9 Particle-in-a-box (PIB)

1. Consider a linear poly-ene.

2. The electrons are completely delocalized inside the poly-ene, but cannot leave the molecular framework.

3. Let us approximate this system by a one-dimensional box, of length L. The potential energy of the electrons inside the polyenes can be approximated by the figure below.

4. We will assume that the electron feels the same potential at all points inside the molecular framework. (An approximation that actually works pretty well and explains results in many physical systems.)

5. The particle-in-a-box is "toy" problem, but it is the starting point for many important modern-day ideas such as:

   (a) A fundamental understanding of resonance on polyenes is possible through PIB.

   (b) Frontier molecular orbital theory, which is the starting point for the Woodward Hoffman rules in organic chemistry, is very easily explained using PIB.

   (c) Quantum dots, wells, and wires become very much accessible.

   (d) And the Thomas Fermi functional in Density Functional Theory (DFT), a very powereful modern-day quantum chemistry method, has its roots in PIB.

6. So PIB is of fundamental importance.

7. Once we study the PIB, we will then derive a conceptually appealing formalism based on "scattering" to write down solutions directly for such problems (without calculus)!!

8. The box edges have infinite repulsive potentials to keep the electrons inside the molecular framework. But inside the molecular framework the electrons are completely free to move as they should be on account of resonance in poly-enes.

   So,

$$
\begin{aligned}
V(x) &= 0, & 0 \leq x \leq L \\
V(x) &= \infty, & x < 0 \ and \ x > L
\end{aligned}
\tag{9.1}
$$

9. In region II, the Hamiltonian for the system is:

$$
H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}
\tag{9.2}
$$

(note that the potential is zero).

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10. We would like to solve the time-independent Schrödinger Equation to obtain the wavefunction for the system inside the box (in region II):

$$
\begin{aligned}
H_{II}\psi(x) &= E\psi(x) \\
-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) &= E\psi(x) \\
\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) &= 0
\end{aligned}
\tag{9.3}
$$

If we make the substitution $\frac{2mE}{\hbar^2} = k^2$,

$$
\frac{\partial^2}{\partial x^2}\psi(x) + k^2\psi(x) = 0
\tag{9.4}
$$

To obtain the solution to this equation, we need to solve for $\psi(x)$. The function should have a form such that, when differentiated twice, it gives the function back multiplied by a constant. The exponential function has this property and hence lets guess the solution to this equation as $\exp\{sx\}$. Substituting this solution into the equation above leads to:

$$
s^2\psi(x) + k^2\psi(x) = 0
\tag{9.5}
$$

which leads to:
$$
s = \pm \imath k
\tag{9.6}
$$

which gives two solutions: $\exp\{\imath kx\}$ and $\exp\{-\imath kx\}$.

11. Hence the general solution has the form:

$$\psi(x) = C_1 \exp\{\imath kx\} + C_2 \exp\{-\imath kx\} \tag{9.7}$$

which reduces to

$$
\begin{aligned}
\psi(x) &= C_1 \exp\{\imath kx\} + C_2 \exp\{-\imath kx\} \\
&= C_1 \left[\cos\{kx\} + \imath \sin\{kx\}\right] + C_2 \left[\cos\{kx\} - \imath \sin\{kx\}\right] \\
&= [C_1 + C_2] \cos\{kx\} + [\imath C_1 - \imath C_2] \sin\{kx\}
\end{aligned}
\tag{9.8}
$$

and since $[C_1 + C_2]$ and $[\imath C_1 - \imath C_2]$ are also constants:

$$\psi(x) = A \cos\{kx\} + B \sin\{kx\} \tag{9.9}$$

But what is A and what is B?

