

## 1.4: Free-Particle Motion in Two Dimensions

### The Schrödinger Equation

*The number of dimensions depends on the number of particles and the number of spatial (and other) dimensions needed to characterize the position and motion of each particle*

Consider an electron of mass  $m$  and charge  $e$  moving on a two-dimensional surface that defines the  $x,y$  plane (perhaps the electron is constrained to the surface of a solid by a potential that binds it tightly to a narrow region in the  $z$ -direction), and assume that the electron experiences a constant potential  $V_0$  at all points in this plane (on any real atomic or molecular surface, the electron would experience a potential that varies with position in a manner that reflects the periodic structure of the surface). The pertinent time independent Schrödinger equation is:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x,y) + V_0 \psi(x,y) = E \psi(x,y)$$

Because there are no terms in this equation that **couple** motion in the  $x$  and  $y$  directions (e.g., no terms of the form  $x^a y^b$  or  $\frac{\partial}{\partial x} \frac{\partial}{\partial y}$  or  $x \frac{\partial}{\partial y}$ ), separation of variables can be used to write  $\phi$  as a product  $\phi(x,y)=A(x)B(y)$ . Substitution of this form into the Schrödinger equation, followed by collecting together all  $x$ -dependent and all  $y$ -dependent terms, gives;

$$-\frac{\hbar^2}{2m} A^{-1} \frac{\partial^2 A}{\partial x^2} - \frac{\hbar^2}{2m} B^{-1} \frac{\partial^2 B}{\partial y^2} = E - V_0$$

Since the first term contains no  $y$ -dependence and the second contains no  $x$ -dependence, both must actually be constant (these two constants are denoted  $E_x$  and  $E_y$ , respectively), which allows two separate Schrödinger equations to be written:

$$\begin{aligned} \frac{-\hbar^2}{2m} A^{-1} \frac{\partial^2 A}{\partial x^2} &= E_x, \text{ and} \\ \frac{-\hbar^2}{2m} B^{-1} \frac{\partial^2 B}{\partial y^2} &= E_y \end{aligned}$$

The total energy  $E$  can then be expressed in terms of these separate energies  $E_x$  and  $E_y$  as  $E_x + E_y = E - V_0$ . Solutions to the  $x$ - and  $y$ - Schrödinger equations are easily seen to be:

$$\begin{aligned} A(x) &= e^{ix\sqrt{\frac{2mE_x}{\hbar^2}}} \text{ and} \\ &e^{-ix\sqrt{\frac{2mE_x}{\hbar^2}}} \\ B(y) &= e^{iy\sqrt{\frac{2mE_y}{\hbar^2}}} \text{ and} \\ &e^{-iy\sqrt{\frac{2mE_y}{\hbar^2}}} \end{aligned}$$

Two independent solutions are obtained for each equation because the  $x$ - and  $y$ -space Schrödinger equations are both second order differential equations.

### Boundary Conditions

The boundary conditions, not the Schrödinger equation, determine whether the eigenvalues will be discrete or continuous

If the electron is entirely unconstrained within the  $x,y$  plane, the energies  $E_x$  and  $E_y$  can assume any value; this means that the experimenter can 'inject' the electron onto the  $x,y$  plane with any total energy  $E$  and any components  $E_x$  and  $E_y$  along the two axes

as long as  $E_x + E_y = E$ . In such a situation, one speaks of the energies along both coordinates as being 'in the continuum' or 'not quantized'.

In contrast, if the electron is constrained to remain within a fixed area in the x,y plane (e.g., a rectangular or circular region), then the situation is qualitatively different. Constraining the electron to any such specified area gives rise to so-called boundary conditions that impose additional requirements on the above A and B functions. These constraints can arise, for example, if the potential  $V_0(x,y)$  becomes very large for x,y values outside the region, in which case, the probability of finding the electron outside the region is very small. Such a case might represent, for example, a situation in which the molecular structure of the solid surface changes outside the enclosed region in a way that is highly repulsive to the electron.

For example, if motion is constrained to take place within a rectangular region defined by  $0 \leq x \leq L_x$ ;  $0 \leq y \leq L_y$ , then the continuity property that all wavefunctions must obey (because of their interpretation as probability densities, which must be continuous) causes A(x) to vanish at 0 and at  $L_x$ . Likewise, B(y) must vanish at 0 and at  $L_y$ . To implement these constraints for

A(x), one must linearly combine the above two solutions  $e^{ix\sqrt{\frac{2mE_x}{\hbar^2}}}$  and  $e^{-ix\sqrt{\frac{2mE_x}{\hbar^2}}}$  to achieve a function that vanishes at x=0:

$$A(x) = e^{ix\sqrt{\frac{2mE_x}{\hbar^2}}} - e^{-ix\sqrt{\frac{2mE_x}{\hbar^2}}}$$

One is allowed to linearly combine solutions of the Schrödinger equation that have the same energy (i.e., are degenerate) because Schrödinger equations are linear differential equations. An analogous process must be applied to B(y) to achieve a function that vanishes at y=0:

$$B(y) = e^{iy\sqrt{\frac{2mE_y}{\hbar^2}}} - e^{-iy\sqrt{\frac{2mE_y}{\hbar^2}}}$$

