Quantum Mechanics 7

Daniel Holleufer

In this exercise we consider a hydrogen atom, given that spin and fine structure effects are neglected. The normalized energy eigenfunctions are denoted as

$$\phi_{nlm}(\vec{r}),$$

where n is the principal quantum number, and l and m are the usual quantum numbers belonging to $\hat{L}^2$ and $\hat{L}_z$ respectively. As usual we introduce the operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y$$
$$\hat{L}_- = \hat{L}_x - i\hat{L}_y$$

1. *It is shown that ϕ_{nlm} is an eigenfunction for the operator $\hat{L}_+\hat{L}_-$, and the eigenvalue is determined.*

   The full expression for ϕ_{nlm} is given as

   $$\phi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}\right] Y_l^m(\theta,\varphi). \tag{1}$$

   To avoid any confusion with the energy eigenfunctions, we write the second angle in Y_l^m as varphi, φ, instead of the usual ϕ. To make things simpler, we can rewrite equation (1) as

   $$\phi_{nlm} = R_{nl}(r) Y_l^m(\theta,\varphi).$$

   Now let us consider the the operator $\hat{L}_+\hat{L}_-$. It can be written as

   $$\hat{L}_+\hat{L}_- = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z,$$

   where $\hat{L}^2$ and $\hat{L}_z$ are the two operators

   $$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin(\theta)^2}\frac{\partial^2}{\partial\varphi^2}\right],$$

and

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}.$$

We see no r dependency in $\hat{L}^2$ and $\hat{L}_z$. We can therefore treat $R_{nl}(r)$ as a constant during the transformation.

$$\begin{aligned}
\hat{L}_+\hat{L}_-\phi_{nlm} &= \hat{L}^2\phi_{nlm} - \hat{L}_z^2\phi_{nlm} + \hbar\hat{L}_z\phi_{nlm} \\
&= \hat{L}^2 R_{nl} Y_l^m - \hat{L}_z^2 R_{nl} Y_l^m + \hbar\hat{L}_z R_{nl} Y_l^m \\
&= \hbar^2 l(l+1) R_{nl} Y_l^m - \hbar^2 m^2 R_{nl} Y_l^m + \hbar^2 m R_{nl} Y_l^m \\
&= \hbar^2[l(l+1) - m(m-1)] R_{nl}(r) Y_l^m(\theta,\varphi) \\
&= \hbar^2[l(l+1) - m(m-1)]\phi_{nlm}.
\end{aligned}$$

So ϕ_{nlm} is indeed an eigenfunction to the operator $\hat{L}_+\hat{L}_-$, with eigenvalue $\hbar^2[l(l+1) - m(m+1)]$.

2. *Consider the state*

$$\psi(\vec{r}) = \frac{1}{\sqrt{2}}(\phi_{21-1}(\vec{r}) + i\phi_{211}(\vec{r})).$$

It is explained why ψ is an eigenfunction for the energy as well as $\hat{L}^2$, but not for $\hat{L}_z$.

Because $n = 2$ for both energy eigenfunctions, they have the same energy. Therefore ψ will only have one possible value for the energy, which means it is an eigenfunction for $\hat{H}$. They also share the same $l = 1$, which is the only quantum number to appear in the eigenvalue for $\hat{L}^2$, so they have the same eigenvalue for that operator. Their m's are different, so they cannot share the same eigenvalue for $\hat{L}_z$, since it depends on m.

3. *Now consider the 3-dimensional subspace $\mathcal{H}$ spanned by ϕ_{21-1}, ϕ_{210}, and ϕ_{211}. The matrix representations of $\hat{L}^2$, $\hat{L}_z$, $\hat{L}_+$, and $\hat{L}_-$ in the subspace $\mathcal{H}$ are determined.*

We choose a basis where ϕ_{21-1}, ϕ_{210}, and ϕ_{211} can be written as the three basis vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$. To obtain the matrix representation, we apply the operators on each basis element, and write the new vectors in a matrix.

