

QUANTUM IN **3D**: SEPARABLE SYSTEMS

1D Systems	3D Systems
\hat{x}	$\hat{\mathbf{r}} = (\hat{x} \ \hat{y} \ \hat{z}) = \hat{\mathbf{i}} \hat{x} + \hat{\mathbf{j}} \hat{y} + \hat{\mathbf{k}} \hat{z}$
$\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$	$\hat{\mathbf{p}} = (\hat{p}_x \ \hat{p}_y \ \hat{p}_z) = \hat{\mathbf{i}} \frac{\hbar}{i} \frac{\partial}{\partial x} + \hat{\mathbf{j}} \frac{\hbar}{i} \frac{\partial}{\partial y} + \hat{\mathbf{k}} \frac{\hbar}{i} \frac{\partial}{\partial z}$
$[\hat{x}, \hat{p}] = i\hbar$	$[\hat{x}, \hat{p}_x] = i\hbar \quad [\hat{y}, \hat{p}_y] = i\hbar \quad [\hat{z}, \hat{p}_z] = i\hbar$
$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$	$\hat{T} = \frac{\hat{\mathbf{p}}^2}{2m} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial z^2}$
$\psi(x)$	$\psi(x, y, z)$
$\langle \hat{O} \rangle = \int \psi^*(x) \hat{O} \psi(x) dx$	$\langle \hat{O} \rangle = \int \psi^*(x, y, z) \hat{O} \psi(x, y, z) dx dy dz$

By fiat, operators corresponding to different axes **commute** with one another.

$$\hat{x}\hat{y} = \hat{y}\hat{x} \quad \hat{p}_z\hat{y} = \hat{y}\hat{p}_z \quad \hat{p}_z\hat{p}_x = \hat{p}_x\hat{p}_z \quad \text{etc.}$$

Further, operators in one variable have no effect on functions of another:

$$\hat{x}f(y) = f(y)\hat{x} \quad \hat{p}_z f(x) = f(x)\hat{p}_z \quad f^*(z)\hat{p}_x = \hat{p}_x f^*(z) \quad \text{etc.}$$

The Time Independent Schrödinger Equation becomes:

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

∇^2 the Laplacian

$$\Rightarrow \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\hat{x}, \hat{y}, \hat{z}) \right] \psi(x, y, z) = E\psi(x, y, z)$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\hat{x}, \hat{y}, \hat{z}) \quad \text{Hamiltonian operator in 3D}$$

$\hat{H}\psi(x, y, z) = E\psi(x, y, z)$

3D Schrödinger equation
(Time Independent)

Separation of variables

$$\underline{\text{IF}} \quad V(\hat{x}, \hat{y}, \hat{z}) = V_x(\hat{x}) + V_y(\hat{y}) + V_z(\hat{z})$$

$$\begin{aligned} \text{then} \quad \hat{H}(x, y, z) &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_x(\hat{x}) \right] + \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + V_y(\hat{y}) \right] + \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + V_z(\hat{z}) \right] \\ &= \hat{H}_x + \hat{H}_y + \hat{H}_z \end{aligned}$$

⇒ Schrödinger's Eq. becomes:

$$\left[\hat{H}_x + \hat{H}_y + \hat{H}_z \right] \psi(x, y, z) = E \psi(x, y, z)$$

Then try solution of form $\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z)$
(separation of variables)

Where we assume that the 1D functions satisfy the appropriate 1D TISE:

$$\hat{H}_x \psi_x(x) = E_x \psi_x(x)$$

$$\hat{H}_y \psi_y(y) = E_y \psi_y(y)$$

$$\hat{H}_z \psi_z(z) = E_z \psi_z(z)$$

First term:

$$\begin{aligned} \hat{H}_x \psi_x(x) \psi_y(y) \psi_z(z) &= \psi_y(y) \psi_z(z) \hat{H}_x \psi_x(x) = \psi_y(y) \psi_z(z) E_x \psi_x(x) \\ &= E_x \psi_x(x) \psi_y(y) \psi_z(z) \end{aligned}$$

Same for \hat{H}_y and $\hat{H}_z \Rightarrow$

$$\begin{aligned} \hat{H} \psi &= E \psi \\ \left[\hat{H}_x + \hat{H}_y + \hat{H}_z \right] \left[\psi_x(x) \psi_y(y) \psi_z(z) \right] &= \underbrace{(E_x + E_y + E_z)}_{E = E_x + E_y + E_z} \left[\psi_x(x) \psi_y(y) \psi_z(z) \right] \end{aligned}$$

Thus, if the Hamiltonian has this special form, the eigenfunctions of the 3D Hamiltonian are just products of the eigenfunctions of the 1D Hamiltonian and the situation is equivalent to doing three separate 1D problems.