Further requiring A(x) and B(y) to vanish, respectively, at  $x=L_x$  and  $y=L_y$ , gives equations that can be obeyed only if  $E_x$  and  $E_y$  assume particular values:

$$e^{iL_x\sqrt{\frac{2mE_x}{\hbar^2}}} - e^{-iL_x\sqrt{\frac{2mE_x}{\hbar^2}}} = 0 \text{ and } e^{iL_y\sqrt{\frac{2mE_y}{\hbar^2}}} - e^{-iL_y\sqrt{\frac{2mE_y}{\hbar^2}}} = 0$$

These equations are equivalent to

$$\sin\left(iL_x\sqrt{\frac{2mE_x}{\hbar^2}}\right) = \sin\left(iL_y\sqrt{\frac{2mE_y}{\hbar^2}}\right) = 0$$

Knowing that  $\sin(\theta)$  vanishes at  $\theta = n\pi$ , for  $n=1,2,3,\dots$ , (although the  $\sin(n\pi)$  function vanishes for  $n=0$ , this function vanishes for all x or y, and is therefore unacceptable because it represents zero probability density at all points in space) one concludes that the energies  $E_x$  and  $E_y$  can assume only values that obey:

$$L_x\sqrt{\frac{2mE_x}{\hbar^2}} = n_x\pi$$

$$L_y\sqrt{\frac{2mE_y}{\hbar^2}} = n_y\pi, \text{ or}$$

$$E_x = \frac{n_x^2\pi^2\hbar^2}{2mL_x^2}, \text{ and}$$

$$E_y = \frac{n_y^2\pi^2\hbar^2}{2mL_y^2}, \text{ with } n_x \text{ and } n_y = 1,2,3,\dots$$

It is important to stress that it is the imposition of boundary conditions, expressing the fact that the electron is spatially constrained, that gives rise to quantized energies. In the absence of spatial confinement, or with confinement only at  $x=0$  or  $L_x$  or only at  $y=0$  or  $L_y$ , quantized energies would not be realized.

In this example, confinement of the electron to a finite interval along both the  $x$  and  $y$  coordinates yields energies that are quantized along both axes. If the electron were confined along one coordinate (e.g., between  $0 \leq x \leq L_x$ ) but not along the other (i.e.,  $B(y)$  is either restricted to vanish at  $y=0$  or at  $y=L_y$  or at neither point), then the total energy  $E$  lies in the continuum; its  $E_x$  component is quantized but  $E_y$  is not. Such cases arise, for example, when a linear triatomic molecule has more than enough energy in one of its bonds to rupture it but not much energy in the other bond; the first bond's energy lies in the continuum, but the second bond's energy is quantized.

Perhaps more interesting is the case in which the bond with the higher dissociation energy is excited to a level that is not enough to break it but that is in excess of the dissociation energy of the weaker bond. In this case, one has two degenerate states- i. the strong bond having high internal energy and the weak bond having low energy ( $\psi_1$ ), and ii. the strong bond having little energy and the weak bond having more than enough energy to rupture it ( $\psi_2$ ). Although an experiment may prepare the molecule in a state that contains only the former component (i.e.,  $\psi = C_1\psi_1 + C_2\psi_2$  with  $C_1 \ll C_2$ ), coupling between the two degenerate functions (induced by terms in the Hamiltonian  $\mathbf{H}$  that have been ignored in defining  $\psi_1$  and  $\psi_2$ ) usually causes the true wavefunction  $\Psi = e^{\left(\frac{-itH}{\hbar}\right)}\psi$  to acquire a component of the second function as time evolves. In such a case, one speaks of internal vibrational energy flow giving rise to unimolecular decomposition of the molecule.

### 3. Energies and Wavefunctions for Bound States

*For discrete energy levels, the energies are specified functions that depend on quantum numbers, one for each degree of freedom that is quantized*

Returning to the situation in which motion is constrained along both axes, the resultant total energies and wavefunctions (obtained by inserting the quantum energy levels into the expressions for  $A(x)B(y)$ ) are as follows:

$$E_x = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2},$$

and

$$E_y = \frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2},$$

$$E = E_x + E_y,$$

$$\psi(x, y) = \left( \sqrt{\frac{1}{2L_x}} \right) \left( \sqrt{\frac{1}{2L_y}} \right) \left[ e^{\frac{in_x \pi x}{L_x}} - e^{\frac{-in_x \pi x}{L_x}} \right] \left[ e^{\frac{in_y \pi y}{L_y}} - e^{\frac{-in_y \pi y}{L_y}} \right]$$

with  $n_x$  and  $n_y = 1, 2, 3, \dots$

The two  $\sqrt{\frac{1}{2L}}$  factors are included to guarantee that  $\psi$  is normalized:

$$\int |\psi(x, y)|^2 dx dy = 1.$$

Normalization allows  $|\psi(x, y)|^2$  to be properly identified as a probability density for finding the electron at a point  $x, y$ .

