

2.57 Nano-to-Macro Transport Processes
Fall 2004
Lecture 5

Quick review of Lecture 4

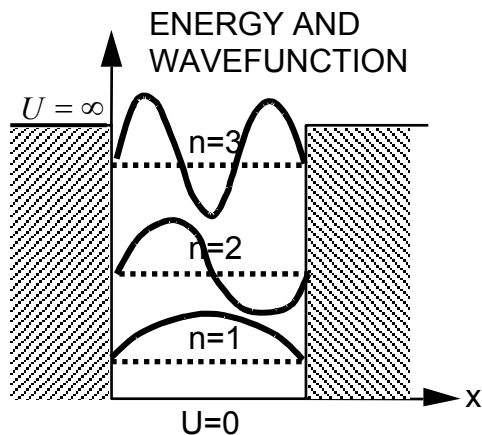
1. Free particles

The energy can be any values determined by the wavelength.

$$E = p^2 / 2m = \frac{(h / \lambda)^2}{2m} = \frac{\hbar^2 k^2}{2m}; k = 2\pi / \lambda, \hbar = h / 2\pi$$



2. Quantum well



Energy has discrete levels, and we have one quantum number n .

$$E = \frac{h^2}{8m} \frac{n^2}{D^2} \quad (n=1,2,\dots)$$

For 2D constraints, we have two quantum numbers n and l . In the discussions, the conception of “degeneracy” is introduced.

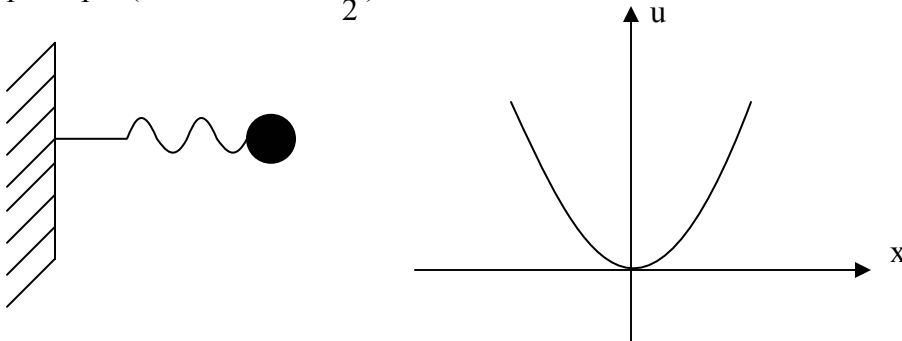
3. Spin

For electrons, we have talked about $s = \pm \frac{1}{2}$, where $s=1/2$ is called spin up and $s=-1/2$ is called spin down.

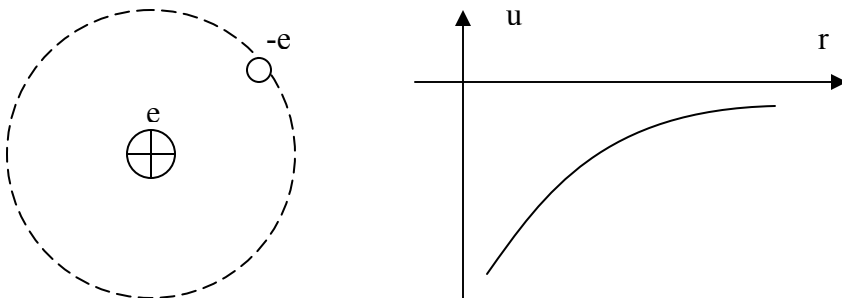
4. Harmonic oscillator

$$E_n = h\nu(n + 1/2); \nu = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$

