Week ⑧

PHY 303 Quantum Mechanics
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4 Quantum mechanics in three dimensions

So far we have dealt with one spatial dimension x only (1D), for simplicity and ease of notation. Of course the real world is 3D. Luckily, most of what we learnt so far straightforwardly generalizes from 1D to 3D, as we shall discuss in this "week" segment. New physics that comes in when we go to 3D is that of angular momentum (which does not exist in 1D). We will discuss angular momentum in the subsequent week, in the context of the Hydrogen atom, which will be the main focus of this chapter.

4.1 Higher-dimensional wavefunctions

We want to preserve the basic feature that $|\Psi|^2$ gives us the probability density of the position of a particle. However that position is now a 3D vector $\mathbf{r} = [x, y, z]^T$. Same as here, we shall use **boldface** to distinguish vectors from scalars. To preserve the probability density interpretation, the wavefunction must now be a complex function in three-dimension, i.e. taking a vector-valued argument. As in the box around Eq. (1.27) we then have:

Probability density and normalisation in 3D Now $|\Psi(\mathbf{r}, t)|^2\, dV$ shall be the probability at time t to find the particle in an infinitesimal cubic volume $dV = dx\, dy\, dz$ near 3D position $\mathbf{r} = [x, y, z]^T$. Hence the normalisation becomes

$$\int d^3\mathbf{r}\, |\Psi(\mathbf{r}, t)|^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, |\Psi(x, y, z, t)|^2 = 1. \qquad (4.1)$$

Note: We can also use ket vectors to represent quantum states as before, with position space representation $\Psi(\mathbf{r}) = \langle\, \mathbf{r}\, |\, \Psi\, \rangle$. Here is one more advantage of the bra-ket notation: we do not have to worry about the number of dimensions initially. Pretty much all of week 6 and week 7 is unchanged, going from 1D to 3D.

Nextly

Operators in 3D Also the position and momentum operators now become vectors (vector operators)

$$\hat{\mathbf{r}} = \begin{bmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{bmatrix}, \quad \hat{\mathbf{p}} = \begin{bmatrix} \hat{p}_x \\ \hat{p}_y \\ \hat{p}_z \end{bmatrix} = \begin{bmatrix} -i\hbar\frac{\partial}{\partial x} \\ -i\hbar\frac{\partial}{\partial y} \\ -i\hbar\frac{\partial}{\partial z} \end{bmatrix}. \tag{4.2}$$

- Since the operators are vectors, also expectation values of operators are vectors, e.g.

$$\langle \hat{x} \rangle = \langle \Psi | \hat{\mathbf{r}} | \Psi \rangle = \begin{bmatrix} \langle \Psi | \hat{x} | \Psi \rangle \\ \langle \Psi | \hat{y} | \Psi \rangle \\ \langle \Psi | \hat{z} | \Psi \rangle \end{bmatrix} = \begin{bmatrix} \int d^3\mathbf{r}\ \Psi^*(\mathbf{r})x\Psi(\mathbf{r}) \\ \int d^3\mathbf{r}\ \Psi^*(\mathbf{r})y\Psi(\mathbf{r}) \\ \int d^3\mathbf{r}\ \Psi^*(\mathbf{r})z\Psi(\mathbf{r}) \end{bmatrix}. \tag{4.3}$$

Note each integration still is a 3D integration!

- Since we now have multiple components of the position and momentum operators, we have to revisit their commutator (compare Eq. (2.46)). You can show that

$$\left[\hat{r}_n, \hat{p}_m\right] = i\hbar\delta_{nm}, \tag{4.4}$$

using the same techniques as in Eq. (2.47) (exercise). We have used $\hat{r}_n$ to label the three components of $\hat{\mathbf{r}}$ and $\hat{p}_m$ for those of $\hat{\mathbf{p}}$.

We similarly generalize the

Schrödinger equations in 3D, which are now

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\Psi(\mathbf{r}, t), \quad \text{(TDSE)} \tag{4.5}$$

$$E_n\phi_n(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\phi_n(\mathbf{r}). \quad \text{(TISE)} \tag{4.6}$$

where we have used the

Laplacian operator:

$$\Delta = \boldsymbol{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{4.7}$$

4.1.1 Simple quantum systems in three dimensions

Most of what we discussed in section 2 straightforwardly generalizes to 3D, and we will now briefly mention how, to serve as examples for section 4.1. However since not much new physics or techniques are added here, we shall be brief. You may notice that most books do not discuss this step at all, for the same reason.