12. To answer the question we must look at the so-called *boundary conditions* for the problem.

13. Let us briefly examine the regions I and III. The potential is infinite in both regions. Hence the Hamiltonian in these regions is:

$$H_I = H_{III} = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \infty \tag{9.10}$$

and the Schrödinger Equation in these regions is:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \infty\right]\psi(x) = E\psi(x) \tag{9.11}$$

The wavefunction must be finite everywhere. The only way that could happen is if

$$\psi(x) = 0 \quad x < 0 \;\; and \;\; x > L \tag{9.12}$$

14. Now lets go back to region II. **The wavefunction must be continuous everywhere.** *This means the value of $\psi(x)$ must be zero at x = 0 and x = L.*

15. Since $\psi(x) = 0$ at x = 0, $A = 0$ in Eq. (9.9). Therefore the solution is now

$$\psi(x) = B\sin\{kx\} \tag{9.13}$$

16. But $\psi(x) = 0$ at x = L. This means:

$$B \sin\{kL\} = 0 \tag{9.14}$$

and since B cannot be zero (there would be no wavefunction if that were the case!!) $\sin\{kL\}$, which can happen when $\{kL\}$ has the values $0, \pi, 2\pi, 3\pi \cdots$, or simply when $kL = n\pi$, or:

$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L} \tag{9.15}$$

where $n = 0, 1, 2, \cdots$, (whole numbers) which leads to

$$\psi(x) = B \sin\{\frac{n\pi x}{L}\} \tag{9.16}$$

17. **The wavefunction must be normalized.** Therefore

$$\int_0^L B^2 \sin^2\{\frac{n\pi x}{L}\} dx = 1 \tag{9.17}$$

If we make the substitution $\frac{n\pi x}{L} = y$, then $dx = \frac{L}{n\pi} dy$ and the integral can be rewritten as

$$B^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2\{y\} dy = 1 \tag{9.18}$$

which leads to

$$B = \sqrt{\frac{2}{L}} \tag{9.19}$$

Thus the solution to $\psi(x)$ is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\{\frac{n\pi x}{L}\} \tag{9.20}$$

18. From Eq. (9.15)

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{k^2\hbar^2}{2m} \tag{9.21}$$

19. What do we have?

   (a) Lets recap the particle in a box wavefunction and energy:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\{\frac{n\pi x}{L}\} \tag{9.22}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{9.23}$$

   (b) Even at $n = 1$, which is the lowest energy state, the particle has a finite energy. This the "zero point energy". As the length of the box gets smaller this energy gets larger!!! It also goes up as the mass decreases. (Note: $n = 0$ is not physically meaningful. Why?)

   (c) The solution is oscillatory. (Trigonometric functions are oscillatory.) Hence it contains points inside the box where the probability is zero. These points are called *nodes*. For example, $\psi_2(x)$ has a node at $x = L/2$.

   (d) Since n can only take on some values ($n = 1, 2, 3, \cdots,$) the energy expression in Eq. (9.21) can have only some discrete values. Thus *the energy is quantized*.

   (e) n can take on only some values due to the boundary conditions. See Points (15) and (16).

   (f) In fact, it is *in general true that boundary conditions enforce quantization*.

   (g) Notice further that for different values of n:

$$\langle \psi_n \mid \psi_{n'} \rangle = \int_0^L \psi_n(x)\psi_{n'}(x)dx = \int_0^L \frac{2}{L}\sin\{\frac{n\pi x}{L}\}\sin\{\frac{n'\pi x}{L}\} = \delta_{n,n'} \tag{9.24}$$

   where we have chosen to label the wavefunctions for the particle in a box in Eq. (9.20) using the "quantum number" n. Also, $\delta_{n,n'}$ is the Kronecker delta: $\delta_{n,n'} = 1$ for $n = n'$ and $\delta_{n,n'} = 0$ for $n \neq n'$. **Homework: Prove the above relation using trigonometric identities for Sine?**

   (h) This means $\{\psi_n(x)\}$ *form an orthonormal set*. (In fact these wavefunctions also form a complete set, in the sense that they satisfy the resolution of the identity (*do you remember what that is, refresh!!*). We will prove this for a general case later in the course.)

