between the two is used to generate an image of the surface. Central to this is a feedback loop that controls the tip-sample distance during scanning in order to maintain a constant interaction, as shown in the figure below. Different types of SPM utilize different interactions, and as a result, map different properties of the system under investigation.

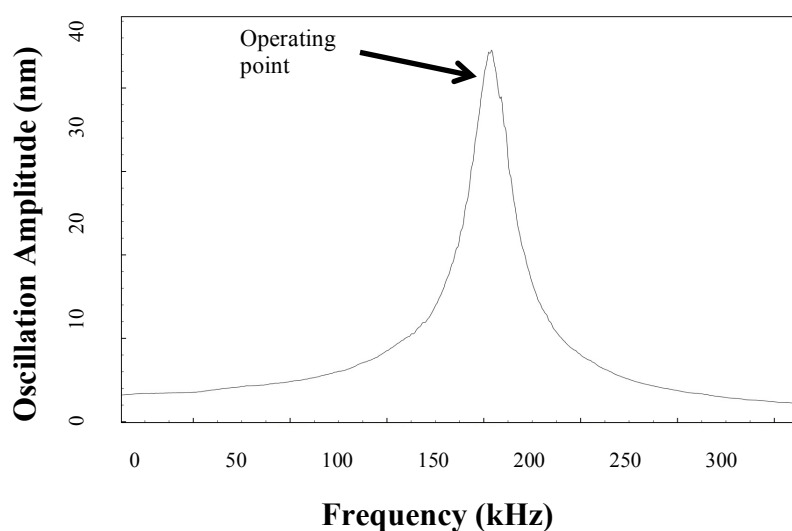


In atomic force microscopy which was developed a few years after the STM, the interaction between tip and sample is based on forces rather than on currents as is the case in the STM. These forces are usually sensed by placing the tip on a micro-machined cantilever beam (these are now mass-produced and may be purchased for a few dollars), the deflection of which is measured using a position-sensitive detector. The simplest way to implement this is to use the “*beam deflection*” method, whereby a laser is focused on the cantilever near the tip end, and as the cantilever bends, the reflected laser beam will move. This motion can easily be detected with a quadrant photodiode (QPD), as illustrated in the figure below.

In this way and using an off-the-shelf laser and photodiode, it is possible to detect cantilever deflections of the order 0.01 nm. AFM has also demonstrated atomic resolution capability in recent years. There exist many different types of force at the nanoscale, including friction, van der Waals, magnetic, electrical and thermal, among others. Different forces can be selectively measured simply by choosing a suitable tip.



In tapping mode, the cantilever is oscillated just below its resonance frequency. The oscillation amplitude is rather large, at several tens of nm. This means the cantilever has enough energy to prevent the tip snapping onto the surface or getting trapped in the contamination layer. It also means that the tip “samples” the entire force gradient all the way from far away to contact, so the force changes from attractive to repulsive, making quantitative measurements of the force impossible. Distance regulation and hence imaging is typically done by maintaining constant oscillation amplitude, usually at around 90–95% of the free amplitude (i.e. the amplitude when the tip is far away from the sample), as shown in the figure below. As an imaging technique, this is perhaps the most commonly used one now, as it has a very good resolution at the same time as having very low lateral forces on the sample. This is the technique of choice for looking at soft matter (mostly biological material).



Resonance curve of a typical intermittent-contact mode AFM cantilever. A typical operating point is indicated on the plot. The difference between non-contact mode and intermittent contact mode is mainly in terms of the operating point and the free oscillation amplitude.

In standard operation, the phase of the cantilever oscillation is monitored at the same time as the amplitude. Phase images, whilst again extremely difficult to quantify, reveal material differences. This is useful when imaging samples, particularly copolymers or self-assembled monolayers with little or no measurable topographic variation, but with distinctly different materials. Tapping-mode can also be used under liquid environments, although the reduced Q-factor of the cantilever due to hydrodynamic damping reduces the sensitivity. Tapping-mode is the most commonly used mode of operation of the AFM today, as it lends itself to imaging of both hard and soft samples.

(b) Bond-level resolution has been achieved by functionalizing the AFM tip, and by operating in non-contact mode under UHV conditions, and generally at low (liquid Nitrogen) temperatures. In non-contact mode, the cantilever is oscillated just above the resonance frequency at an amplitude of typically a fraction of a nm, and the frequency shift is monitored and used as the feedback control signal. The tip is functionalized by picking up a molecule, usually by picking one up from the surface under study. Experiments have shown that by adding a CO molecule to the tip apex,

the spatial resolution of the resulting images is high enough to be able to resolve the individual bonds between atoms, hence bond-level resolution, on the order of 0.1 nm. By comparison, the resolution of STM is around 0.2 nm, at the atomic scale, so not sufficient to observe bonds.

