Quantum Mechanics

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1 p-orbitals

In this exercise we investigate the spherical harmonics corresponding to the angular momentum quantum number $l = 1$. However, let us first briefly consider the case $l = 0$. Since $-l \leq m \leq l$, the only possibility is $m = 0$, and the corresponding spherical harmonics is $Y_{l=0}^{m=0}(\theta, \phi) = (4\pi)^{-1/2}$. One can think of Y_0^0 as a uniform sphere, and is commonly referred to as an s-orbital. The next possibility is $l = 1$, for which $m = -1, 0, 1$, and which correspond to the p-orbitals.

a) In spherical coordinates the orbital angular momentum operators take the form

$$\begin{aligned}
\langle \theta, \phi | L_x | \psi \rangle &= i\hbar \Big(\sin\phi \frac{\partial}{\partial \theta} + \frac{\cos\phi}{\tan\theta} \frac{\partial}{\partial \phi} \Big) \psi(\theta, \phi), \\
\langle \theta, \phi | L_y | \psi \rangle &= i\hbar \Big(-\cos\phi \frac{\partial}{\partial \theta} + \frac{\sin\phi}{\tan\theta} \frac{\partial}{\partial \phi} \Big) \psi(\theta, \phi), \\
\langle \theta, \phi | L_z | \psi \rangle &= -i\hbar \frac{\partial}{\partial \phi} \psi(\theta, \phi).
\end{aligned}$$

Show that the ladder operators $L_\pm$, expressed in the spherical coordinate system, are

$$\langle \theta, \phi | L_\pm | \psi \rangle = \hbar e^{\pm i\phi} \Big(\pm \frac{\partial}{\partial \theta} + i \frac{1}{\tan\theta} \frac{\partial}{\partial \phi} \Big) \psi(\theta, \phi).$$

(2 points)

b) It is the case that

$$Y_1^1(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi},$$

where one might note that $Y_1^1(\theta, \phi) = \langle \theta, \phi | l = 1, m = 1 \rangle$. *Apply the ladder operators onto Y_1^1, in order to show that*

$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta, \quad Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}.$$

(4 points)

c) In the following we take a closer look at these functions, and construct the corresponding p-orbitals. As the first step, we put $p_z(\theta, \phi) = Y_1^0(\theta, \phi)$. *Sketch the graph of $|p_z|$ in the x-z-plane, i.e., make a polar plot of $|p_z(\theta, \phi = 0)|$.* (Hence, at the angle θ with respect to the z-axis, put a point at the radius $|p_z(\theta, 0)|$.) *Next, sketch the shape of $|p_z|$ in $\mathbb{R}^3$.* Rough sketches are enough (but you can use some plotting tool if you want to). **(2 points)**

d) The complex valued functions $Y_1^{\pm 1}$ are a bit harder to interpret, but we can make linear combinations of them in order to get real-valued functions. *Determine the functions*

$$p_x(\theta, \phi) = -\frac{1}{\sqrt{2}} \big(Y_1^1(\theta, \phi) - Y_1^{-1}(\theta, \phi) \big), \quad p_y(\theta, \phi) = -\frac{1}{i\sqrt{2}} \big(Y_1^1(\theta, \phi) + Y_1^{-1}(\theta, \phi) \big).$$

(2 points)

e) *Show that p_x, p_y, p_z form an orthonormal basis of the space $\mathcal{H}_l$ that is spanned by Y_1^1, Y_1^0, Y_1^{-1}.*

Hint: Keep in mind that Y_1^1, Y_1^0, Y_1^{-1} are orthonormal. Also, there is no need to calculate any integrals.

(2 points)

Remark: Since p_x, p_y, p_z and Y_1^1, Y_1^0, Y_1^{-1} both span $\mathcal{H}_l$, it is a matter of convenience which one to use. It turns out that the p-orbitals p_x, p_y, p_z are convenient for molecular physics and chemistry. In particular, these orbitals distribute the particle[1] (the electron, in case of chemistry) in distinct manners over space, which is useful when describing the formation of chemical bonds. In **c)** you have already seen how p_x is distributed, and in the next problem we consider p_y and p_z.

f) *Sketch the graph of $|p_x|$ in the x-z-plane, i.e., make a polar plot of $|p_x(\theta, \phi = 0)|$. Similarly, sketch the graph of $|p_y|$ in the y-z-plane, i.e., make a polar plot of $|p_y(\theta, \phi = \pi/2)|$.*

(2 points)

Remark: In case you are using some plot-tool, it is instructive to make 3D plots of $|p_x|$ and $|p_y|$ and compare with your plot of $|p_z|$.

g) The orbital p_z is an eigenfunction of L_z. However, neither p_x nor p_y are eigenfunctions of L_z (since both are linear combinations of eigenfunctions with different eigenvalues). *Show that p_x is an eigenfunction of L_x and that p_y is an eigenfunction of L_y. What are the eigenvalues?*

(4 points)

h) *Show that p_x is symmetric under rotations around the x-axis and show that p_y is symmetric under rotations around the y-axis.* Looking at the concrete functions p_x and p_y, these symmetries are not obvious (at least not to me). However, if you think about what you have learned, there is a very direct argument.

(2 points)

[1] To be more precise, the p's and the Y's only give the angular part of the wave function, and are accompanied by radial wave-functions. The absolute value square of the joint wave-function gives the probability density of where to find the electron. For the p-orbitals, these distributions are oriented in a distinct manner around the atom. This can be compared with the s-orbital, where the probability distribution is rotation symmetric.