20. **Homework:**

    (a) Sketch out the first five eigenstates of the particle in a box. Do you notice any symmetry about the center of the box? Comment. (Hint: In general, there are two different kinds of functions, based on symmetry about the center. Do you see this? Comment.)

    (b) As n increases the difference between neighboring energy levels increases. Prove this statement. Hint: Calculate $(E_{n+1} - E_n)$. What happens to this expression as n increases? How about when L goes to infinity?

    (c) Write down the probability distribution $\rho_n(x) = |\psi_n(x)|^2$. How does this change as n increases? Comment on the oscillatory nature of this function with increasing n. (Does it get more or less oscillatory?) Sketch out $\rho_n(x)$ for $n = 1, 2, 3, 4$.

    (d) I have a detector through which I look into the box to locate the position of the particle. My detector, however, has a restriction. It has a least count of a. This means I cannot measure the probability of the particle with infinite precision. At any point x that I look at using the detector, I end up measuring the following quantity:

    $$\int_{x-a/2}^{x+a/2} \rho_n(x')dx' \tag{9.25}$$

    Which is the total probability inside the interval $[x - a/2, x + a/2]$. (Do you see this? This detector is similar to an electron microscope!) Lets assume for this problem that $a = L/5$. Plot the value of the function above for n=1,2,3,4,5,11,21,31,51,501. (Note: The integral above will be a function of x after integration.) Describe what you see. Comment on the generality of your result. That is, is this description always valid for any a, however small (but never zero).

21. *If you got the correct answer for the above problem, you have just derived what is known as the* **Bohr's correspondence rule between quantum mechanics and classical mechanics**. *For larger n you should see little change in the probability across the box. Hence the particle becomes more and more "classical-like" (*i.e. *devoid of the nodes which are a manifestation of quantization and wave-like behavior) as we increase n.*

22. This is actually an important result. In the early 20th century many great minds sat down to "make-sense" out of quantum mechanics. Bohr was one of them. Dirac was another and so was Heissenberg. These guys tried to see if there were certain limits where quantum theory would approach classical mechanics. In this homework you have arrived at one such general limit above.

9.1 The time-dependent Schrödinger Equation in three dimensions

$$\imath\hbar\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi(\vec{r},t) \tag{9.26}$$

The Hamiltonian for a particle whose position is given by a vector $\vec{r}$ is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V \tag{9.27}$$

In Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{9.28}$$

The *time-independent Schrödinger Equation* of the Particle-in-a-box in 3D would then look like:

$$\left[-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\}\right]\phi(x,y,z) = E\phi(x,y,z) \tag{9.29}$$

To proceed further in solving this equation, we have to assume:

$$\phi(x,y,z) = \phi_1(x)\phi_2(y)\phi_3(z) \tag{9.30}$$

Note: This is very similar to the space-time separation we used earlier to obtain the time-independent Schrödinger Equation from the time-dependent Schrödinger Equation. In that case we said that space and time are independent and write $\psi(x,t)$ as a product of $\phi(x)$ and $f(t)$. In this case we have done the same thing for x, y and z. This can always be done when a differential equation has the so-called separable form as in Eq. (9.29).

After some algebra (which I will do on the board) we will be able to reduce Eq. (9.29) to the following three equations:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi_1(x) = E_x\phi_1(x) \tag{9.31}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\phi_2(y) = E_y\phi_2(y) \tag{9.32}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\phi_3(z) = E_z\phi_3(z) \tag{9.33}$$

You will notice that these three equations are essentially similar. *And they are identical to the one-dimensional case that we already solved.* So we can write down the solution straight.

