1 Review of analytically solvable problems

1.1 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 as follows:

$$
\begin{aligned}
V(x) &= 0, & 0 \leq x \leq L \\
V(x) &= \infty, & x < 0 \ \ and \ \ x > L
\end{aligned}
\tag{1.1.1}
$$

4. 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.

5. 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 other physical systems too!!) 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. Region I, to the left of the box ($x < 0$), Region II is the box ($0 \leq x \leq L$) and Region III to the right side of the box ($x > L$).

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

$$
H = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}
\tag{1.1.2}
$$

(note that the potential is zero).

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

$$
\begin{aligned}
H_{II}\psi(x) &= E\psi(x) \\
-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) &= E\psi(x) \\
\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) &= 0
\end{aligned}
\tag{1.1.3}
$$

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

$$
\frac{\partial^2}{\partial x^2}\psi(x) + k^2\psi(x) = 0
\tag{1.1.4}
$$

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:

$$
s^2\psi(x) + k^2\psi(x) = 0
\tag{1.1.5}
$$

which leads to:

$$
s = \pm\imath k
\tag{1.1.6}
$$

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

10. Hence the general solution has the form:

$$
\psi(x) = C_1\exp\{\imath kx\} + C_2\exp\{-\imath kx\}
\tag{1.1.7}
$$

which reduces to

$$
\begin{aligned}
\psi(x) &= C_1\exp\{\imath kx\} + C_2\exp\{-\imath kx\} \\
&= C_1\left[\cos\{kx\} + \imath\sin\{kx\}\right] + C_2\left[\cos\{kx\} - \imath\sin\{kx\}\right] \\
&= \left[C_1 + C_2\right]\cos\{kx\} + \left[\imath C_1 - \imath C_2\right]\sin\{kx\}
\end{aligned}
\tag{1.1.8}
$$

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

$$
\psi(x) = A\cos\{kx\} + B\sin\{kx\}
\tag{1.1.9}
$$

So you see that Eq. (1.1.9) and Eq. (1.1.7) are completely equivalent. We will choose Eq. (1.1.9) for further development and will soon see why. (It may be a good exercise to use Eq. (1.1.7) and continue further.)

But what is A and what is B?

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

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

$$H_I = H_{III} = \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \infty \qquad (1.1.10)$$

and the Schrödinger Equation in these regions is:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \infty\right]\psi(x) = E\psi(x) \qquad (1.1.11)$$

Lets recall a postulate of quantum mechanics: **Postulate: The wavefunction must be finite everywhere.** (Why is this important?) The only way that could happen is if

$$\psi(x) = 0 \quad x < 0 \ and \ x > L \qquad (1.1.12)$$

13. Now lets go back to region II. **Postulate: The wavefunction must be continuous everywhere.** (Why? This is slightly more tricky.) *This means the value of $\psi(x)$ must be zero at x = 0 and x = L.*

14. Since $\psi(x) = 0$ at x = 0, $A = 0$ in Eq. (1.1.9). Therefore the solution is now

$$\psi(x) = B\sin\{kx\} \qquad (1.1.13)$$

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

$$B\sin\{kL\} = 0 \qquad (1.1.14)$$

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:

$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L} \qquad (1.1.15)$$

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

$$\psi(x) = B\sin\{\frac{n\pi x}{L}\} \qquad (1.1.16)$$

16. **Postulate: The wavefunction must be normalized.** (Why?) Therefore

$$\int_0^L B^2\sin^2\{\frac{n\pi x}{L}\}dx = 1 \qquad (1.1.17)$$

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

$$B^2\frac{L}{n\pi}\int_0^{n\pi}\sin^2\{y\}dy = 1 \qquad (1.1.18)$$

which leads to

$$B = \sqrt{\frac{2}{L}} \tag{1.1.19}$$

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

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\{\frac{n\pi x}{L}\} \tag{1.1.20}$$

17. From Eq. (1.1.15)

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{\hbar^2 k^2}{2m} \tag{1.1.21}$$

18. Summary:

    (a) The particle in a box wavefunction and energy are:

    $$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\{\frac{n\pi x}{L}\} \tag{1.1.22}$$

    $$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{\hbar^2 k^2}{2m} \tag{1.1.23}$$

    (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. (1.1.21) 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 (14) and (15) above.

    (f) What happens to the energy levels when $L \to \infty$?

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

    (h) What happens to the energy levels when $n \to \infty$?

19. **Completeness and orthonormality:**

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

    $$\int_0^L \psi_n(x)\psi_{n'}(x)dx = \int_0^L dx \frac{2}{L} \sin\{\frac{n\pi x}{L}\} \sin\{\frac{n'\pi x}{L}\} = \delta_{n,n'} \equiv \langle n|n'\rangle \tag{1.1.24}$$

    where we have chosen to label the wavefunctions for the particle in a box in Eq. (1.1.20) 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?**

(b) On the last part of Eq. (1.1.24), we have defined the Dirac notation, but we will see this in much more detail, with more life, later in the class.

