# ONE FREE ELECTRON

## 0. Quick review of Quantum Mechanics: the quantum aspects for the electron:

Recall from PHYS 252 that **$E = \hbar\omega$** and the **DeBroglie relation** : **$\lambda = h/p$** , where h is Planck's constant and p is the momentum (p=mv) of the particle; recall also that for sine waves $k = 2\pi/\lambda$, so that: $k = 2\pi/\lambda = 2\pi p/h = p/\hbar$ ; or **$p = \hbar k$** .

For a free electron (no potential energy): $E = KE = \frac{1}{2}mv^2 = p^2/2m = \hbar^2k^2/2m$. Schrodinger's Equation can be "derived" from this relation with the idea of operators. For a nice free wave, we would have $\psi(x,t) = C\sin(kx-\omega t)$ or $\psi(x,t) = Ce^{i(kx-\omega t)}$ . Note that $\partial\psi/\partial x = ik\psi$ and $\partial\psi/\partial x = -i\omega\psi$ [these are called operators], so that KE = E can be written **$(-\hbar^2/2m)\,[\partial^2\psi(x,t)/\partial x^2] \;=\; i\hbar[\partial\psi(x,t)/\partial t]$** . Now we just add in the PE function and we have Schrodinger's Equation.

Note that k is related to $\partial\psi/\partial x$, and p is related to k, so the momentum, p, is related to $\partial\psi/\partial x$. This means that $\psi$ must be continuous everywhere, and this leads to the boundary conditions in step 5 below.

## 1. Schrodinger's Equation:

Schrodinger's Equation was quickly developed in PHYS 252 and is more fully developed in PHYS 447 Modern Physics. It can be thought of as the basic LAW of quantum systems much as Newton's Second Law can be thought of as the basic LAW of macroscopic systems. In differential equation form, **Schrodinger's Equation** (in one dimension) is:

$$(-\hbar^2/2m)\,[\partial^2\psi(x,t)/\partial x^2] + PE(x)\,\psi(x,t) \;=\; i\hbar[\partial\psi(x,t)/\partial t] \,,$$

where $\psi(x,t)$ is the "wavefunction" which is related to the probability of finding the particle at position x at time t by:

$$\text{Prob}(x,t) \;=\; \psi^*(x,t)\,\psi(x,t) \,;$$

[$\psi$ can be complex, and $\psi^*$ is its complex conjugate so the multiplication of the two gives a real value]

And since if we add up all the probabilities we should get one:

$$\int \text{Prob}(x,t)\,dx \;=\; 1 \,; \quad \text{therefore} \quad \int_{-\infty}^{+\infty} \psi^*(x,t)\,\psi(x,t)\,dx \;=\; 1 \,.$$

To put this in context, recall that Newton's 2nd Law is a differential equation that we try to solve to get x as a function of time for a particle that exists at a point in space specified by x at a specific time specified by t, where the forces can depend on x, v, and t, and where $v = dx/dt$ and $a = dv/dt = d^2x/dt^2$ so $\Sigma F(x,dx/dt,t) = m\,d^2x/dt^2$ . We try to solve this differential equation for x(t).

For electrons, though, we have a wave/particle duality. Waves do not exist at just one point in space. Recall that light consists of photons (particles that exist at position x at time t) **and** as electromagnetic waves that exist throughout space where the electric (and magnetic) fields are functions of both space and time: E(x,t). The energy in an electromagnetic field oscillation (wave) depends on $\boldsymbol{E}\times\mathbf{B}$ (vector cross product of the electric field vector, $\boldsymbol{E}$, and the magnetic field vector, $\mathbf{B}$), and the $\mathbf{B}$ field depends on the $\boldsymbol{E}$ field, so essentially the energy depends on $\boldsymbol{E}^2$, the square of the electric field in space; so $\boldsymbol{E}^2$ is related to the probability of finding a photon at that location in space. Our wavefunction, $\Psi$, will be like the electric field, and it will be a function of both space and time, and $\Psi(x,t)$, [via $\psi^*(x,t)\,\psi(x,t)$] will be related to the probability of finding an electron at position x at time t.