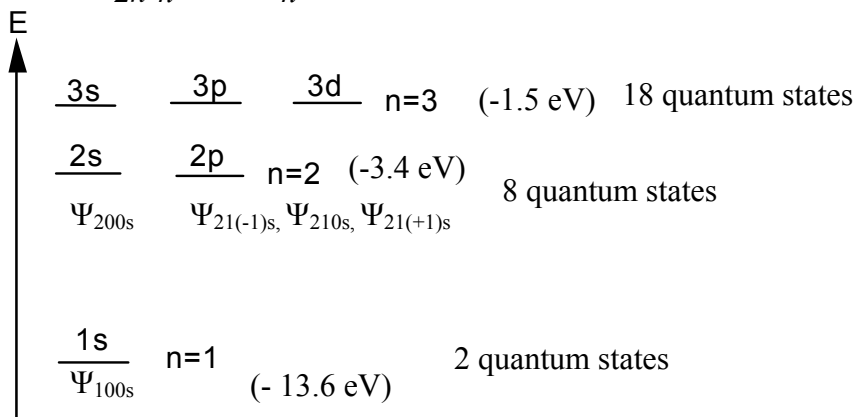
Note: the zero point (intrinsic) energy $\frac{h\nu}{2}$ is required by the Heisenberg uncertainty principle ($\langle \Delta t \rangle \langle \Delta E \rangle \geq \frac{\hbar}{2}$).



5. Electrons moving around the nucleus



$$E_n^{el} = -\frac{Mc_1^2}{2\hbar^2 n^2} = -\frac{13.6 \text{ eV}}{n^2} \quad (n \geq 1, n \geq \ell + 1 \text{ and } |m| \leq \ell, \ell = 0, 1, 2, \dots)$$



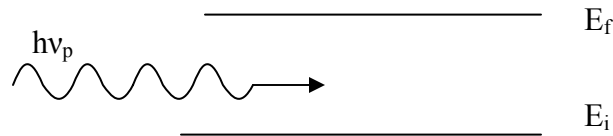
The corresponding Ψ_{nlms} are marked in the figure for some energy levels. The degeneracy follows $g(n)=2n^2$.

Note: As electrons number goes up, the orbit will split. The energy of 3d is lifted up above 4s because of the electron-electron interaction. For the element potassium (K), it has 19 electrons but the $n=3$ energy levels are not totally filled and one electron goes to the 4s orbit.

2.3.5 Energy Quantization observation

Absorption or emission of photon happening only

$$E(\text{photon}) = h\nu_p = E_f - E_i$$



The allowable energy levels of the electron-nucleus system (hydrogen atom) are

$$E_n^{el} = -\frac{13.6 \text{ eV}}{n^2}.$$

The emission occurring between $n=1,2$ is

$$h\nu_p = -13.6 \text{ eV} \left(\frac{1}{2^2} - \frac{1}{1^2} \right) \sim 10 \text{ eV}.$$

The corresponding wavelength is

$$\lambda_p = c / \nu_p.$$

Sometimes, we also use the wave number as

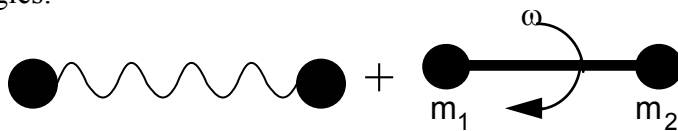
$$\frac{1}{\lambda_p} = \frac{\nu_p}{c} [\text{cm}^{-1}].$$

These units are used interchangeably and you should be able to do the conversion yourself. One good number to remember is that 1eV is 1.24 μm .

Now we are in a position to discuss the total energy of an atom or molecule. The total energy can be approximated as the summation of translational, vibrational, rotational, and electronic energies:

$$E^{tot} = E^{trans} + E^{el} + E^{vib} + E^{rot}.$$

We talk about the translational energy as a particle in a box. To simplify, for hydrogen molecules we neglect other effects and only consider the vibrational and rotational energies.



If the emission and absorption occur between two energy levels of vibration, we have

$$E_n = h\nu(n + 1/2).$$

Thus

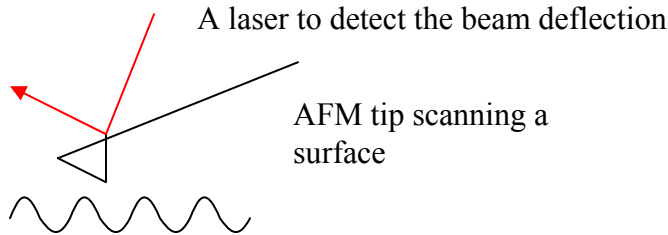
$$h\nu_p = h\nu(n_f - n_i); \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}},$$

where the reduced mass is $m = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_1}{2}$ ($m_1 = m_2$), and the selection rule states

$n_f - n_i = \pm 1$. Positive for absorption and negative for emission. We can measure the vibrational frequency from which, to deduce the spring constant. For hydrogen, the

vibrational wavelength is 2.3 micron, corresponding to a $k \sim 500$ N/m. This is a large spring constant.