(c) But essentially, this means $\{\psi_n(x)\}$ *form an orthonormal set of functions*.

(d) Or to say it a different way, $\{|n\rangle\}$ represents a family of vectors that are solutions to the SE for PIB and Eq. (1.1.24) tells us that $\{|n\rangle\}$ *form an orthonormal set of vectors*. If this is not clear, it will become so when we embark on the foundation of quantum mechanics later in the semester when we probe the connections to vector spaces further.

(e) There is something even more strange to consider next. In Eq. (1.1.24), we fixed $[n, n']$ and summed over all x. (An integral is just a sum correct?) Now lets do the opposite, sum over n and fix $[x, x']$. To make life easier we will choose $x' \equiv 0$. We now look at the cosine functions and for simplicity we assume $L = \pi$.
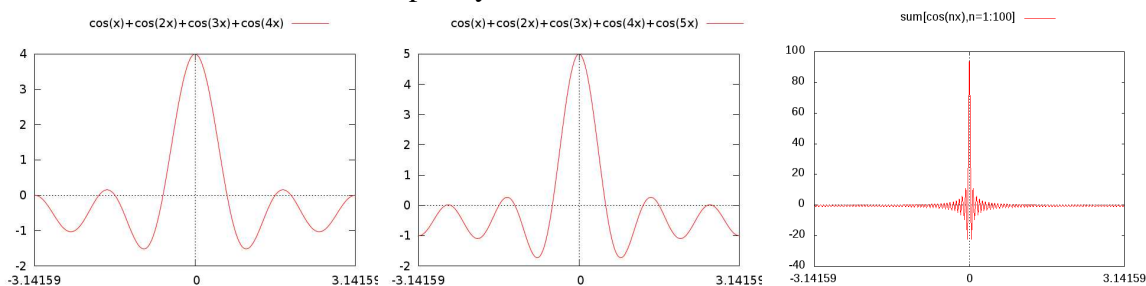

As we add more and more of these cosine functions together, the result becomes quite strongly peaked near the origin. (Try this out for yourself using your favorite plotting routine.)

What do you think this looks like when you start adding even more functions?

This leads to, what we will later see in a very general way, the idea that these functions also form a complete set. More on this later.

We will notice that the sine functions also have a similar property and for illustration we choose $x' \equiv \pi/2$.
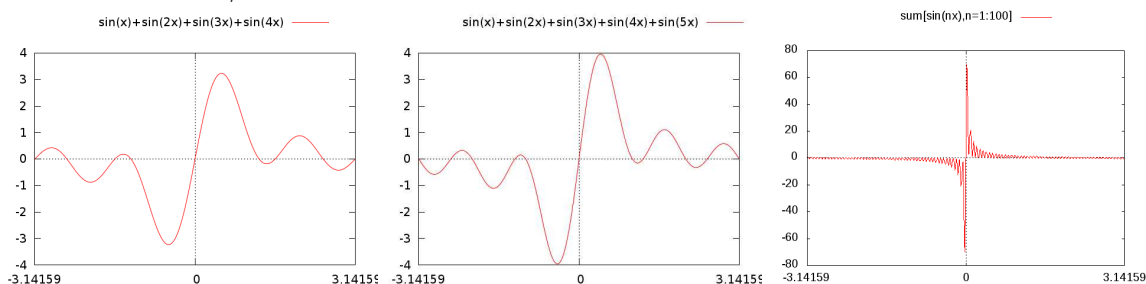
(f) How about,

$$\sum_n \exp\frac{-\imath n\pi x}{L} * \exp\frac{\imath n\pi x'}{L} = ? \qquad (1.1.25)$$

Do you see a connection to the figures above? What will it look like? We put a minus sign on the left exponential for a reason. Why do you think that is? Can you try this at home using your favorite plotting program? Or maple?

(g) If you did the last problem right you would have invented the continuous form of $\delta_{n,n'}$, or $\delta(x - x')$. Can you define that from your analysis?

(h) This would be a good time to start look at the linear algebra handouts.

(i) What happens to the expression above (Eq. (1.1.25)) when $L \to \infty$? Likewise what happens to Eq. 1.1.24 when $L \to \infty$? How would work this out? Thoughts?

20. **Sommerfeld quantization:**

(a) Let us look at the energy expression for the PIB again.

$$k = n\pi/L. \tag{1.1.26}$$

Thus k is also quantized. What is k? It is related to the wavelength. How so? For the n-th quantum state, the wavefunction is n-half sine waves inside the box. Thus the wavelength of the particle in the n-th quantum state is

$$\lambda = 2L/n. \tag{1.1.27}$$

(Can you confirm this by checking for a set of quantum numbers?) Thus,

$$k = n\pi/L = 2\pi/\lambda \tag{1.1.28}$$

or

$$\hbar k = 2\pi\hbar/\lambda = h/\lambda = p \tag{1.1.29}$$

(For the last part, we have remember what Dr. de Broglie told us.) Now, does the energy expression look obvious?