**2. Setting up the equation(s) for the free electron:**

For an electron to be free, it must not be subject to any force and hence its potential energy must be zero [PE(x)=0]. Therefore for this case, Schrodinger's Equation becomes:

$$(-\hbar^2/2m)\,[\partial^2\psi(x,t)/\partial x^2] + 0 \;=\; i\hbar[\partial\psi(x,t)/\partial t]\,.$$

To solve this equation for $\psi(x,t)$, that is, to find the function, $\psi$, that satisfies this equation, we can try the technique of separation of variables. To do this, we try: $\psi(x,t) = X(x)\,T(t)$, where X(x) denotes that X is a function only of x and T(t) denotes that T is a function only of t:

$$(-\hbar^2/2m)\,[\partial^2\{X(x)\,T(t)\}/\partial x^2] \;=\; i\hbar\,[\partial\{X(x)\,T(t)\}/\partial t] \quad , \quad \text{or}$$

since T(t) does not depend on x, and X(x) does not depend on t:

$$(-\hbar^2/2m)\,T(t)\,[d^2X(x)/dx^2] \;=\; i\hbar\,X(x)\,[dT(t)/dt]\,.$$

We can get rid of the time variance on the left side by dividing out T(t) and we can get rid of the spatial variance on the right side by dividing out X(x) to get:

$$[(-\hbar^2/2m)\,T(t)\,d^2X(x)/dx^2]\,/\,[X(x)T(t)] \;=\; [ih\,X(x)\,dT(t)/dt]\,/\,[X(x)T(t)]$$

or $$[(-\hbar^2/2m)\,d^2X(x)/dx^2]\,/\,[X(x)] \;=\; [i\hbar\,dT(t)/dt]\,/\,[T(t)]\,.$$

Note that the left side depends only on x, and therefore as far as time is concerned it is a constant! Note that the right side depends only on t, therefore as far as position goes it is a constant! Therefore this one equation can be broken into two equations where we let the constant just mentioned be called E. (We call this constant E because the constant needs to have units of energy and later on we will see that it is in fact the energy of the electron!)

$$[(-\hbar^2/2m)\,d^2X(x)/dx^2]/[X(x)] \;=\; E, \quad \text{or} \quad \mathbf{d^2X(x)/dx^2 \;=\; (-2mE/\hbar^2)\,X(x)}\,; \quad \text{and}$$

$$[i\hbar\,dT(t)/dt]/[T(t)] \;=\; E\,, \quad \text{or} \quad \mathbf{dT(t)/dt \;=\; (E/i\hbar)\,T(t)}\,.$$

**3. Solving the equation for the spatial part of $\psi$ (that is, solving for X)**

$$d^2X(x)/dx^2 \;=\; (-2mE/\hbar^2)\,X(x)$$

Notice that the x differential equation says that we need a function whose second derivative gives the function back again with a constant that is negative. We know from our basic knowledge of functions that either a sine (or cosine) function or an exponential with an imaginary argument will satisfy this. Therefore we try the function:

$$X(x) = A\sin(kx+\theta)\,,$$

where A and $\theta$ are determined by the boundary conditions, and k has units of radians/meter and will be related to the $(2mE/\hbar^2)$ constant:

$$d^2[A\sin(kx+\theta)]/dx^2 \;=\; (-2mE/\hbar^2)\,[A\sin(kx+\theta)]\,,$$

or taking the derivatives:

$$-k^2 A\sin(kx+\theta) \;=\; (-2mE/\hbar^2)\,A\sin(kx+\theta)\,.$$

This equation will be true as long as $k = (2mE/\hbar^2)^{1/2}$ , or $\mathbf{E = \hbar^2k^2/2m}$ .

**Important note:** in solving the differential equation (Schrodinger's Eq.) for $\psi$ (the wavefunction), we obtained a condition on part of the solution (the value of k) – we couldn't have just any k, we could only have a k that was related to the mass of the electron and the energy of the electron: $k = (2mE/\hbar^2)^{1/2}$. From the wave-particle duality, having a condition on k is equivalent to having a condition on the momentum (since $p=\hbar k$, the de Broglie relation).