Note: The large spring constant between atoms is one reason we can use atomic force microscopy to measure the topology of a surface without damaging the surface. The cantilever of the AFM has a spring constant much smaller than that of the spring constant between atoms. When a sharp tip built on the cantilever scans over a solid surface, because the spring constant of the beam is much lower than that of the atomic vibration, the beam will deform instead of deforming the atoms on the surface. The beam deformation can be further measured by a laser and the topography-scanning resolution can reach nm level and even atomic resolution.



For rotational energy, we have 2 degrees of freedom. The energy eigenvalues are

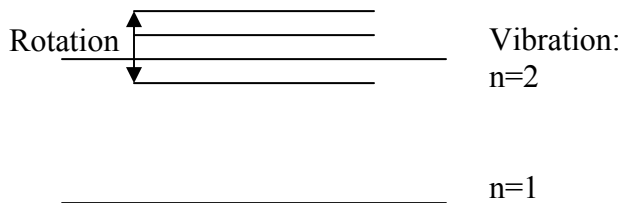
$$E_l = \frac{\hbar^2}{2I} l(l+1) = hB l(l+1) \quad (\text{for } |m| \leq l, l=0,1,2, \dots).$$

$$h\nu_p = hB[l_f(l_f+1) - l_i(l_i+1)],$$

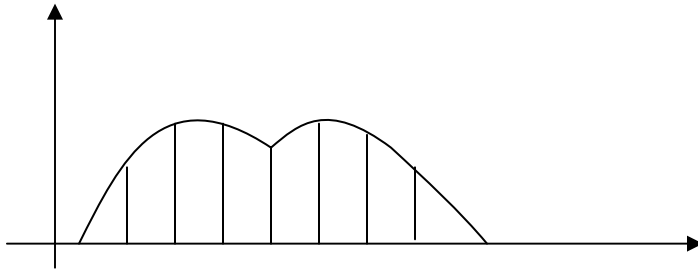
where $B=1.8e12$ Hz. Similarly we have $l_f - l_i = \pm 1, 0$. As an example, $l_f - l_i = 1$ (absorption) gives $\nu_p = 2B(l_i + 1)$. The normal wavelength for rotational energy is around $100 \mu\text{m}$ (far infrared regime), which is much larger than the emission wavelength at the room temperature ($10 \mu\text{m}$).

The energy bands are shown in the following figure, in which rotational energy accounts for small energy sub bands.

$$\nu_p = \nu_{\text{vibration}} \pm 2B(l+1).$$



The degeneracy $g(l)=2l+1$. In the following figure, the density of bands increases with increasing l .

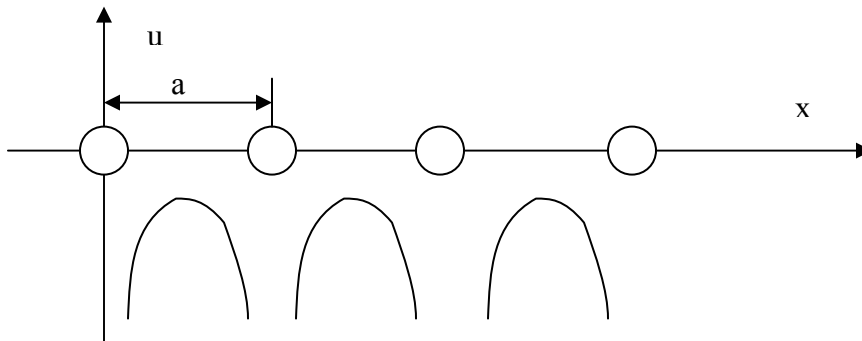


For CO_2 ($O=C=O$), three basic modes exist: symmetric stretching, asymmetric stretching, and bending. The absorption wavelength is around $10\ \mu\text{m}$, which is just the earth emission wavelength at the room temperature.