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Harmonic oscillator in 3D: In three dimensions, the harmonic oscillator potential is

$$V(\mathbf{r}) = \frac{1}{2}m\left(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right). \tag{4.8}$$

Note that this is of the <u>separable</u> form

$$V(\mathbf{r}) = V_x(x) + V_y(y) + V_z(z), \tag{4.9}$$

which is not true for all 3D potentials. However whenever the potential takes this form, it is easy to see that we can just reduce the solution of the 3D TISE (4.6) to three separate solutions of a 1D TISE (one for each dimension).

Using the argumentation around Eq. (1.56), you can see (exercise) that the 3D TISE:

$$E\phi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\phi(\mathbf{r}), \tag{4.10}$$

with $V(\mathbf{r})$ given by (4.8) and using the Ansatz $\phi(\mathbf{r}) = \varphi_{n_x}(x)\varphi_{n_y}(y)\varphi_{n_z}(z)$ is equivalent to three separate TISEs for each dimension:

$$E_{n_x}\varphi_{n_x}(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(x)\right)\varphi_{n_x}(x),$$

$$E_{n_y}\varphi_{n_y}(y) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_y(y)\right)\varphi_{n_y}(y),$$

$$E_{n_z}\varphi_{n_z}(z) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V_z(z)\right)\varphi_{n_z}(z). \tag{4.11}$$

The total energy E in Eq. (4.10) is $E = E_{n_x} + E_{n_y} + E_{n_z}$, so that we should give the eigenvalue and eigenstate in Eq. (4.10) a vector subscript $\mathbf{n} = [n_x n_y n_z]$.

- Since each 1D equation in (4.11) takes the same form as (2.42), we immediately know the solution and energy eigenvalues.

- Note that for the approach it was crucial that we can write the potential as a sum of terms for each dimension, as in (4.8). Without that, the separation of variables near Eq. (1.56) would not work.

Example 28, Quantum states of the three-dimensional oscillator: A problem with 3D states is, that it becomes difficult to draw them
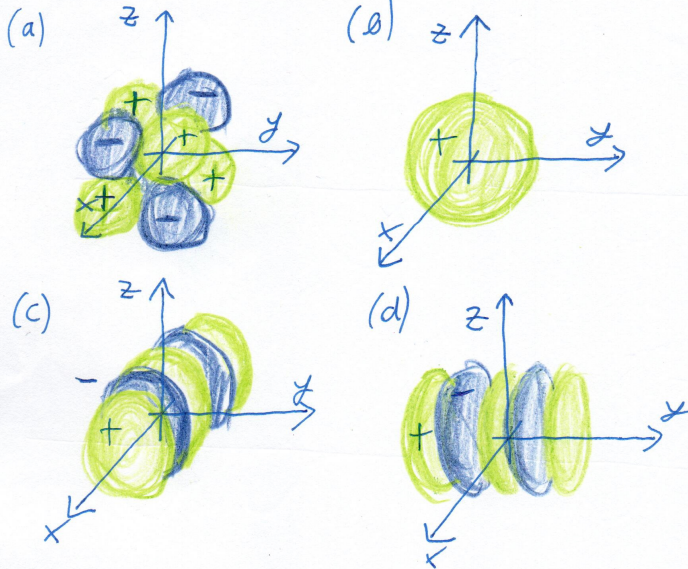
left: On the left we tried anyway, showing 3D equal-probability surfaces for selected states (a) $\mathbf{n} = [n_x = 1, n_y = 1, n_z = 1]$, (b) $\mathbf{n} = [000]$, (c) $\mathbf{n} = [400]$, b) $\mathbf{n} = [040]$ assuming $\omega_x = \omega_y = \omega_z = \omega$.

We see that "each dimension can be excited or not excited separately". A new feature emerging for the isotropic oscillator in 3D, is that all excited states are degenerate, since $E = \hbar\omega(n_x + n_y + n_z + \frac{3}{2})$. Hence e.g. $\mathbf{n} = [400]$ and $\mathbf{n} = [040]$ have the same energy. The physical difference between the states, is the <u>direction</u> along which the oscillator is moving.

Infinite square well potential: Consider the infinite square well in 3D, which is

$$V(\mathbf{r}) = \infty, \quad \text{if } x < 0,\ x > a,\ y < 0,\ y > a,\ z < 0,\ z > a,$$

$$V(\mathbf{r}) = 0 \quad \text{else.} \tag{4.12}$$

We can again write this as a sum of a potential of the type (2.10) for each dimension separately, similar to (4.8). Hence also here the solution follows as a product $\phi(\mathbf{r}) = \varphi_{n_x}(x)\varphi_{n_y}(y)\varphi_{n_z}(z)$ of 1D solution and the energy as a sum $E = E_{n_x} + E_{n_y} + E_{n_z}$.

