The Hydrogen Atom

The hamiltonian H_{ep} is

$$H_{ep} = \frac{\vec{p}_e^{\,2}}{2m_e} + \frac{\vec{p}_p^{\,2}}{2m_p} - \frac{e^2}{|\vec{r}_e - \vec{r}_p|} \qquad (1)$$

in which e and p respectively refer to the electron and the proton, and e^2 is given by

$$\frac{e^2}{\hbar c} = \alpha = \frac{1}{137.036} \qquad (2)$$

In terms of

$$\vec{P} = \vec{p}_e + \vec{p}_p$$

$$\vec{R} = \frac{m_e r_e + m_p r_p}{m_e + m_p} \qquad (3)$$

$$r = r_e - r_p \qquad (4)$$

$$\vec{p} = \frac{m_p p_e - m_e p_p}{m_e + m_p} \qquad (5)$$

$$M = m_e + m_p \qquad (6)$$

and

$$\mu = \frac{m_e m_p}{M}, \qquad (7)$$

H_{ep} is

$$H_{ep} = \frac{\vec{P}^2}{2M} + \frac{\vec{p}^2}{2\mu} - \frac{e^2}{r} \tag{8}$$

where

$$r = |\vec{r}| = |\vec{r}_e - \vec{r}_p|. \tag{9}$$

We seek e-vecs of H, $\vec{P}^2$, L, and L_z in which

$$\vec{L} = \vec{r} \times \vec{p}. \tag{10}$$

These states $|\vec{P}', n, l, m\rangle$ satisfy

$$\vec{P}^2 \, |\vec{P}', n, l, m\rangle = \vec{P}'^2 \, |P, n, l, m\rangle \tag{11}$$

$$H_{ep} |\vec{P}' n l m\rangle = \left(\frac{\vec{P}'^2}{2M} + E_{nl} \right) |P' n l m\rangle \tag{12}$$

$$L^2 |\vec{P}' n l m\rangle = \hbar^2 l(l+1) \, |\vec{P}', n l m\rangle \tag{13}$$

$$L_3 |P' n l m\rangle = m\hbar \, |P' n l m\rangle. \tag{14}$$

These are direct-product states

$$|\vec{P}', n l m\rangle = |\vec{P}'\rangle \otimes |n l m\rangle. \tag{15}$$

Evidentally

$$H_{ep} = \frac{\vec{P}^2}{2M} + H \tag{16}$$

where

$$H = \frac{\vec{p}^2}{2m} - \frac{e^2}{r} . \tag{17}$$

By (12-14),

$$H|n\ell m\rangle = E_{n\ell}|n\ell m\rangle \tag{18}$$

$$L^2|n\ell m\rangle = \hbar^2 \ell(\ell+1)\,|n\ell m\rangle \tag{19}$$

$$L_3\,|n\ell m\rangle = m\hbar\,|n\ell m\rangle . \tag{20}$$

We know the solution will be of the form

$$\langle \vec{r}\,|n\ell m\rangle = \langle r\theta\varphi|n\ell m\rangle \tag{21}$$

$$= R_{n\ell}(r)\; Y_\ell^m(\theta,\varphi) \tag{22}$$

$$= \frac{u_{n\ell}(r)}{r}\; Y_\ell^m(\theta,\varphi) . \tag{23}$$

The radial equation is

$$-\frac{\hbar^2}{2\mu} u''_{n\ell}(r) + \left[-\frac{e^2}{r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right] u_{n\ell}(r) = E_{n\ell} u_{n\ell}(r). \quad (24)$$

First, we change from r to

$$\rho = r/a_0 \quad (25)$$

where $a_0 = \hbar^2/\mu e^2 = 0.529\,177\ \text{Å}$ (26)
is the Bohr radius. So we set

$$u_{n\ell}(r) = v_{n\ell}(r/a_0) = v_{n\ell}(\rho) \quad (27)$$

so that the argument of $v_{n\ell}$ now is dimensionless.

