Phys 506 Hydrogen in position space ①

The Hydrogen atom Hamiltonian is

$$\hat{H} = \frac{\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2}{2\mu} - \frac{e^2}{\hat{r}} \qquad \mu = \frac{M_e M_N}{M_e + M_N} = \text{reduced mass}$$

recall the kinetic energy can be decomposed into its radial and angular pieces

$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu\hat{r}^2} - \frac{e^2}{\hat{r}}$$

Note how $\hat{H}$ commutes with $\hat{L}^2$ and $\hat{L}_z$, because $\hat{p}$ is a vector operator as is $\hat{r}$ and this is a function of $\hat{p}^2$ and $\hat{r}^2$ only.

This means we can simultaneously diagonalize $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ $\Rightarrow$ $|\psi\rangle = |\psi_r\rangle \otimes |l,m\rangle$

This is because we know that the eigenstates of $\hat{L}^2$ and $\hat{L}_z$ are $|l,m\rangle$.

If we operate $\hat{H}$ on $|\psi\rangle$ then since $\hat{L}^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle$ we have

$$\hat{H}_l|\psi_r\rangle = E|\psi_r\rangle$$

with $\hat{H}_l = \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 l(l+1)}{2\mu\hat{r}^2} - \frac{e^2}{\hat{r}}$ the Hamiltonian for angular momentum $l$.

Our job is to factorize each of these $\hat{H}_l$ Hamiltonians and find all of their eigenvalues. There are two ways to do this and we will use a shortcut solution here. You will use the standard Schrödinger method in the homework.

With a little thought, we realize we should try

$$\hat{B}_r(l) = \frac{1}{\sqrt{2\mu}}\left(\hat{p}_r - i\hbar\left(\frac{\alpha}{a_0} + \frac{\beta}{\hat{r}}\right)\right)$$

with $\alpha$ and $\beta$ dimensionless numbers

Here $a_0 = \frac{\hbar^2}{\mu e^2}$ = Bohr radius = 0.529 Å

The choice of constant + $\frac{1}{\hat r}$ is governed by the square of $\vec\nabla$ and the commutator with $\hat p_r$ keeping constant, $\frac{1}{\hat r}$ and $\frac{1}{\hat r^2}$ terms — just what we need.

We compute

$$\hat B_r^+(l)\,\hat B_r(l) = \frac{\hat p_r^2}{2\mu} - \frac{i\hbar}{2\mu}\left[\hat p_r, \frac{\alpha}{a_0} + \frac{\beta}{\hat r}\right] + \frac{\hbar^2}{2\mu}\left[\frac{\alpha}{a_0} + \frac{\beta}{\hat r}\right]^2$$

recall $[\hat p_r, \hat r] = -i\hbar$ $\quad [\hat p_r, \frac{1}{\hat r}] = \frac{i\hbar}{\hat r^2}$

Hence $\hat B_r^+(l)\,\hat B_r(l) = \frac{\hat p_r^2}{2\mu} + \frac{\hbar^2}{2\mu \hat r^2}(\beta+\beta^2) + \frac{\hbar^2}{\mu}\frac{\alpha\beta}{a_0 \hat r} + \frac{\hbar^2}{2\mu}\frac{\alpha^2}{a_0^2}$

note, we use $l$ here to make rest of notation easier

$\Rightarrow \quad \beta(\beta+1) = l(l+1) \qquad \alpha\beta = -1 \qquad \tilde E_l = -\frac{\hbar^2\alpha^2}{2\mu a_0^2}$

so $\beta = l$ or $\beta = -l-1 \qquad \alpha = -\frac{1}{\beta} \qquad \tilde E_l = -\frac{1}{2}\frac{1}{a_0}\frac{e^2}{\beta^2}$

so $\tilde E_l = -\frac{1}{2}\frac{e^2}{a_0}\frac{1}{l^2}$ or $-\frac{1}{2}\frac{e^2}{a_0}\frac{1}{(l+1)^2}$

our rule is to choose $\beta = -l-1 \quad \alpha = \frac{1}{l+1}$ so $W(r) > 0$ as $r \to \infty$

$$\Rightarrow \quad \hat B_r(l) = \frac{1}{\sqrt{2m}}\left[\hat p_r - i\hbar\left(\frac{1}{a_0(l+1)} - \frac{l+1}{\hat r}\right)\right]$$

and $\hat H_l = \hat B_r^+(l)\,\hat B_r(l) + \tilde E_l$

Next is intertwining:

First compute the opposite order

$$\hat B_r(l)\,\hat B_r^+(l) = \frac{1}{2\mu}\left[\hat p_r^2 - i\hbar\left[\hat p_r, \frac{l+1}{\hat r}\right] + \hbar^2\left(\frac{1}{a_0^2(l+1)^2} - \frac{1}{a_0\hat r} + \frac{(l+1)^2}{\hat r^2}\right)\right]$$

$$= \frac{\hat p_r^2}{2\mu} + \frac{\hbar^2(l+1)(l+2)}{2\mu\hat r^2} - \frac{e^2}{\hat r} + \frac{e^2}{2a_0(l+1)^2}$$

$$= \hat H_{l+1} - \tilde E_l$$

so
$$\hat H_l\,\hat B_r^+(l) = \left(\hat B_r^+(l)\,\hat B_r(l) + \tilde E_l\right)\hat B_r^+(l)$$
$$= \hat B_r^+(l)\left(\hat B_r(l)\,\hat B_r^+(l) + \tilde E_l\right)$$
$$= \hat B_r^+(l)\,\hat H_{l+1}$$

We use these results to construct the eigenstates

we label the energies with $n = l+1$

$$E_n = -\frac{e^2}{2a_0 n^2} = \tilde{E}_{l=n-1}$$

The state, which is the ground state of $\hat{H}_l$ is obviously

$$\hat{B}_r(l)\,|n = l+1, l\rangle = 0$$

with energy $E_n = -\dfrac{e^2}{2a_0(l+1)^2}$ $(n = l+1)$

or $\hat{B}_r(n-1)\,|n, l=n-1\rangle = 0 \qquad E_n = -\dfrac{e^2}{2a_0 n^2}$

note when we index by $n$, the energy is defined as above

claim is the state

$$|n\, l\rangle = \hat{B}^+_r(l)\,\hat{B}^+_r(l+1)\cdots\hat{B}^+_r(n-2)\,|n, l=n-1\rangle$$

is an eigenstate of $\hat{H}_l$ with energy $E_n = -\dfrac{e^2}{2a_0 n^2}$

$$\hat{H}_l|n\, l\rangle = \hat{H}_l\,\hat{B}^+_r(l)\,\hat{B}^+_r(l+1)\cdots\hat{B}^+_r(n-2)\,|n, l=n-1\rangle$$

intertwining $\qquad = \hat{B}^+_r(l)\,\hat{H}_{l+1}\,\hat{B}^+_r(l+1)\cdots\hat{B}^+_r(n-2)\,|n, l=n-1\rangle$

$$= \hat{B}^+_r(l)\,\hat{B}^+_r(l+1)\cdots\hat{B}^+_r(n-2)\,\hat{H}_{n-1}\,|n, l=n-1\rangle$$

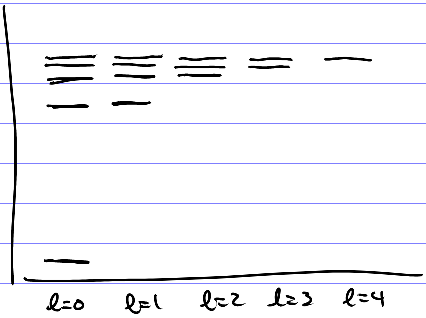
$$= E_n\,\hat{B}^+_r(l)\,\hat{B}^+_r(l+1)\cdots\hat{B}^+_r(n-2)\,|n, l=n-1\rangle$$

$$= E_n\,|n, l\rangle$$

so, it is an eigenstate as claimed.

Note, we have found a chain of states with $0 \le l \le n-1$ that all have energy $E_n$

The spectrum looks like



Our next step is to find the wave function. Although it might not seem like it, the string of $\hat{B}_r$ operators multiplying $|n, l=n-1\rangle$ is a polynomial in $\hat{r}$. We see this when we notice that the condition

$$\hat{B}_r(n-1)\,|n, l=n-1\rangle = 0$$

can be rewritten as

$$\hat{p}_r\,|n, l=n-1\rangle = i\hbar\left(\frac{1}{n a_0} - \frac{n}{\hat{r}}\right)|n, l=n-1\rangle$$

This means the $\hat{p}_r$'s in the string of $\hat{B}^+$'s becomes polynomials in $\frac{1}{\hat{r}}$. We need to determine how to find their form. Obviously, we need to use induction.