(c)

(i) Phase imaging could be used to distinguish between the polymers A & B, and as they will have different mechanical & chemical properties, there will be a contrast in the phase between both materials. This is not quantitative, and cannot be used to uniquely determine which is which material, as the phase contrast is a complex function of setpoint, frequency and other forces present, and can easily become inverted.

(ii) One could operate in contact mode and measure the friction on each polymer – generally the coefficient of static friction is known for materials, so it is possible to determine which is which. Alternatively, force spectroscopy could be employed, and it could be determined which polymer is harder, again something that is often known. A final option would be to combine optical spectroscopy, e.g. Raman spectroscopy with AFM, as each polymer will have a unique signature.

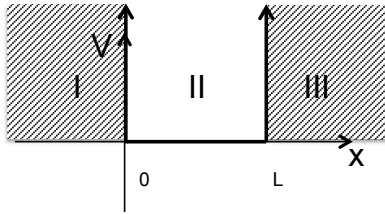
Assessor's comments:

This was not well-answered in general and was unpopular, probably as it was a bit more descriptive than many of the other questions (however, it was favoured by the graduate students taking the module). Few students were able to describe tapping mode AFM in sufficient detail, and the answers were too general. A disappointing set of answers.

5.
(a)

1. Bound states – electron in an infinite potential well

Consider the situation whereby the electron is in a “Potential well” of infinite height, i.e.:



In regions I & III, the potential is infinite. That means there is no possibility of finding the particle there, so it must be confined to region II. What is its configuration, i.e. can the particle have any energy and sit in any position within the well?

The form of the potential is:

$$V = 0 \text{ for } 0 < x < L$$

$$V = \infty \text{ for } x < 0, x > L$$

Schrödinger's equation in region II is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_I(x) = E \psi_I(x)$$

$$\psi(x) = A e^{ikx} + B e^{-ikx} \quad \text{where } k = \frac{\sqrt{2mE}}{\hbar}$$

Since the wave-function is zero outside the well, it must also be zero just at the boundaries (for continuity).

matching at left side

$$\psi(0) = A + B \Rightarrow A = -B$$

i.e.

$$\psi(x) = A(e^{ikx} - e^{-ikx}) = A \sin(kx)$$

matching at right side

$$\psi(L) = 0 \Rightarrow A \sin(kL) = 0 \Rightarrow k = n\pi/L, \quad n = 1, 2, \dots$$

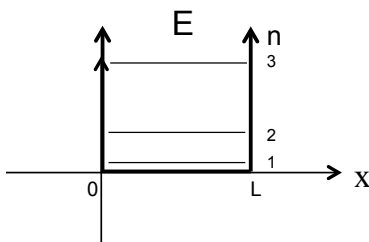
In other words, the wave-function for an electron in an infinite potential well is of the form

$$\psi(x) = A \sin(n\pi x/L)$$

To find the value of A, we need to normalise the function, i.e.

$$\int_{\text{allspace}} \Psi^* \Psi d^3r = 1$$

$$\Rightarrow \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$



This gives us a value for $A = (2/L)^{1/2}$
Remember, Energy, $E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

If $k = n\pi/L$, then the Energy levels of an electron confined in an infinite well are

$$E = \frac{\hbar^2 n^2}{8mL^2}$$

(b)

(i) The energy of the n^{th} state is

$$E_n = \frac{h^2 n^2}{8mL^2} = \frac{(6.6 \times 10^{-34})^2 n^2}{8 \times 0.3 \times 9.1 \times 10^{-31} (10^{-8})^2} = 2n^2 \times 10^{-21} \text{ J}$$

$$= 12.5n^2 \text{ meV}$$

Therefore, the energy of the first 4 states is:

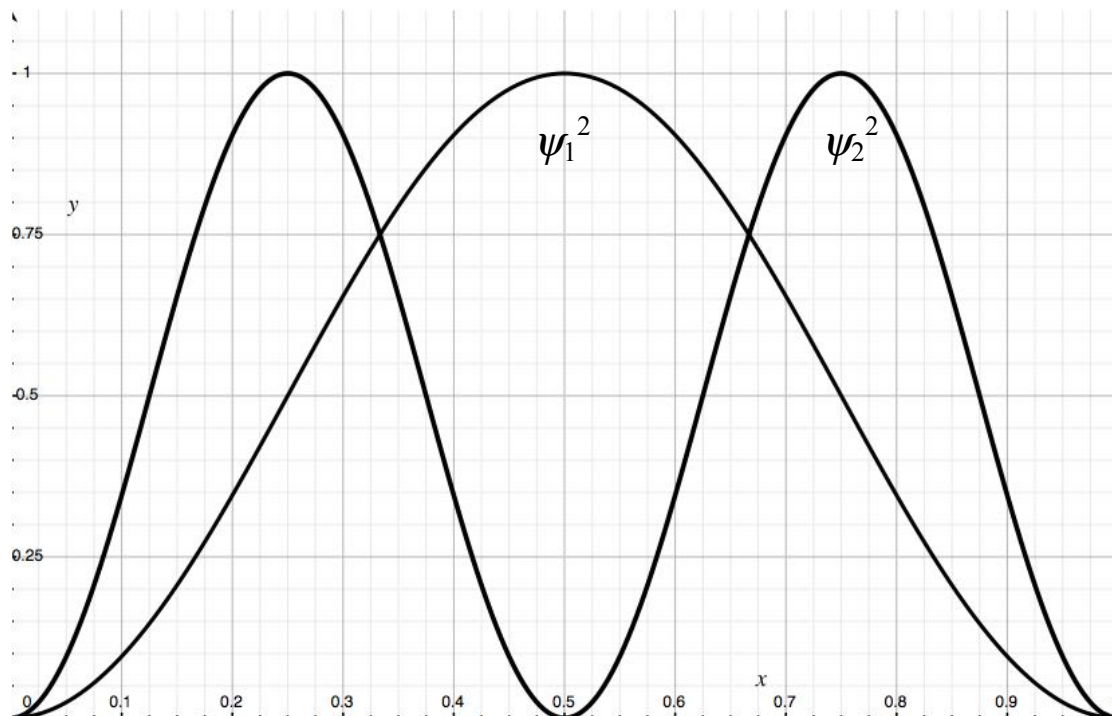
$$n_1 = 12.5 \text{ meV}, n_2 = 50 \text{ meV}, n_3 = 112.5 \text{ meV}, n_4 = 200 \text{ meV}.$$

(ii) The wavefunctions for the first two states are :

$$\psi_1 = \sqrt{\frac{2}{10^{-8}}} \sin\left(\frac{\pi x}{10^{-8}}\right) = 1.414 \times 10^4 \sin(3.14 \times 10^8 x)$$

$$\text{and } \psi_2 = \sqrt{\frac{2}{10^{-8}}} \sin\left(\frac{2\pi x}{10^{-8}}\right) = 1.414 \times 10^4 \sin(6.28 \times 10^8 x)$$

The probability densities are the wavefunctions squared, which look as follows:



(c) The boundary conditions are that (i) the wavefunctions squared and (ii) the first spatial derivatives of the wavefunctions are continuous at the boundaries. The significance of these is (i) the wavefunction squared is a measure of the probability density – the wavefunction squared at any point is equal to the probability of finding the particle at that point. As this is a probability, it must be single-valued at all points and continuous, hence the requirement for continuity at the boundary. As regards the second condition, $d^2\psi/dx^2$ is proportional to the kinetic energy of a particle, so if $d\psi/dx$ has any discontinuities, then the second derivative would be infinite, corresponding to infinite kinetic energy, which does not make physical sense.

(d) If the well is finite, then there is no longer a strict requirement that the wavefunction outside the well should be zero. As a result, the value of the wavefunction at the boundary no longer needs to be zero, and it will have a finite value. The consequence is that the wavefunctions have an exponential tail into the outside well regions. The confinement is therefore slightly less, and the energy levels will drop relative to their infinite well values. The nature of the wavefunctions outside the well is that they are exponentially decaying, and have a complex k-vector, which means they carry no momentum or energy outside the well. From the standpoint of classical mechanics, the probability of being found outside the well is zero, as a complex k-vector corresponds to a negative kinetic energy, which is unphysical.

Assessor's comments:

This question was well-answered across the board. Being quite mathematical it is favoured by the undergraduates taking the course, and they mostly demonstrated a very secure understanding of the course material.