$$u'_{n\ell}(r) = v'_{n\ell}(\rho)\rho' = \frac{v'_{n\ell}(\rho)}{a_0} \quad (28)$$

in which $u' = du/dr$ and $v' = dv/d\rho$. So (24) gives

$$-\frac{\hbar^2}{2\mu}\frac{1}{a_0^2} v''_{n\ell}(\rho) + \left[-\frac{e^2}{a_0\rho} + \frac{\hbar^2 \ell(\ell+1)}{2\mu a_0^2 \rho^2}\right] v_{n\ell}(\rho)$$

$$= E_{n\ell} v_{n\ell}(\rho) \quad \text{or} \quad (29)$$

$$-\frac{\hbar^2 \mu^2 e^4}{2\mu \hbar^4} v''_{n\ell} + \left[-\frac{\mu e^4}{\hbar^2 \rho} + \frac{\mu e^4 \ell(\ell+1)}{2\hbar^2 \rho^2}\right] v_{n\ell} = E_{n\ell} v_{n\ell}. \quad (30)$$

This equation has $\mu e^4/\hbar^2$ as a common factor, which is closely related to the energy

$$E_I = \frac{1}{2}\mu c^2 \alpha^2$$

$$= \frac{1}{2}\mu c^2 \left(\frac{e^2}{\hbar c}\right)^2 = \frac{1}{2}\mu \frac{e^4}{\hbar^2} \qquad (31)$$

which will turn out to be the energy needed to ionize an atom of hydrogen in its ground state.

$$-E_I\, V''_{n\ell} + \left[E_I \frac{\ell(\ell+1)}{\rho^2} - \frac{2}{\rho} E_I\right] V_{n\ell} = E_{n\ell} V_{n\ell} \qquad (32)$$

or

$$V''_{n\ell} + \left(\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) V_{n\ell} = -\frac{E_{n\ell}}{E_I} V_{n\ell}. \qquad (33)$$

We are looking for the bound state with negative $E_{n\ell}$. For them, the ratio

$$-\frac{E_{n\ell}}{E_I} = \lambda_{n\ell}^2 > 0 \qquad (34)$$

is positive.

So our radial equation now is

$$V''_{n\ell} + \left[\frac{z}{\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] V_{n\ell} = \lambda_{n\ell}^2 \, V_{n\ell} \,, \qquad (35)$$

As we saw in class, as $\rho \to \infty$, the main terms in this equation are

$$V''_{n\ell}(\rho) = \lambda_{n\ell}^2 V_{n\ell}(\rho) \qquad (36)$$

whence

$$V_{n\ell}(\rho) = y_{n\ell}(\rho)\, e^{-\lambda_{n\ell}\rho} \qquad (37)$$

in which $y_{n\ell}(\rho)$ behaves quietly, compared to an exponential, as $\rho \to \infty$.

$$\begin{aligned} V' &= y' e^{-\lambda\rho} - \lambda y \, e^{-\lambda\rho} \\ &= (y' - \lambda y)\, e^{-\lambda\rho} \end{aligned} \qquad (38)$$

and

$$\begin{aligned} V'' &= (y'' - \lambda y') e^{-\lambda\rho} - \lambda(y' - \lambda y)\, e^{-\lambda\rho} \\ &= (y'' - 2\lambda y' + \lambda^2 y)\, e^{-\lambda\rho} . \end{aligned} \qquad (39)$$

So $y_{n\ell}(\rho)$ satisfies

$$\left(y''_{n\ell} - 2\lambda_{n\ell} y'_{n\ell} + \lambda^2_{n\ell} y_{n\ell}\right) e^{-\lambda_{n\ell}\rho}$$

$$+ \left[\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] y_{n\ell} e^{-\lambda_{n\ell}\rho} = \lambda^2_{n\ell} y_{n\ell} e^{-\lambda_{n\ell}\rho} \qquad (40)$$

or

$$y''_{n\ell} - 2\lambda_{n\ell} y'_{n\ell} + \left[\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] y_{n\ell} = 0. \qquad (41)$$