Conclusion: Wavefunctions multiply and the energies add if \hat{H} is separable into

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z.$$

The 3D product states are naturally normalized if the 1D wavefunctions are normalized:

$$\begin{aligned} \iiint \psi_x^*(x) \psi_y^*(y) \psi_z^*(z) \psi_x(x) \psi_y(y) \psi_z(z) dx dy dz = \\ \underbrace{\int \psi_x^*(x) \psi_x(x) dx}_{1} \underbrace{\int \psi_y^*(y) \psi_y(y) dy}_{1} \underbrace{\int \psi_z^*(z) \psi_z(z) dz}_{1} = 1 \end{aligned}$$

Notice that for ψ we are free to choose **any** eigenfunction, ψ_{n_x} , of \hat{H}_x together with **any** eigenfunction, ψ_{n_y} , of \hat{H}_y and **any** eigenfunction, ψ_{n_z} , of \hat{H}_z . Thus, while in 1D we usually had one quantum number, in 3D we will have three (n_x, n_y, n_z). Further, for two product states to be orthogonal, we do not have to have all three 1D functions be different. If **any one** of the three 1D wavefunctions (x,y or z) is orthogonal to its counterpart, then the two 3D wavefunctions are also orthogonal. For example, consider the two wavefunctions $\psi_{111}(x, y, z) = \psi_{x1}(x) \psi_{y1}(y) \psi_{z1}(z)$ and $\psi_{311}(x, y, z) = \psi_{x3}(x) \psi_{y1}(y) \psi_{z1}(z)$.

$$\begin{aligned} \iiint \psi_{111}^*(x, y, z) \psi_{311}(x, y, z) dx dy dz \\ \Rightarrow \iiint \psi_{x1}^*(x) \psi_{y1}^*(y) \psi_{z1}^*(z) \psi_{x3}(x) \psi_{y1}(y) \psi_{z1}(z) dx dy dz \\ \Rightarrow \underbrace{\int \psi_{x1}^*(x) \psi_{x3}(x) dx}_{0} \underbrace{\int \psi_{y1}^*(y) \psi_{y1}(y) dy}_{1} \underbrace{\int \psi_{z1}^*(z) \psi_{z1}(z) dz}_{1} = 0 \end{aligned}$$

Because the product states are orthogonal and normalized, they're orthonormal and we summarize this by writing:

$$\iiint \psi_{n_x n_y n_z}^*(x, y, z) \psi_{m_x m_y m_z}(x, y, z) dx dy dz = \delta_{n_x, m_x} \delta_{n_y, m_y} \delta_{n_z, m_z}$$

Example 1:3-D Harmonic Oscillator

Let's consider a particle in 3D subject to a Harmonic potential in x,y and z. Further, assume the force constants in each direction are different. This might be true, for example, for a particle trapped inside a protein: the resorting force for moving it in the x direction will be different from y or z because the protein has a different shape along x than y or z (see below right). Multidimensional

Harmonic potentials are also important for describing the vibrations of polyatomic molecules. For example, in HCO x might correspond to the CH stretch, y to the C-O stretch and z to the H-C-O bend.

In either case, the general potential is given by

$$V(x, y, z) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2 = V_x(x) + V_y(y) + V_z(z)$$

Now, because the potential is a sum of an x potential, a y potential and a z potential, we can easily write the

Hamiltonian down as a sum:

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

$$\hat{H}_x = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}k_x \hat{x}^2$$

$$\hat{H}_y = \frac{\hat{p}_y^2}{2m} + \frac{1}{2}k_y \hat{y}^2$$

$$\hat{H}_z = \frac{\hat{p}_z^2}{2m} + \frac{1}{2}k_z \hat{z}^2$$

where each 1D Hamiltonian describes a particle subject to a Harmonic potential with the appropriate spring constant (k_x , k_y or k_z). Based on the discussion above, we can immediately write down all the eigenfunctions and eigenvalues:

$$\psi_{n_x n_y n_z}(x, y, z) = N_x H_{n_x}(\alpha_x^{1/2} x) e^{-\frac{\alpha_x x^2}{2}} N_y H_{n_y}(\alpha_y^{1/2} y) e^{-\frac{\alpha_y y^2}{2}} \left(\frac{\alpha_z}{\pi}\right)^{\frac{1}{4}} N_z H_{n_z}(\alpha_z^{1/2} z) e^{-\frac{\alpha_z z^2}{2}}$$

$$E_{n_x n_y n_z} = \left[\left(n_x + \frac{1}{2} \right) \hbar \omega_x \right] + \left[\left(n_y + \frac{1}{2} \right) \hbar \omega_y \right] + \left[\left(n_z + \frac{1}{2} \right) \hbar \omega_z \right]$$

$$\alpha_x = \frac{(mk_x)^{1/2}}{\hbar} \quad \omega_x = \sqrt{\frac{k_x}{m}} \text{ etc.}$$

Notice again that for the 3D problem we have 3 quantum numbers, and the energy and wavefunction depend on all three simultaneously.

Degeneracies

In 3D, there are a number of interesting things that can happen that we didn't see in 1D. One example of this is that, in 3D it is possible for two different

eigenfunctions of the Hamiltonian to have the same energy. When this happens, these two states are called *degenerate*. If there are three, four... states with the same energy, they are said to be threefold, fourfold ... degenerate. This never happened for the Particle in a Box or the Harmonic Oscillator. In fact, one can show that for bound states in 1D, one never has degeneracy; every state has its own energy. However, in 3D we can find degeneracy very easily. For example, if our spring constants are all the same:

$$k_x = k_y = k_z \equiv k \quad \Rightarrow \quad \omega_x = \omega_y = \omega_z \equiv \omega$$

$$\Rightarrow E_{n_x, n_y, n_z} = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right)$$

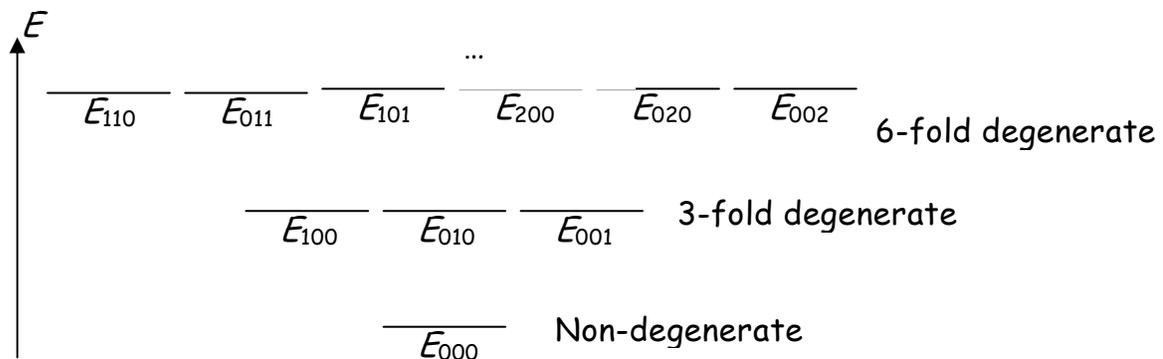
The ground state has an energy $E_{000} = \frac{3}{2}\hbar\omega$. There is only one way I can get this energy ($n_x = 0, n_y = 0, n_z = 0$), so it is not degenerate. However, there are three ways I can get the first excited state energy $\frac{5}{2}\hbar\omega$: $n_x = 1, n_y = 0, n_z = 0$, $n_x = 0, n_y = 1, n_z = 0$ or $n_x = 0, n_y = 0, n_z = 1$. So we find that if we choose all the spring constants to be equal,

$$E_{000} = \frac{3\hbar\omega}{2} \quad \text{nondegenerate level}$$

$$E_{100} = E_{010} = E_{001} = \frac{5\hbar\omega}{2} \quad \text{3-fold degenerate level}$$

etc.