## 4. Solving the equation for the temporal part of $\psi$, that is, solving for T(t)

$$dT(t)/dt = (E/i\hbar)\,T(t) = (-iE/\hbar)\,T(t)$$

Notice that the t differential equation says that we need a function whose first derivative gives the function back again with a constant (actually, an imaginary constant). Again from our knowledge of functions we know that an exponential function has this property. Therefore we **try** the function: $\mathbf{T(t) = B\,e^{-i\omega t}}$, where B is determined by the initial conditions, and $\omega$ has units of radians/second and will be related to the constants out front:

$$d[B\,e^{-i\omega t}]/dt = (-iE/\hbar)\,B\,e^{-i\omega t},$$

or taking the derivative: $-i\,\omega\,B\,e^{-i\omega t} = (-iE/\hbar)\,B\,e^{-i\omega t}$.

This equation will be true as long as $\boldsymbol{\omega = E/\hbar = E/\hbar}$.

## 5. Applying the initial and boundary conditions

We are now in a position to put $\psi$ back together again and then to try and determine the constants from the initial and boundary conditions:

$$\psi(x,t) = X(x)\,T(t) = A\sin(kx+\theta)\,B\,e^{-i\omega t} = C\sin(kx+\theta)\,e^{-i\omega t},$$

where we have simply combined the two constants A and B into one: A*B=C, and where $k = (2mE/\hbar^2)^{1/2}$ and $\omega = E/\hbar$.

We have no real restrictions with regard to time, but we can restrict the electron so **that it must stay in the solid**. To do this, the probability of the electron being outside the solid must be zero, and hence the value of $\psi$ must also be zero if x is outside the solid. This condition can be equated to making $\psi = 0$ at the boundaries of the solid, at x=0 and x=L, because we can't have $\psi$ be discontinuous at x=0 or x=L since the momentum is related to k which is related to $d\psi/dx$ (see step 0 above) which would be essentially infinite at x=0 or x=L if $\psi$ were discontinuous there. Applying these two boundary conditions (at x=0 and x=L):

$$\psi(0,t) = C\sin(0+\theta)\,e^{-i\omega t} = 0, \quad \text{and} \quad \psi(L,t) = C\sin(kL+\theta)\,e^{-i\omega t} = 0.$$

Since sine is zero only at 0 or $n\pi$, we see that from the **first condition** that $\theta$ must be zero or $n\pi$; the only difference between zero and $n\pi$ is the possibility of a minus sign, but that could be incorporated into the constant, C. Therefore it is easiest to choose 0 for $\theta$: $\boldsymbol{\theta = 0}$.

The **second condition** indicates that $kL + \theta = n\pi$ (where n is any integer) for sine to be zero and since we know from above that $\theta=0$ already, we need to have:

$\mathbf{k = n\pi/L}$, where n is any integer.

Note that if n is zero, k is zero and $\psi$ would then be zero everywhere. This would mean that the probability of finding the electron anywhere would be zero - that is, the electron does not exist. We do not wish to consider this trivial case, so we require that **n be a non-zero integer**.

We are only left with C to determine. This can be done using the fact mentioned in step 1 above that:

$$\int_{-\infty}^{+\infty} \psi^*(x,t)\, \psi(x,t)\, dx \;=\; 1 \;=\; \int_0^L [C \sin(kx)\, e^{-i\omega t}]\, [C \sin(kx)\, e^{+i\omega t}]\, dx$$

or

$$C^2 = 1 / [\int_0^L \sin^2(kx)\, dx]\ .$$

**6. Getting energy levels for the free electron in the solid:**

From part 3 (solving Schrodinger's Equation for a free electron) we get that k is related to the energy

$$E = \hbar^2 k^2/2m\ ,$$

and from part 5 (applying the boundary conditions) we get that we can only have certain values of k:

$$k = n\pi/L\ ;$$

so putting the two together gives us the condition that we can only have certain values of the energy:

$$\mathbf{E = [n^2\hbar^2\pi^2]/[2mL^2]}\ ,$$

which says that **energy is quantized** with a quantum number, n! This is just like the E&M wave energy was quantized (in photons) and the lattice vibration energies were quantized (in phonons). Also note that this k is not limited to the first Brillion zone like the K for phonons since the electron can be anywhere in the metal, not just at the lattice points.