So the wavelength, the momentum and k are discrete!!

(b) The wavelength quantization was originally proposed by Sommerfeld. This was the old quantum theory that predates Schrödinger. Here we see that he had it right!! There is one more important contribution that Sommerfeld made to quantum theory. Do you know what it is?

21. **Homework: Consider the free-particle case. Here $L \to \infty$ and hence there are no boundary conditions. How does this change our solution above?**

22. **Homework: Can you confirm that the free-particle eigenstates are also momentum eigenstates? What is the eigenvalue? Did you expect this?**

23. **Homework: Do the momentum operator and the free-particle Hamilitonian commute? Check. How does your answer connect with your answer to the previous question?**

24. **Homework: Particle in a ring. How is this case different? How do you think the solutions would differ? Explain.**

1.2   The time-independent Schrödinger Equation in three dimensions

$$H\phi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\phi(\vec{r}) \tag{1.2.30}$$

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

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V \tag{1.2.31}$$

In Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.2.32}$$

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

$$\left[-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\}\right]\phi(x,y,z) = E\phi(x,y,z) \tag{1.2.33}$$

The Hamiltonian is separable and hence the product wave-function is a valid approximation. (What does the product wave-function mean in terms of probabilities? As a result what is not contained in a product wavefunction?)

$$\phi(x,y,z) = \phi_1(x)\phi_2(y)\phi_3(z) \tag{1.2.34}$$

We can reduce Eq. (1.2.33) to the following three equations:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi_1(x) = E_x\phi_1(x) \tag{1.2.35}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\phi_2(y) = E_y\phi_2(y) \tag{1.2.36}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\phi_3(z) = E_z\phi_3(z) \tag{1.2.37}$$

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.

$$
\begin{aligned}
\psi_{n_x,n_y,n_z}(x,y,z) &= \phi_{1_{n_x}}(x)\phi_{2_{n_y}}(y)\phi_{3_{n_z}}(z) \\
&= \sqrt{\frac{2}{L_x}\frac{2}{L_y}\frac{2}{L_z}} \times \\
&\quad \sin\{\frac{n_x\pi x}{L_x}\}\sin\{\frac{n_y\pi y}{L_y}\}\sin\{\frac{n_z\pi z}{L_z}\}
\end{aligned}
\tag{1.2.38}
$$

$$
\begin{aligned}
E_{n_x,n_y,n_z} &= E_x + E_y + E_z \\
&= \frac{n_x^2\pi^2\hbar^2}{2mL_x^2} + \frac{n_y^2\pi^2\hbar^2}{2mL_y^2} + \frac{n_z^2\pi^2\hbar^2}{2mL_z^2} \\
&= \frac{\hbar^2}{2m}\left[\frac{\pi^2 n_x^2}{L_x^2} + \frac{\pi^2 n_y^2}{L_y^2} + \frac{\pi^2 n_z^2}{L_z^2}\right]
\end{aligned}
\tag{1.2.39}
$$

So thats your general result for a higher dimensional particle in a box. We could also write this using the wave-vector component in each direction ($\vec{k}$ is the wave-vector, remember how this quantity is related to λ as exposed in the Sommerfeld quantization section):

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{2m} \left[k_x^2 + k_y^2 + k_z^2 \right] \tag{1.2.40}$$

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

It is good to think of the above expression in the following pictorial form. This is the k-space
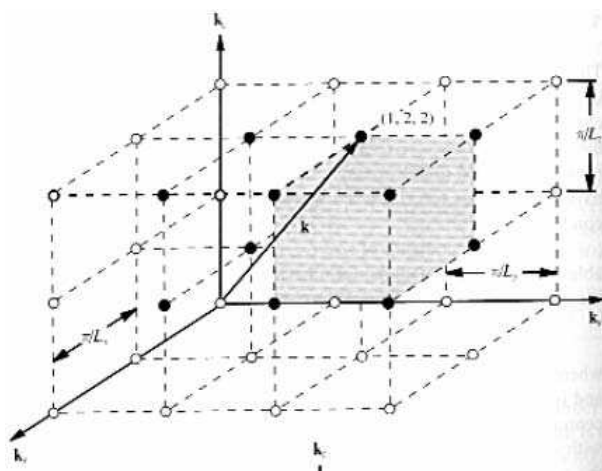

Figure 1: This figure shows a cube in k-space. The axes in k-space are k_x, k_y, k_z.

or momentum space representation of the eigenvalues of the particle in a box. (Why is it called the momentum space?)

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. (We will not go through this, but the picture above should allow you to derive the density of states on your own.)

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 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. (1.2.40) is simply equal to **k** · **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.

  Homework: We have solved the Schrödinger Equation for the free-particle case and the PIB. We know what the eigenfunctions are. I would like you to now think about how to represent these eigenfunctions in the k-space that I have described above. This is the question that summarizes your understanding of PIB and free-particle.
  Homework: Assuming you solved the problem above, discuss the implications of your solution towards uncertainty.