To organize the work, we need to establish some notation, which, like in the SHO, uses the answer so everything is neat.

$$|n\,l\rangle = \hat{B}^+_r(l)\,\hat{B}^+_r(l+1)\cdots\hat{B}^+_r(n-2)\,|n, l=n-1\rangle$$
$$= \left(\frac{-i\hbar}{\sqrt{2\mu}\,n a_0}\right)^{n-l-1}\left(\frac{n a_0}{2\hat{r}}\right)^{n-l-1}\frac{(2n-1)!}{(n+l)!}\,\frac{(n-l-1)!\,l!}{(n-1)!}$$
$$L^{2l+1}_{n-l-1}\left(\frac{2\hat{r}}{n a_0}\right)|n, l=n-1\rangle$$

which defines our polynomial operator $L^{2l+1}_{n-l-1}\left(\frac{2\hat{r}}{n a_0}\right)$

$n-l-1$ appears because that is how many $\hat{B}^+_r$ operators we have. The factorials are used to put the result in "standard" form.

We write $$L^{2l+1}_{n-l-1}\left(\frac{2\hat{r}}{n a_0}\right) = \sum_{j=0}^{n-l-1} a_j^{2l+1}\left(\frac{2\hat{r}}{n a_0}\right)^j$$

To find the recurrence relation, we do the same as with the SHO, factor of a $\hat{B}^+_r(l)$ from the left

$$\left(\frac{-i\hbar}{\sqrt{2\mu}\,n a_0}\right)^{n-l-1}\left(\frac{n a_0}{2\hat{r}}\right)^{n-l-1}\frac{(2n-1)!}{(n+l)!}\,\frac{(n-l-1)!\,l!}{(n-1)!}\sum_{j=0}^{n-l-1} a_j^{2l+1}\left(\frac{2\hat{r}}{n a_0}\right)^j|n, l=n-1\rangle$$

$$= \left(\frac{-i\hbar}{\sqrt{2\mu}\,n a_0}\right)^{n-l-2}\frac{(2n-1)!}{(n+l+1)!}\,\frac{(n-l-2)!\,(l+1)!}{(n-1)!}\,\hat{B}^+_r(l)\left(\frac{n a_0}{2\hat{r}}\right)^{n-l-2}\sum_{j=0}^{n-l-2} a_j^{2l+3}\left(\frac{2\hat{r}}{n a_0}\right)^j|n, l=n-1\rangle$$

Compute $\hat{B}^+_r(l)\left(\frac{2\hat{r}}{n a_0}\right)^{n-l-2-j}|n, l=n-1\rangle$

$$= \frac{1}{\sqrt{2\mu}} \left[ \hat{p}_r + i\hbar \left[ \frac{1}{(l+1)a_0} - \frac{l+1}{\hat{r}} \right] \right] \left( \frac{2\hat{r}}{na_0} \right)^{-n+l+2+j} |n, l=n-1\rangle$$

$$= \frac{i\hbar}{\sqrt{2\mu}} \left[ \frac{1}{na_0} - \frac{n}{\hat{r}} - (-n+l+2+j)\frac{1}{\hat{r}} + \frac{1}{(l+1)a_0} - \frac{l+1}{\hat{r}} \right] \left( \frac{2\hat{r}}{na_0} \right)^{-n+l+2+j} |n, l=n-1\rangle$$

from $[\hat{p}_r, \hat{r}^{\,n-l-2-j}]$

from $\hat{p}_r |n, l=n-1\rangle$

$$= \frac{i\hbar}{\sqrt{2\mu}} \left[ \frac{n+l+1}{n(l+1)a_0} - \frac{2l+j+3}{\hat{r}} \right] \left( \frac{2\hat{r}}{na_0} \right)^{-n+l+2+j} |n, l=n-1\rangle$$

$$\Rightarrow \left( \frac{-i\hbar}{\sqrt{2\mu}\, na_0} \right) \frac{(n+l+1)(n-l-1)}{l+1} \sum_{j=0}^{n-l-1} a_j^{2l+1} \left( \frac{2\hat{r}}{na_0} \right)^j |n, l=n-1\rangle$$

$$= \frac{-i\hbar}{\sqrt{2\mu}} \sum_{n=0}^{n-l-2} \left( \frac{2}{na_0}(2l+j+3) - \frac{2(n+l+1)\hat{r}}{(na_0)^2(l+1)} \right) a_j^{2l+3} \left( \frac{2\hat{r}}{na_0} \right)^j |n, l=n-1\rangle$$

$$\frac{n^2-(l+1)^2}{l+1} \sum_{j=0}^{n-l-1} a_j^{2l+1} \left( \frac{2\hat{r}}{na_0} \right)^j |n, l=n-1\rangle$$