Note: the green housing effects occur when solar emission ($\sim 0.5\ \mu\text{m}$) can pass CO_2 and heat up the earth. Then the emission of the earth will be absorbed by CO_2 and the heat is trapped on earth, leading to global warming.

Chapter 3 Energy states in a solid

3.1.1 A crystal is periodic arrangement of atoms



Consider a one-dimensional lattice. The potential energies of adjacent atoms overlap and form a periodic potential field, i.e. $u(x+na) = u(x)$. Instead of the boundary conditions used for particles with constraints, now we will employ the periodicity to calculate the energy levels of electrons.

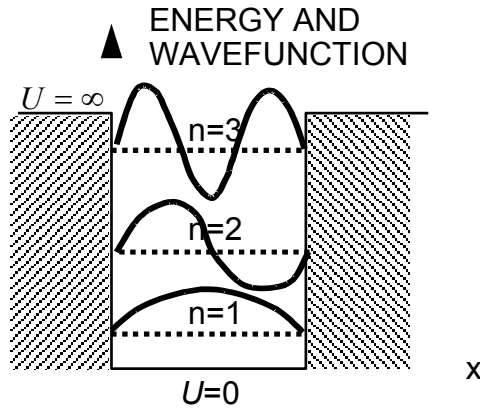
3.1.2 Possible approaches

First we will review the problems solved in Lecture 4.

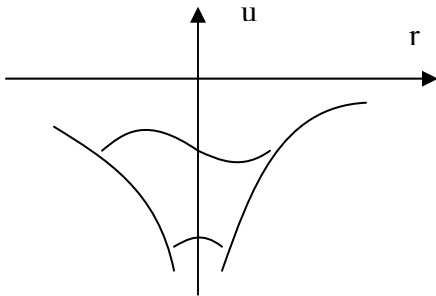
(1) Free electron $E = p^2 / 2m$



(2) Quantum well $E \propto n^2$

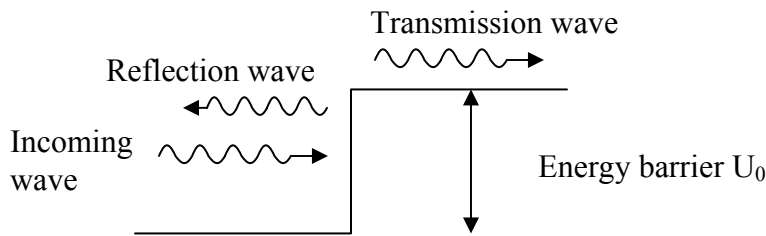


(3) Electron-nucleus system (hydrogen atom) $E_n^{el} = -\frac{13.6 eV}{n^2}$

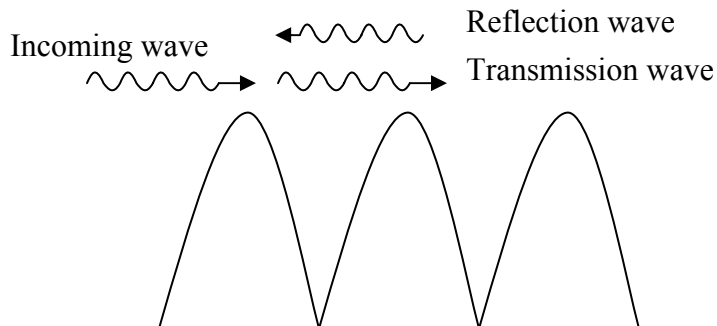


(4) Homework 2.5. At a potential step, there are reflections and transmissions of waves.

- $\left\{ \begin{array}{l} E > U_0, \text{ transmission wave } \Psi_t \text{ propagates.} \\ E < U_0, \text{ transmission wave } \Psi_t \text{ decays from the interface.} \end{array} \right.$

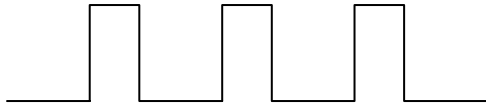


Later we will talk more about the interface influence. In the following figure, there will be interference effects of the reflection waves from different interfaces.