Frobenius's trick for solving such an equation is to write

$$y_{n\ell}(\rho) = \rho^s \sum_{q=0}^{\infty} c_q \rho^q = \sum_{q=0}^{\infty} c_q \rho^{s+q} \qquad (42)$$

in which we stipulate that $c_0 \neq 0$ so that

$$y_{n\ell}(\rho) \sim \rho^s \quad \text{as} \quad \rho \to 0. \qquad (43)$$

$$y' = \sum_{q=0}^{\infty} (s+q) c_q \rho^{s+q-1} \qquad (44)$$

$$y'' = \sum (s+q)(s+q-1) c_q \rho^{s+q-2}. \qquad (45)$$

So

$$\sum_q (s+q)(s+q-1)c_q\rho^{s+q-2} - 2\lambda\sum(s+q)c_q\rho^{s+q-1} \tag{46}$$

$$+\ 2\sum c_q\rho^{s+q-1} - \ell(\ell+1)\sum c_q\rho^{s+q-2} = 0. \tag{47}$$

The terms that dominate as $\rho \to 0$ have $q=0$ and are

$$s(s-1)c_0\rho^{s-2} - \ell(\ell+1)c_0\rho^{s-2} = 0 \tag{48}$$

whence

$$s(s-1) = \ell(\ell+1) \tag{49}$$

or

$$s = \ell+1 \quad \text{or} \quad -\ell \tag{50}$$

The choice $s=-\ell$ is absurdly singular, so we conclude

$$y_{n\ell}(\rho) = \rho^{\ell+1}\sum_{q=0}^{\infty} c_q\rho^q \tag{51}$$

which tells us that $V_{n\ell} \sim \rho^{\ell+1}$ and $u_{n\ell} \sim r^{\ell+1}$ and $R_{n\ell} \sim r^{\ell}$ as $\rho, r \to 0$. (52)

Now we shift the indices in (46) so that the power of ρ is the same in every term:

$$\sum_{q=0}^{\infty}(\ell+1+q)(\ell+q)c_q\rho^{\ell+q-1} - 2\lambda\sum_q(\ell+q)c_{q-1}\rho^{\ell+q-1} \qquad (53)$$

$$+2\sum_q c_{q-1}\rho^{\ell+q-1} - \ell(\ell+1)\sum_q c_q\rho^{\ell+q-1} = 0$$

We set the coefficient of $\rho^{\ell+q-1}$ equal to zero:

$$0 = \sum_q\left[(\ell+1+q)(\ell+q)c_q - 2\lambda(\ell+q)c_{q-1} + 2c_{q-1} - \ell(\ell+1)c_q\right]\rho^{\ell+q-1} \qquad (54)$$

that is,

$$0 = \left[(\ell+1+q)(\ell+q) - \ell(\ell+1)\right]c_q - 2\left[\lambda(\ell+q)-1\right]c_{q-1} \qquad (55)$$

or

$$\left[(\ell+1+q)(\ell+q) - \ell(\ell+1)\right]c_q = 2\left[(\ell+q)\lambda - 1\right]c_{q-1} \qquad (56)$$

or

$$\left[(\ell+1)q + q\ell + q^2\right]c_q = 2\left[(\ell+q)\lambda - 1\right]c_{q-1} \qquad (57)$$

$$(2\ell+1+q)\,q\,c_q = 2\left[(\ell+q)\lambda_{n\ell} - 1\right]c_{q-1}, \qquad (58)$$

which is our recursion relation.

Note that as $q \to \infty$

$$c_q \sim \frac{2q\lambda c_{q-1}}{q^2} \sim \frac{2\lambda}{q} c_{q-1} , \qquad (59)$$

so c_q looks like

$$c_q \sim \frac{(2\lambda)^q}{q!} C_0 \qquad (60)$$

which means that the full series looks like

$$Y_{nl}(\rho) = \sum \frac{(2\lambda_{nl})^q}{q!} \rho^q$$

$$\sim e^{2\lambda_{nl}\rho} \qquad (61)$$

which would leave us with

$$V_{nl}(\rho) = e^{-\lambda\rho} Y_{nl} \sim e^{\lambda_{nl}\rho} \qquad (62)$$

which is not normalizable.