We will typically draw this with a picture like:



Note the wavefunctions are distinct:

$$\psi_{100}(x, y, z) \neq \psi_{010}(x, y, z) \neq \psi_{001}(x, y, z)$$

This leads to an interesting effect. Suppose we make up a wavefunction that is a sum of two degenerate states, say

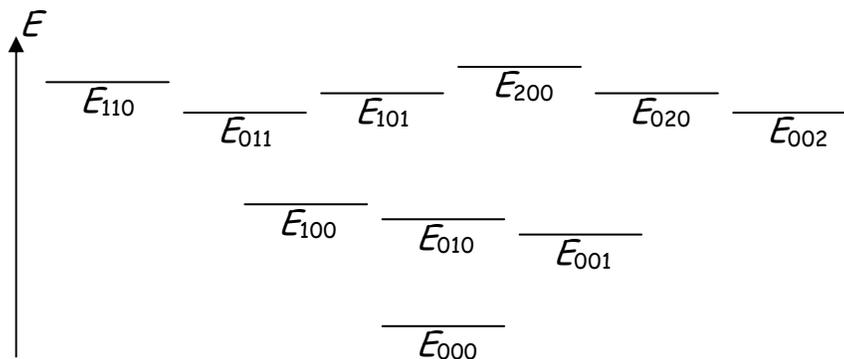
$$\psi(x, y, z) = a \psi_{010}(x, y, z) + b \psi_{001}(x, y, z)$$

where a and b are constants. Then it turns out that ψ is also an eigenstate of the Hamiltonian! To see this,

$$\begin{aligned}\hat{H}\psi &= \hat{H}(a\psi_{010} + b\psi_{001}) = a\hat{H}\psi_{010} + b\hat{H}\psi_{001} \\ &= a\frac{5\hbar\omega}{2}\psi_{010} + b\frac{5\hbar\omega}{2}\psi_{001} = \frac{5\hbar\omega}{2}(a\psi_{010} + b\psi_{001}) \\ &= \frac{5\hbar\omega}{2}\psi\end{aligned}$$

This illustrates the important point that **any sum of degenerate eigenstates is also an eigenstate of the Hamiltonian with the same eigenvalue.**

Setting the spring constants equal amounts to assuming the well is symmetric with respect to x , y and z . If the symmetry is "broken", i.e. $k_x \neq k_y \neq k_z$ then the 100, 010 and 001 states will become non-degenerate. In this case, we will usually say that the degeneracy has been "lifted" or that the degenerate states have been split. The latter language comes from the pictorial view; if the spring constants are only slightly different, then the energy levels might look like:



Here, you can see that the $n=1$ levels are *almost* degenerate (they've been "split") and the $n=2$ levels are *almost* degenerate, but not quite, because the force constants are slightly different. Notice that it is possible to break some degeneracies but keep others. For example, if we choose:

$$k_x = k_y \equiv k \neq k_z \quad \Rightarrow \quad \omega_x = \omega_y \equiv \omega \neq \omega_z$$

Then the energies become:

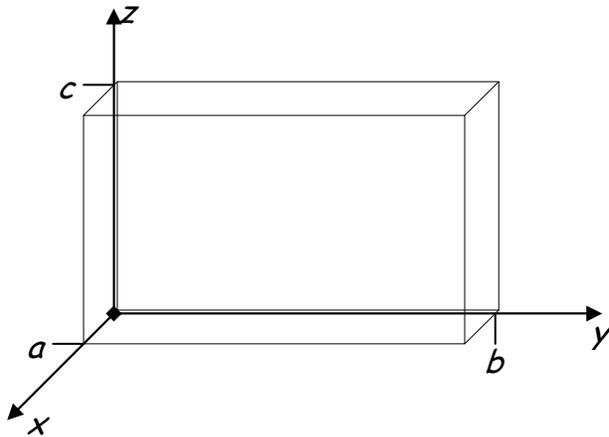
$$E_{n_x n_y n_z} = \hbar\omega(n_x + n_y + 1) + \hbar\omega_z\left(n_z + \frac{1}{2}\right)$$

and we find

$$E_{000} = \hbar\omega + \frac{1}{2}\hbar\omega_z \quad \text{nondegenerate level}$$

$$E_{100} = E_{010} = 2\hbar\omega + \frac{1}{2}\hbar\omega_z \quad \text{2-fold degenerate level}$$

$$E_{001} = \hbar\omega + \frac{3}{2}\hbar\omega_z \quad \text{nondegenerate level}$$