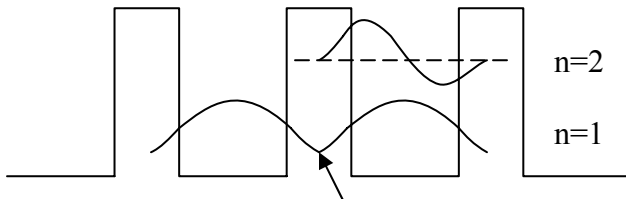
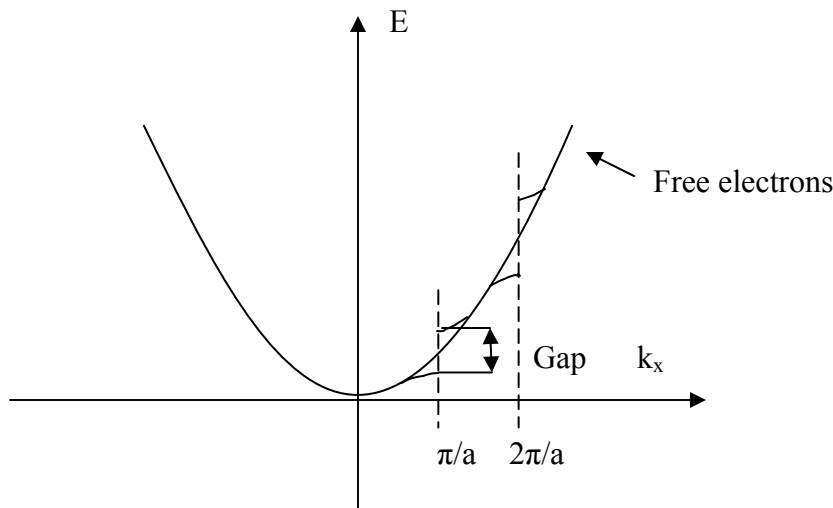


Now we will start solving the Schrödinger equation with periodic u :

(1) First we will consider periodic quantum wells with finite depth, and electrons with energy larger than the barrier function as free electrons. Basically we approximate the potential field as rectangular wells.



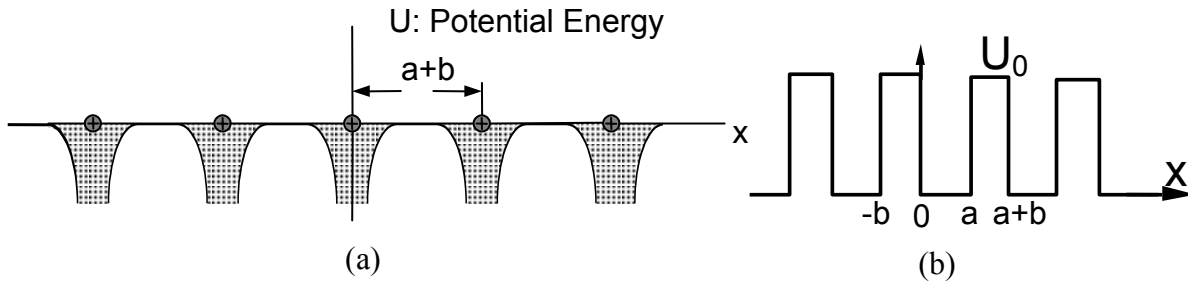
Compared with a free electron, there will be small energy gaps on the energy curve for $k_x = n\pi/a$ ($n = \pm 1, \pm 2, \dots$). No electrons are allowed on the energy levels within the gaps. This is caused by the interference effect, which we will learn in details in chapter 5.



NOT allowed by Pauli exclusion principle

Now let us go back to the quantum wells. Due to the finite depth, the wave functions will not be zero at the boundary like standing waves. Instead, they will decay exponentially from the interface. However, this indicates two wavefunctions overlap in the middle of the barrier, which conflicts with the Pauli exclusion principle. The waves will split in this situation. We will talk more about this later.