$$= \sum_{n=0}^{n-l-2} \left( 2(2l+j+3) - \frac{n+l+1}{l+1} \frac{2\hat{r}}{na_0} \right) \left( \frac{2\hat{r}}{na_0} \right)^j a_j^{2l+3}$$

$$\Rightarrow \frac{n^2-(l+1)^2}{(l+1)} a_j^{2l+1} = \begin{cases} -\frac{n+l+1}{l+1} a_{n-l-2}^{2l+3} & j=n-l-1 \\ 2(2l+j+3) a_j^{2l+3} - \frac{n+l+1}{l+1} a_{j-1}^{2l+3} & 1 \le j \le n-l-2 \\ 2(2l+3) a_0^{2l+3} & j=0 \end{cases}$$

note: there is no $\frac{1}{na_0}$ here

So
$$\frac{a_{j+1}^{2l+1}}{a_j^{2l+1}} = \frac{2(2l+j+4) a_{j+1}^{2l+3} - \frac{n+l+1}{l+1} a_j^{2l+3}}{2(2l+j+3) a_j^{2l+3} - \frac{n+l+1}{l+1} a_{j-1}^{2l+3}}$$

$$= \frac{2(2l+j+4) \dfrac{a_{j+1}^{2l+3}}{a_j^{2l+3}} - \dfrac{n+l+1}{l+1}}{2(2l+j+3) - \dfrac{n+l+1}{l+1} \left( \dfrac{a_j^{2l+3}}{a_{j-1}^{2l+3}} \right)^{-1}}$$

We can check that this is solved by

$$\frac{a_j^{2l+3}}{a_{j-1}^{2l+3}} = \frac{l+j-n+1}{j(2l+j+3)} \qquad \frac{a_{j+1}^{2l+1}}{a_j^{2l+1}} = \frac{l+j-n+1}{(j+1)(2l+j+2)}$$

check:
$$\frac{l+j-n+1}{(j+1)(2l+j+2)} = \frac{2(2l+j+4) \dfrac{l+j-n+2}{(j+1)(2l+j+4)} - \dfrac{n+l+1}{l+1}}{2(2l+j+3) - \dfrac{n+l+1}{l+1} \dfrac{j(2l+j+3)}{l+j-n+1}}$$

$$= \frac{\frac{2(l+j-n+2)}{j+1} - \frac{n+l+1}{l+1}}{(2l+j+3)\left(2 - \frac{(n+l+1)j}{(l+1)(l+j-n+1)}\right)}$$

$$= \frac{2(l+j-n+2)(l+1) - (n+l+1)(j+1)}{2(l+j-n+1)(l+1) - (n+l+1)j} \quad \frac{l+j-n+1}{2l+j+3} \quad \frac{1}{j+1}$$

$$= \frac{1}{j+1} \frac{(l+1)(2l+j+3) - (2l+j+3)n}{(l+1)(2l+2j+2-j) - n(2l+2+j)} \quad \frac{(l+j-n+1)}{(2l+j+3)}$$

$$= \frac{1}{j+1} \frac{l-n+1}{l-n+1} \quad \frac{l+j-n+1}{2l+j+2}$$

$$= \frac{l+j-n+1}{(j+1)(2l+j+2)} \quad \checkmark$$

So, up to a normalization question you will answer on the HW, this establishes that

$$a^{2l+1}_{j} = -\frac{(n-l-j)}{j(2l+j+1)} a^{2l+1}_{j-1}$$

$$= (-)^{j} \frac{(n-l-1)!}{(n-l-j-1)!} \frac{1}{j!} \frac{(2l+1)!}{(2l+j+1)!} a^{2l+1}_{0}$$

But the Laguerre polynomial satisfies

$$L^{2l+1}_{n-l-1}(x) = \sum_{j=0}^{n-l-1} \frac{(l+n)!}{(n-l-j-1)!\,(2l+j+1)!\,j!} (-x)^{j}$$

and one can see with a proper choice of $a^{2l+1}_{0}$ (which we can calculate), we will have a Laguerre polynomial in the wavefunction. More details are on the HW.

Also note $\langle r| \otimes \langle \theta\phi| \, |nl\rangle \otimes |lm\rangle$

$$= \langle r|nl\rangle \underbrace{\langle \theta\phi|lm\rangle}_{Y_{lm}(\theta,\phi)}$$

$$\underset{\text{number}}{C} \; L^{2l+1}_{n-l-1}(r) \, \langle r|n, \underset{\psi_{n,n-1}(r)}{l=n-1}\rangle$$

$\psi_{n,n-1}(r)$, need to use radial translation operator to find this.