Example 2: Particle in 3-D box

$$V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$$

$$V_x(x) = 0 \quad 0 \leq x \leq a$$

$$V_y(y) = 0 \quad 0 \leq y \leq b$$

$$V_z(z) = 0 \quad 0 \leq z \leq c$$

$$V_x(x), V_y(y), V_z(z) = \infty \quad \text{otherwise}$$

Inside the box:

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

Outside the box:

$$\psi(x, y, z) = 0$$

We can again apply separation of variables since $\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$ where $\hat{H}_x, \hat{H}_y, \hat{H}_z$ are each 1D particle in a box Hamiltonians. So the solutions to the 3D equation are products of the 1D solutions

$$\Rightarrow \psi(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

where from the 1D problem we have the solutions

$$\psi_{n_x}(x) = \left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \left(\frac{n_x \pi x}{a} \right) \quad n_x = 1, 2, 3, \dots \quad E_{n_x} = \frac{\hbar^2 n_x^2}{8m a^2}$$

$$\psi_{n_y}(y) = \left(\frac{2}{b} \right)^{\frac{1}{2}} \sin \left(\frac{n_y \pi y}{b} \right) \quad n_y = 1, 2, 3, \dots \quad E_{n_y} = \frac{\hbar^2 n_y^2}{8m b^2}$$

$$\psi_{n_z}(z) = \left(\frac{2}{c} \right)^{\frac{1}{2}} \sin \left(\frac{n_z \pi z}{c} \right) \quad n_z = 1, 2, 3, \dots \quad E_{n_z} = \frac{\hbar^2 n_z^2}{8m c^2}$$

Where the energy is now a function of all three Quantum numbers:

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Degeneracies

Degeneracies occur in a similar fashion for the PiB. e.g. if $a = b = c$ in our 3-D box:

$$\Rightarrow E_{n_x n_y n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$E_{111} = \frac{3h^2}{8ma^2} \quad \text{is nondegenerate}$$

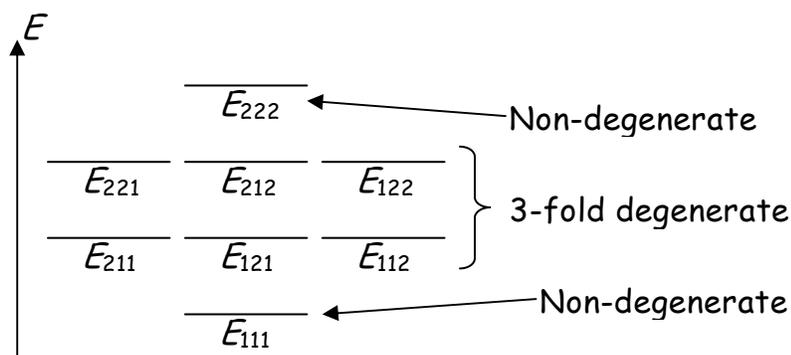
$$\psi_{111}(x, y, z) = \psi_1(x)\psi_1(y)\psi_1(z) = \left(\frac{8}{a^3}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{a}\right) \sin\left(\frac{\pi z}{a}\right)$$

But...

$$E_{211} = E_{121} = E_{112} = \frac{h^2}{8ma^2} (2^2 + 1^2 + 1^2) \quad \text{3-fold degeneracy}$$

Note the wavefunctions are again distinct:

$$\psi_{211}(x, y, z) \neq \psi_{121}(x, y, z) \neq \psi_{112}(x, y, z)$$



If the symmetry is "broken", i.e. $a \neq b \neq c$ then the degeneracy is lifted.

$$E_{112} = \frac{h^2}{8m} \left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{4}{c^2} \right) \neq E_{121} = \frac{h^2}{8m} \left(\frac{1}{a^2} + \frac{4}{b^2} + \frac{1}{c^2} \right)$$

Summary

3-D box

$$\psi_{n_x n_y n_z}(x, y, z) = \left(\frac{8}{abc} \right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad n_x = 1, 2, 3, \dots \quad n_y = 1, 2, 3, \dots \quad n_z = 1, 2, 3, \dots$$