(2) Kronig-Penney model



Here we will solve the Schrödinger equation for one period

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + (U - E)\Psi = 0 \quad (0 < x < a+b).$$

Recall homework 2.5. We have one positive-direction wave and one negative-direction wave in the same region. Two coefficients A and B need to be determined in

$$\Psi = Ae^{-iKx} + Be^{iKx}.$$

For $[0, a]$ and $[a, a+b]$ regions, we have totally four unknown coefficients. The continuity boundary condition at $x=a$ only gives two equations

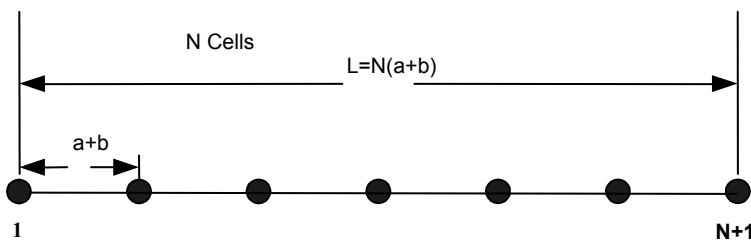
$$\Psi_1(x=a) = \Psi_2(x=a), \quad \Psi_1'(x=a) = \Psi_2'(x=a).$$

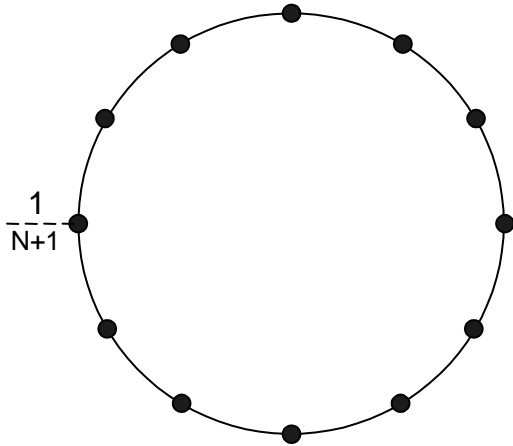
The other two equations come from the potential periodicity. Because the potential is periodic, the wavefunctions between different periods are related through the Bloch theorem, i.e.

$$\Psi[x + (a+b)n] = \Psi(x)e^{ikn(a+b)},$$

Therefore, we finally have four equations to determine the constants. Please note this k is different from K in the Ψ expression.

We now determine the value of the wvector k in the Bloch theorem, using the **Born-von Karman** periodic boundary condition. The Born-von Karman boundary condition deals with the end points of a crystal. Ordinarily, we would think that the two end points are different from the internal points. For many applications, however, distinguishing the boundary points from the internal points is not necessary, because a crystal usually has a tremendous number of lattice points (this is not true for quantum wells, quantum wires, and quantum dots). The Born-von Karman boundary condition requires that the wave functions at the two end points be equal to each other, i.e., the two end points are overlapped to form a lattice loop as shown in the figure.





First we have

$$\Psi[x + N(a + b)] = \Psi(x).$$

Using Bloch's theorem, it can be written as

$$\Psi(x) = \Psi(x) \exp[ikN(a + b)],$$

which yields

$$k = \frac{2\pi n}{N(a + b)} = \frac{2\pi n}{L} \quad (n=0, \pm 1, \pm 2, \dots),$$

where L is the length of the crystal.

To get a better idea of the solution form, now we simply let b approach zero. The following figure shows that for each wavevector k , there are many possible values for the electron energy E . These values form quasi-continuous bands as a function of k (because k itself is quasi-continuous as to be discussed latter). Because both the wavefunctions and the eigen energy for the states correspond to the wavevectors k and $[k+m(2\pi/a)]$ are identical, these are actually the same quantum state and should be counted only once. Thus, rather than plotting the energy eigenvalues for all the wavevectors, we can plot them in one period, as shown in the subsequent figure. This way of representation is called the **reduced-zone** representation. Often, only half of the band, $[0, \pi/a]$, needs to be drawn because the band is symmetric for both positive and negative wavevector values. The relationship between the energy and the wave vector is the dispersion relation.