$$
\begin{aligned}
\psi_{n_x,n_y,n_z}(x,y,z) &= \phi_{1n_x}(x)\phi_{2n_y}(y)\phi_{3n_z}(z) \\
&= \sqrt{\frac{2}{L_x}\frac{2}{L_y}\frac{2}{L_z}} \times \\
&\quad \sin\{\frac{n_x\pi x}{L_x}\}\sin\{\frac{n_y\pi y}{L_y}\}\sin\{\frac{n_z\pi z}{L_z}\}
\end{aligned} \tag{9.34}
$$

$$
\begin{aligned}
E_{n_x,n_y,n_z} &= E_x + E_y + E_z \\
&= \frac{n_x^2\pi^2\hbar^2}{2mL_x^2} + \frac{n_y^2\pi^2\hbar^2}{2mL_y^2} + \frac{n_z^2\pi^2\hbar^2}{2mL_z^2} \\
&= \frac{\hbar^2}{2m}\left[\frac{\pi^2 n_x^2}{L_x^2} + \frac{\pi^2 n_y^2}{L_y^2} + \frac{\pi^2 n_z^2}{L_z^2}\right]
\end{aligned} \tag{9.35}
$$

So thats your general result for a higher dimensional particle in a box. We could also write this using the wave-vector in each direction:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left[k_x^2 + k_y^2 + k_z^2\right] \tag{9.36}$$

where $k_x = \frac{n_x\pi}{L_x}$ and similarly for y and z.

It is this final relation that will be useful for us in deriving the density of states for a quantum dot and also the Thomas Fermi functional.

It is good to think of the above expression in the following pictorial form. This is the k-space or momentum space representation of the eigenvalues of the particle in a box.

Thomas and Fermi used this idea to describe the "uniform electron gas". That is a collection of electrons inside a "uniform" (or constant or zero) potential just like the case we have constructed, that is the particle in a box. This was used by Thomas and Fermi to explain the behavior of electrons in crystals.

1. From the expression for the energy of PIB in terms of k_x, k_y, k_z, we note that exactly one state exists inside the shaded volume shown in the figure. (Exactly one state exists along the
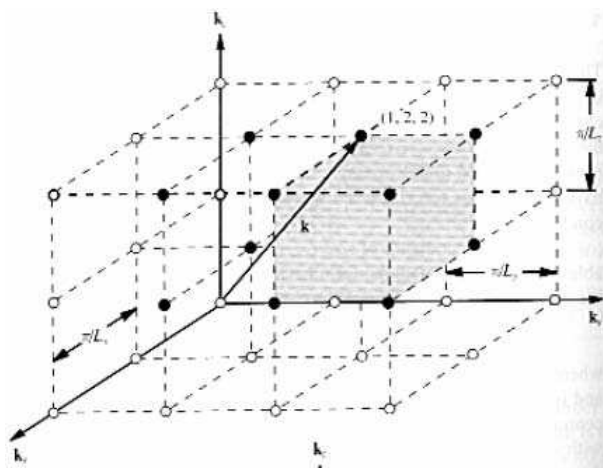
Figure 14: This figure shows a cube in k-space. The axes in k-space are k_x, k_y, k_z.

k_x-direction inside a length of $\frac{\pi}{L_x}$. Similar one state exists in the k_y-direction inside a length of $\frac{\pi}{L_y}$ and one state exists inside k_z-direction inside a length of $\frac{\pi}{L_z}$. Consequently one state exists inside this closed volume.)

2. Hence cartesian grid points on this 3D k-space represent energy levels for the particle in a box!

3. Also the energy value is proportional to the length of the **k** vector. (Note that the bracketed term in Eq. (9.36) is simply equal to $\mathbf{k} \cdot \mathbf{k}$.

4. Consequently we can construct a sphere inside this space centered around the origin and all grid points inside this sphere represent an energy level.

5. If we had a metal with say N electrons these electrons would occupy the states corresponding to these grid points upto a maximum value of energy or a maximum value of $\mathbf{k} \cdot \mathbf{k}$.

6. Hence all grid points inside a "sphere" (note this sphere is defined only on this octant since n_x, n_y and n_z have to be positive!) are occupied states. **Such a sphere is called the Fermi sphere.**

7. This gives us a nice pictorial way to think about states in the PIB. It also provides us an important machinary which we will use to derive density of states in the next section.