Scattering: We had seen a 1D scattering problem in section 2.2.3 for the example of the finite well. Here there were two possible outcomes: (i) transmission and (ii) reflection. In 3D, if an incoming, non-bound quantum particle impacts on a potential $V(\mathbf{r})$, there are of course many more outcomes:
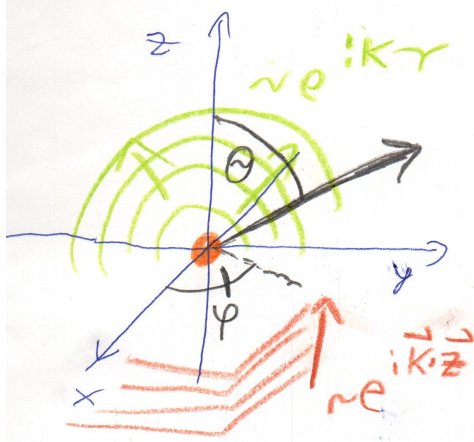
left: The particle can afterwards be scattered into any direction $\mathbf{k}$ in 3D space, parametrised by two scattering angles as shown in the figure on the left.

It is the subject of <u>quantum scattering theory</u>, which we will learn in the next semester, to find out the probability for each direction.

Free particle and Gaussian wavepacket: Turning the free-particle Hamiltonian (2.1) into a 3D version we find

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta, \tag{4.13}$$

with Laplacian Δ from (4.7). From this we find the

Momentum eigenstates (3D) (plane wave solutions)

$$\phi(\mathbf{p}, \mathbf{r}) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{\mathbf{p}}{\hbar}\cdot\mathbf{r}} \tag{4.14}$$

with $\hat{\mathbf{p}}\phi(\mathbf{p}, \mathbf{r}) = \mathbf{p}\phi(\mathbf{p}, \mathbf{r})$.

- Alternatively we can use the <u>wave vector</u> $\mathbf{k} = \frac{\mathbf{p}}{\hbar}$ in the notation above.

- These are now 3D plane waves, with propagation direction along $\mathbf{k}$.

- You can verify that these are eigenstates of (4.13) by simple differentiation.

Similarly we can generalize the

Gaussian Fourier transform pair (in 3D) Using $\sigma_k = 1/\sigma$, we have

$$\phi(\mathbf{r}) = \frac{1}{(\pi\sigma^2)^{3/4}} e^{-\frac{(\mathbf{r}-\mathbf{r_0})^2}{2\sigma^2}} e^{i\mathbf{k_0}\cdot(\mathbf{r}-\mathbf{r_0})}, \tag{4.15}$$

$$\tilde{\phi}(\mathbf{k}) = \frac{1}{(\pi\sigma_k^2)^{3/4}} e^{-\frac{(\mathbf{k}-\mathbf{k_0})^2}{2\sigma_k^2}} e^{-i\mathbf{r_0}\cdot\mathbf{k}}. \tag{4.16}$$

- This is not the most general Gaussian, for that the widths in the three cartesian directions might differ $\sigma_x \neq \sigma_y \neq \sigma_z$

4.1.2 Angular momentum operator

In 3D we can meaningfully form one more operator our of the position and momentum ones, that did not make sense to define in 1D, the

Angular momentum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \tag{4.17}$$

in the position representation $\hat{\mathbf{L}} = [\hat{L}_x, \hat{L}_y, \hat{L}_z]^T$, with

$$\hat{L}_x = \hat{L}_1 = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right),$$

$$\hat{L}_y = \hat{L}_2 = -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right),$$

$$\hat{L}_z = \hat{L}_3 = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right). \tag{4.18}$$

- This follows from the classical definition of angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{4.19}$$

  Same like that one, the angular momentum depends on the origin of your coordinate system (i.e. one should always say " angular momentum with respect to ...."). Often (but not necessarily), angular momentum is used to characterise some sort of circular or orbital motion, such as a planet around the sun, or an electron around a proton.

When dealing with cross-products $\times$, it is often helpful to use the

Component notation for cross-product: For the cross-product $\mathbf{a} \times \mathbf{b} = \mathbf{c}$, we can write

$$c_i = \sum_{jk} \epsilon_{ijk} a_j b_k, \tag{4.20}$$

where ϵ_{ijk} is called Levi-Civita symbol or perfectly anti-symmetric tensor. Its indices i, j, k can take the values $1, 2, 3$ or x, y, z for the three dimensions of space, and $\epsilon_{123} = 1$. Whenever two indices are equal, it is zero, $\epsilon_{ijj} = 0$. Whenever you swap two indices, it changes sign, e.g. $\epsilon_{132} = -1$. A useful consequence is that the ϵ tensor remains constant under a cyclic change of indices, e.g. $1 = \epsilon_{123} = \epsilon_{231} = \epsilon_{312}$.
To use the Levi-Civita symbol, we often need the identity

$$\sum_i \epsilon_{ijk} \epsilon_{inm} = \delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}. \tag{4.21}$$

