The radial Hamiltonian for the Hydrogen atom with orbital angular momentum quantum number l is

$$H_l = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{r} \qquad 1)$$

We wish to find the energies $E_{n_r,l}$ and corresponding wave functions $P_{n_r,l}(r)$. It is convenient to define a radial quantum number n_r which is equal to the number of nodes in the wavefunction.

For small r, the wavefunctions must be proportional to r^{l+1}. At large r, they must decay as $e^{-\kappa r}$, where $\kappa = \sqrt{-2\mu E/\hbar^2}$. The lowest energy level for any l must have no zero crossings. Thus an educated guess for the wave function for the lowest energy level for a given l is

$$P_{0,l}(r) = r^{l+1} e^{-\frac{r}{a}} \qquad 2)$$

If we plug this into the Schrodinger equation, as in the accompanying *Mathematica* notebook, we find

$$\frac{e^{-\frac{r}{a}}\, r^l \left(-2\, a\, (1+l)\, \hbar^2 + r\, \hbar^2 + 2\, a^2 \left(e^2 + r\, \mathcal{E}\right) \mu\right)}{a\, \mu} == 0$$

For this to hold at any r, each power of r in the numerator must individually vanish. Thus

$$-2\, a\, (1+l)\, \hbar^2 + 2\, a^2\, e^2\, \mu == 0,\ r\, \hbar^2 + 2\, a^2\, r\, \mathcal{E}\, \mu == 0$$

which has the solution

$$a = (l+1)a_B, \qquad E_{0,l} = -\frac{Ry}{(l+1)^2}$$

where the Bohr radius is $a_B = \hbar^2/\mu e^2$ and the Rydberg constant is $Ry = \mu e^4/2\hbar^2$. We now have the lowest energy level and its wavefunction for each *l*.

Now we want to find the excited state energy levels. We will use a trick similar to the raising and lowering operators for the harmonic oscillator. We define a "superpotential"

$$W_l(r) = \frac{e^2\mu}{(l+1)\hbar^2} - \frac{l+1}{r} \qquad 3)$$

and we define operators

$$\begin{aligned} A_l &= \frac{d}{dr} + W_l \\ A_l^\dagger &= -\frac{d}{dr} + W_l \end{aligned} \qquad 4)$$

then we can show (see *Mathematica*)

$$\begin{aligned} \frac{\hbar^2}{2\mu} A_l^\dagger\, A_l &= H_l - E_{0l} \\ \frac{\hbar^2}{2\mu}\, A_l A_l^\dagger &= H_{l+1} - E_{0l} \end{aligned} \qquad 5)$$

Now we wish to show that $A^\dagger P_{n_r,l+1} = P_{n_r+1,l}$, and $E_{n_r+1,l} = E_{n_r,l+1}$. The creation operator adds a node to the wavefunction and reduces its angular momentum, but keeps the energy the same.

Let us operate H_l on $A^\dagger P_{n_r,l+1}$:

$$\begin{aligned} H_l A_l^\dagger P_{n_r,l+1} &= \left(\frac{\hbar^2}{2\mu} A_l^\dagger\, A_l + E_{0l}\right) A_l^\dagger P_{n_r,l+1} \\ &= A_l^\dagger \left(\frac{\hbar^2}{2\mu}\, A_l A_l^\dagger + E_{0l}\right) P_{n_r,l+1} \\ &= A_l^\dagger H_{l+1} P_{n_r,l+1} = E_{n_r,l+1} A_l^\dagger P_{n_r,l+1} \end{aligned} \qquad 6)$$

Therefore $A^\dagger P_{n_r,l+1}$ is an eigenfunction of H_l with eigenvalue $E_{n_r,l+1}$. We therefore have

$$E_{n_r,l} = E_{0,n_r+l} = -\frac{Ry}{(n_r + l + 1)^2} \qquad 7)$$

The action of the operator $A_l^\dagger$ gives us a new eigenstate of one less l, and one greater n_r. Defining the principal quantum number $n = n_r + l + 1$, it follows that the energy levels of the hydrogen atom energy levels are

$$E_{nl} = -\frac{Ry}{n^2} \qquad 8)$$

and the eigenfunctions can be generated by successively operating on $P_{0n}(r)$:

$$P_{nl}(r) = A_l^\dagger \ldots A_{n-3}^\dagger A_{n-2}^\dagger P_{0n-1}(r) \qquad 9)$$

where $A_l^\dagger$ is the lowering operator corresponding to superpotential W_l.

hydrogen atom Hamiltonian

In[277]:= $$\mathbf{H_{l\_}[f\_] := \frac{-\hbar^2}{2\,\mu} D[f, \{r, 2\}] + \frac{\hbar^2\, l\, (l+1)}{2\,\mu\, r^2}\, f - \frac{e^2}{r}\, f}$$