### 4. Quantized Action Can Also be Used to Derive Energy Levels

There is another approach that can be used to find energy levels and is especially straightforward to use for systems whose Schrödinger equations are separable. The so-called classical **action** (denoted  $S$ ) of a particle moving with momentum  $\mathbf{p}$  along a path leading from initial coordinate  $\mathbf{q}_i$  at initial time  $t_i$  to a final coordinate  $\mathbf{q}_f$  at time  $t_f$  is defined by:

$$S = \int_{\mathbf{q}_i, t_i}^{\mathbf{q}_f, t_f} \mathbf{p} \cdot d\mathbf{q}$$

Here, the momentum vector  $\mathbf{p}$  contains the momenta along all coordinates of the system, and the coordinate vector  $\mathbf{q}$  likewise contains the coordinates along all such degrees of freedom. For example, in the two-dimensional particle in a box problem considered above,  $\mathbf{q} = (x, y)$  has two components as does  $\mathbf{p} = (p_x, p_y)$ , and the action integral is:

$$S = \int_{x_i, y_i, t_i}^{x_f, y_f, t_f} (p_x dx + p_y dy).$$

In computing such actions, it is essential to keep in mind the sign of the momentum as the particle moves from its initial to its final positions. An example will help clarify these matters.

For systems such as the above particle in a box example for which the Hamiltonian is separable, the action integral decomposed into a sum of such integrals, one for each degree of freedom. In this two-dimensional example, the additivity of  $H$ :

$$\begin{aligned} H &= H_x + H_y = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + V(x) + V(y) \\ &= \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + V(y) \end{aligned}$$

means that  $p_x$  and  $p_y$  can be independently solved for in terms of the potentials  $V(x)$  and  $V(y)$  as well as the energies  $E_x$  and  $E_y$  associated with each separate degree of freedom:

$$\begin{aligned} p_x &= \pm \sqrt{2m(E_x - V(x))} \\ p_y &= \pm \sqrt{2m(E_y - V(y))}; \end{aligned}$$

the signs on  $p_x$  and  $p_y$  must be chosen to properly reflect the motion that the particle is actually undergoing. Substituting these expressions into the action integral yields:

$$\begin{aligned} S &= S_x + S_y \\ &= \int_{x_i, t_i}^{x_f, t_f} \pm \sqrt{2m(E_x - V(x))} dx + \int_{y_i, t_i}^{y_f, t_f} \pm \sqrt{2m(E_y - V(y))} dy. \end{aligned}$$

The relationship between these classical action integrals and existence of quantized energy levels has been shown to involve equating the classical action for motion on a closed path (i.e., a path that starts and ends at the same place after undergoing motion away from the starting point but eventually returning to the starting coordinate at a later time) to an integral multiple of Planck's constant:

$$S_{\text{closed}} = \int_{\mathbf{q}_i, t_i}^{\mathbf{q}_f = \mathbf{q}_i, t_f} \mathbf{p} \cdot d\mathbf{q} = nh \quad (n = 1, 2, 3, 4, \dots).$$

Applied to each of the independent coordinates of the two-dimensional particle in a box problem, this expression reads:

$$\begin{aligned} n_x h &= \int_{x=0}^{x=L_x} \sqrt{2m(E_x - V(x))} dx + \int_{x=L_x}^{x=0} -\sqrt{2m(E_x - V(x))} dx \\ n_y h &= \int_{y=0}^{y=L_y} \sqrt{2m(E_y - V(y))} dy + \int_{y=L_y}^{y=0} -\sqrt{2m(E_y - V(y))} dy. \end{aligned}$$

Notice that the sign of the momenta are positive in each of the first integrals appearing above (because the particle is moving from  $x = 0$  to  $x = L_x$ , and analogously for y-motion, and thus has positive momentum) and negative in each of the second integrals (because the motion is from  $x = L_x$  to  $x = 0$  (and analogously for y-motion) and thus with negative momentum). Within the region bounded by  $0 \leq x \leq L_x$ ;  $0 \leq y \leq L_y$ , the potential vanishes, so  $V(x) = V(y) = 0$ . Using this fact, and reversing the upper and lower limits, and thus the sign, in the second integrals above, one obtains:

$$n_x h = 2 \int_{x=0}^{x=L_x} \sqrt{2mE_x} dx = 2\sqrt{2mE_x} L_x$$

$$n_y h = 2 \int_{y=0}^{y=L_y} \sqrt{2mE_y} dy = 2\sqrt{2mE_y} L_y.$$

Solving for  $E_x$  and  $E_y$ , one finds:

$$E_x = \frac{(n_x h)^2}{8mL_x^2}$$

$$E_y = \frac{(n_y h)^2}{8mL_y^2}$$

These are the same quantized energy levels that arose when the wavefunction boundary conditions were matched at  $x = 0$ ,  $x = L_x$  and  $y = 0$ ,  $y = L_y$ . In this case, one says that the Bohr-Sommerfeld quantization condition:

$$nh = \int_{\mathbf{q}_i; t_i}^{\mathbf{q}_f; t_f} \mathbf{q} \cdot d\mathbf{q}$$

has been used to obtain the result.

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