With that we can write

$$\hat{L}_i = \sum_{jk} \epsilon_{ijk} \hat{x}_j \hat{p}_k. \tag{4.22}$$

Using the definitions (4.18) and the known commutators for position and momentum (4.4), you can (and should) show yourself the following commutator(s):

Commutator of angular momentum operator

$$\left[\hat{L}_n, \hat{L}_m\right] = i\hbar \sum_\ell \epsilon_{nm\ell} \hat{L}_\ell. \tag{4.23}$$

- You can either use the explicit definitions (4.18) and show this three times (for $[nm\ell] = [xyz, yzx, zxy]$, or use the epsilon tensor notation (4.22) and the properties of ϵ plus (4.21) together with $\frac{\partial}{\partial_k} x_\ell = \delta_{k\ell}$ to show it only once.

Defining further the

Square of angular momentum

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \tag{4.24}$$

we can show further that

$$\left[\hat{\mathbf{L}}^2, \hat{L}_n\right] = 0 \tag{4.25}$$

for any n. Let's see now what all these commutation relations tell us: We can immediately insert those into the generalized uncertainty principle (3.41), to see (exercise) the

Angular momentum uncertainty relation

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle \hat{L}_z \rangle|. \tag{4.26}$$

similarly for $xyz \leftrightarrow yzx \leftrightarrow zyx$.

- We again see a deep difference to classical mechanics. In classical mechanics we can have a well defined position and momentum of the particle, and thus via (4.19) know all three components of the angular momentum perfectly.

- Quantum mechanically, (4.26) tells us that for non-zero angular momentum, you can know <u>at most one</u> component of the angular momentum vector perfectly.

- However, from using the generalized HUP with (4.25) we see that it IS possible to simultaneously have complete knowledge of the squared angular momentum $\hat{\mathbf{L}}^2$ and $\hat{L}_n$ for <u>any one out of three</u> cartesian components $n \in \{x, y, z\}$.

4.1.3   More particles

So far we considered the quantum mechanics of a single particle only. Of course most real world systems are made of many. We will start looking more seriously at that case in chapter 5, but we

shall require the most basic statements regarding this already for our discussion of the Hydrogen atom (which is made of two particles, electron and proton, of course).

The first question is, what is the wavefunction of a two-particle system? For a single particle, $|\Psi(\mathbf{r}, t)|^2 \, dV$ is the probability at time t to find the particle within volume dV near $\mathbf{r} = [x, y, z]^T$. For two particles, we now have two 3D coordinates $\mathbf{r}_a$ and $\mathbf{r}_b$. Whenever either of these differs, the two-particle configuration has changed. The generalisation of our earlier single particle treatment is thus to use the

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Two particle wavefunction

$$\Psi(\mathbf{r}_a, \mathbf{r}_b, t) \tag{4.27}$$

that has now one 3D coordinate $\mathbf{r}_k$ for each particle $k \in \{a, b\}$. We now say that the probability at time t to find particle a within volume dV near $\mathbf{r}_a = [x_a, y_a, z_a]^T$ and particle b within volume dV near $\mathbf{r}_b = [x_b, y_b, z_b]^T$ is $|\Psi(\mathbf{r}_a, \mathbf{r}_b, t)|^2 \, dV^2$.

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- Similarly the Hamiltonian now must contain kinetic energy and potential energy contributions for each particle. Stick with the example of two (non-interacting) particles:

$$\hat{H} = -\frac{\hbar^2}{2m_a}\Delta_{\mathbf{r}_a} - \frac{\hbar^2}{2m_b}\Delta_{\mathbf{r}_b} + V(\mathbf{r}_a) + V(\mathbf{r}_b), \tag{4.28}$$

where $\Delta_{\mathbf{r}_a}$ denotes the Laplacian wrt. the components in vector $\mathbf{r}_a$ only.

- You hopefully see, that this gets nasty really fast, once we are looking at genuinely many particles. Even the wavefunction for just 10 particles is a 30 dimensional function.

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Example 29, Many-body quantum problem: Assume we try to handle N distinguishable particles in 3D on a computer as we did in assignment 2,3. For that we now have to discretise each dimension of the wavefunction. Let's suppose we choose M discrete points for each, where typically $M \geq 64$ say, to get reasonable results. A typical floating point complex number takes 16 bytes of memory. How much memory do we need to store the 3D wavefunction of just $N = 3$ particles with $M = 64$ gridpoints per dimension?

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