Schrodinger equation

In[278]:= $$\mathbf{Sch[f\_] := H_l @ f == \mathcal{E}\, f}$$

In[279]:= $$\mathbf{Sch[P0[r]]}$$

Out[279]= $$-\frac{e^2\, \mathrm{P0}[r]}{r} + \frac{l\,(1+l)\,\hbar^2\, \mathrm{P0}[r]}{2\, r^2\, \mu} - \frac{\hbar^2\, \mathrm{P0}''[r]}{2\,\mu} == \mathcal{E}\, \mathrm{P0}[r]$$

educated guess for the ground state wavefunctions for different *l*s

In[280]:= $$\mathbf{Sch\left[r^{l+1}\, e^{-r/a}\right] // Simplify}$$

Out[280]= $$\frac{e^{-\frac{r}{a}}\, r^l \left(-2\, a\,(1+l)\,\hbar^2 + r\,\hbar^2 + 2\, a^2 \left(e^2 + r\,\mathcal{E}\right)\mu\right)}{a\,\mu} == 0$$

to satisfy for all r, each power of r must separately vanish

In[281]:= $$\mathbf{Solve\left[\left\{-2\, a\,(l+1)\,\hbar^2 + 2\, a^2\, e^2\, \mu == 0,\ r\,\hbar^2 + 2\, a^2\, r\,\mathcal{E}\,\mu == 0\right\}, \{a, \mathcal{E}\}\right]}$$

Out[281]= $$\left\{\left\{a \to \frac{(1+l)\,\hbar^2}{e^2\,\mu},\ \mathcal{E} \to -\frac{e^4\,\mu}{2\,(1+l)^2\,\hbar^2}\right\}\right\}$$

so the n_r=0 energy levels for arbitrary *l* are

In[282]:= $$\mathbf{E0[l\_] := -\frac{e^4\,\mu}{2\,(l+1)^2\,\hbar^2}}$$

$$\mathbf{P0[l\_] := r^{l+1}\, e^{-r/a}\ /.\ a \to \frac{(l+1)\,\hbar^2}{e^2\,\mu}}$$

define “superpotential”

In[284]:= $$\mathbf{W_{l\_}[r] = \frac{\mu\, e^2}{(l+1)\,\hbar^2} - \frac{l+1}{r};}$$

define operators analogous to SHO raising and lowering operators

In[287]:= $$\mathbf{A_{l\_}[f\_] := D[f, r] + W_l[r]\, f}$$

In[288]:= $$\mathbf{A\dagger_{l\_}[f\_] := -D[f, r] + W_l[r]\, f}$$

Show that A†A and AA† are equal to $H_l - E_{0\,l}$ and $\mathrm{H}_{l+1} - \mathrm{E}_{0\;l}$

In[289]:= $$\mathbf{\left(\frac{\hbar^2}{2\,\mu}\, A\dagger_l @ A_l @ P[r] == H_l @ P[r] - E0[l]\, P[r]\right) // Simplify}$$

Out[289]= True

In[290]:=

$$\left(\frac{\hbar^2}{2\,\mu}\,\mathtt{A}_{\mathtt{l}}\mathtt{@At}_{\mathtt{l}}\mathtt{@P[r] == H}_{\mathtt{l+1}}\mathtt{@P[r] - E0[l]\ P[r]}\right)\ \mathtt{//\ Simplify}$$

Out[290]= `True`

now in terms of the principal quantum number n:

In[291]:=

$$\mathtt{Enl[n\_,\ l\_]\ :=\ -}\frac{e^4\,\mu}{2\,n^2\,\hbar^2}$$

In[292]:=

$$\mathtt{P[n\_,\ l\_]\ :=\ Module}\left[\{\mathtt{P0l = P0[n-1]}\},\ \mathtt{Do}\left[\mathtt{P0l = At}_{\mathtt{lp}}\mathtt{@P0l},\ \{\mathtt{lp},\ \mathtt{n-2},\ \mathtt{l},\ \mathtt{-1}\}\right];\ \mathtt{P0l}\right]$$

verify that the wavefunctions satisfy the Schrodinger eqn, and print them out. They are unnormalized.

In[299]:=

$$\mathtt{With}\Big[\{\mathtt{n = 17,\ l = 10}\},\ \mathtt{Print[(H}_{\mathtt{l}}\mathtt{@P[n,\ l] == Enl[n,\ l]\ P[n,\ l])\ //\ Simplify];}$$

$$\quad\mathtt{P[n,\ l]\ /.\ }\mu\ \mathtt{->}\ \frac{\hbar^2}{e^2\,a_B}\ \mathtt{//\ Simplify}\Big]$$

`True`

Out[299]=

$$\frac{1}{313\,788\,397\,a_B^6}\,899\,e^{-\frac{r}{17\,a_B}}\,r^{11}\left(2\,r^6 - 2754\,r^5\,a_B + 1\,521\,585\,r^4\,a_B^2 - 431\,115\,750\,r^3\,a_B^3 + 65\,960\,709\,750\,r^2\,a_B^4 - 5\,158\,127\,502\,450\,r\,a_B^5 + 160\,761\,640\,493\,025\,a_B^6\right)$$