For $\hat{L}^2$, we observe that each of the functions that span the current subspace, have $l = 1$, so they have the same eigenvalue $2\hbar^2$ for $\hat{L}^2$. This comes from

$$\hat{L}^2 f_l^m = \hbar^2 l(l+1) f_l^m.$$

The matrix representation becomes

$$\hat{L}^2 = 2\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

The three functions have different values for m, so their eigenvalues for $\hat{L}_z$ will be different. They are given by

$$\hat{L}_z f_l^m = \hbar m f_l^m.$$

When applied to the three functions we get the eigenvalues -1, 0, and 1 respectively. The matrix representation becomes

$$\hat{L}_z = \hbar \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For the operators $\hat{L}_+$, we use the results proven in G3.21

$$\hat{L}_+ f_l^m = \hbar\sqrt{(l-m)(l+m+1)} f_l^{m+1}$$

When this is used on the three basis functions, we get

$$\begin{aligned} \hat{L}_+ \phi_1^{-1} &= \sqrt{2}\hbar\phi_1^0 \\ \hat{L}_+ \phi_1^0 &= \sqrt{2}\hbar\phi_1^1 \\ \hat{L}_+ \phi_1^1 &= 0 \end{aligned}$$

The last one becomes zero because m becomes greater than l. The matrix representation becomes

$$\hat{L}_+ = \sqrt{2}\hbar \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}.$$

The matrix representation for $\hat{L}_-$ is easily found by using $\hat{L}_+^\dagger = \hat{L}_-$.

$$\hat{L}_- = \sqrt{2}\hbar \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix}.$$

4. *The matrix representation of $\hat{L}_x$ in $\mathcal{H}$ is determined.*

   By adding $\hat{L}_+$ and $\hat{L}_-$ we get $2\hat{L}_x$. Dividing by two yields

$$\hat{L}_x = \frac{\hat{L}_+ + \hat{L}_-}{2}.$$

   The matrix representation for $\hat{L}_x$ becomes the sum of the matrix representations for $\hat{L}_+$ and $\hat{L}_-$ divided by two.

$$\hat{L}_x = \frac{\hbar}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}.$$

5. *All eigenvalues and eigenvectors for $\hat{L}_x$ in the subspace $\mathcal{H}$ are determined.*

   The eigenvalues are found by determining the roots of the characteristic polynomial for $\hat{L}_x$,

$$\begin{aligned} 0 &= \det(\hat{L}_x - t\,\mathrm{I}_3) \\ &= \det\left(\begin{bmatrix} -t & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & -t & \frac{\hbar}{\sqrt{2}} \\ 0 & \frac{\hbar}{\sqrt{2}} & -t \end{bmatrix}\right) \\ &= -t^3 + \hbar^2 t. \end{aligned}$$

   The solutions to this equations (and therefore the eigenvalues to $\hat{L}_x$) are $\lambda = 0$, $\lambda = \hbar$, and $\lambda = -\hbar$. We determine the eigenvectors by finding the null space for the matrix $\hat{L}_x - \lambda\,\mathrm{I}_3$. First $\lambda = 0$.

$$\begin{bmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & \frac{\hbar}{\sqrt{2}} \\ 0 & \frac{\hbar}{\sqrt{2}} & 0 \end{bmatrix} \sim \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

   The only free variable is the third one. Therefore the eigenvector for 0 is $[-1, 0, 1]^T$. For $\lambda = \hbar$, we have

$$\begin{bmatrix} -\hbar & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & -\hbar & \frac{\hbar}{\sqrt{2}} \\ 0 & \frac{\hbar}{\sqrt{2}} & -\hbar \end{bmatrix} \sim \begin{bmatrix} 1 & 0 & -1 \\ 0 & 1 & -\sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}$$

Again, the free variable is the third one. The eigenvector for $\hbar$ is $[1, \sqrt{2}, 1]^T$.

For $\lambda = -\hbar$, we have

$$\begin{bmatrix} \hbar & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & \hbar & \frac{\hbar}{\sqrt{2}} \\ 0 & \frac{\hbar}{\sqrt{2}} & \hbar \end{bmatrix} \sim \begin{bmatrix} 1 & 0 & -1 \\ 0 & 1 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix}$$

And again, the only free variable is the third one. The eigenvector for $-\hbar$ is $[1, -\sqrt{2}, 1]^T$.