The only way out is to require that for some finite integer

$$q = 1, 2, 3 \quad \text{etc} \qquad (63)$$

$$c_q = \frac{2\left[(\ell+q)\lambda_{n\ell} - 1\right] c_{q-1}}{(2\ell+1+q)\,q} = 0 \tag{64}$$

That is, for some $q = k$ a positive integer

$$(\ell+k)\,\lambda_{n\ell} - 1 = 0 \tag{65}$$

That is,

$$\lambda_{n\ell} = \frac{1}{\ell+k} \tag{66}$$

for $k = 1, 2, 3$ etc. But this means that

$$\lambda_{n\ell}^2 = -\frac{E_{n\ell}}{E_I} = \frac{1}{(\ell+k)^2} \tag{67}$$

or

$$E_{n\ell} = -\frac{E_I}{(\ell+k)^2} \, . \tag{68}$$

The value of $q = k$ that makes c_q zero must be a positive integer because $C_0 \neq 0$ by construction. The sum

$$n = \ell + k \tag{69}$$

is called the principical quantum number. The energy depends only on the principal quantum number

$$n = \ell + k \tag{70}$$

and

$$E_{n\ell} = E_n = -\frac{E_I}{n^2} = -\frac{1}{2}\mu c^2 \frac{\alpha^2}{n^2} . \tag{71}$$

The ground state has $k=1$ and $\ell = 0$ and $n=1$

$$E_n = -\frac{1}{2}\mu c^2 \alpha^2 \simeq -13.6\,eV. \tag{72}$$

In terms of n, since $k = 1, 2, 3$ etc.,

$$\ell = n - k \tag{73}$$

so for a given principal quantum number n, the possible values of the angular-momentum quantum number ℓ run from 0 for $k = n$ to $n-1$ for $k=1$

$$0 \leq \ell \leq n-1 \tag{74}$$

in steps of unity. For each ℓ, there are $2\ell+1$ possible values of m. The degeneracy of the nth energy level (due to a hidden symmetry) is

$$g_n = \sum_{\ell=0}^{n-1} (2\ell+1) = \frac{2(n-1)n}{2} + n = n^2 \text{ states.} \tag{75}$$

One may show that c_q is

$$C_q = (-1)^q \left(\frac{2}{k+\ell}\right)^q \frac{(k-1)!}{(k-q-1)!} \frac{(2\ell+1)!}{q!(q+2\ell+1)!} C_0 \qquad (76)$$

in which c_0 is determined by the normalization condition

$$1 = \int_0^\infty dr\, r^2 \, |R_{n\ell}(r)|^2 , \qquad (77)$$

The first three R's are

$$R_{10}(r) = 2(a_0)^{-3/2} e^{-r/a_0} \qquad (78)$$

$$R_{20}(r) = 2(2a_0)^{-3/2}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \qquad (79)$$

$$R_{21}(r) = (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0} . \qquad (80)$$

The historical jargon is s for $\ell=0$, p for $\ell=1$, d for $\ell=2$, f for $\ell=3$, g for $\ell=4$, h for $\ell=5$, i for $\ell=6$, and so on down the alphabet.

The quantity $r^2 R_{n0}^2(r)$ has a maximum at

$$r_n = n^2 a_0 \quad \text{for s-states.} \qquad (81)$$

The $\ell = 1$ wave functions are

$$\psi_{n,1,1}(\vec{r}) = -\sqrt{\frac{3}{8\pi}}\, R_{n1}(r) \sin\theta\, e^{i\varphi} \qquad 82$$

$$\psi_{n,1,0}(\vec{r}) = \sqrt{\frac{3}{4\pi}}\, R_{n1}(r) \cos\theta \qquad 83$$

$$\psi_{n,1,-1}(r) = \sqrt{\frac{3}{8\pi}}\, R_{n1}(r) \sin\theta\, e^{-i\varphi} \qquad 84$$

and from them we can form the linear combinations

$$\psi_{npx}(r) = -\frac{1}{\sqrt{2}}\left[\psi_{n11}(r) - \psi_{n1-1}(r)\right]$$

$$= \sqrt{\frac{3}{4\pi}}\, R_{n1}(r)\, \frac{x}{r} \qquad (85)$$

$$\psi_{npy}(r) = \frac{i}{\sqrt{2}}\left[\psi_{n11}(r) + \psi_{n1-1}(r)\right]$$

$$= \sqrt{\frac{3}{4\pi}}\, R_{n1}(r)\, \frac{y}{r} \qquad (86)$$

and

$$\psi_{npz}(\vec{r}) = \psi_{n10}(r) = \sqrt{\frac{3}{4\pi}}\, R_{n1}(r)\, \frac{z}{r}. \qquad (87)$$

Such orbitals are useful in chemistry and exist for all values of n and ℓ, and they are real.