The Hydrogen Atom

In SI units with $\frac{q^2}{4\pi\epsilon_0 r} = \frac{e^2}{r}$, 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

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

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

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

The radial equation is

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

First, we change from r to

$$\rho = r/a_0 \tag{25}$$

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

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

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

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

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

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

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

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

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 states with negative $E_{n\ell}$. For them, the ratio

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

is positive.

So our radial equation now is

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

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 $\rho \to \infty$.

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

and

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

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 $y_{n\ell} \sim \rho^{\ell+1}$ 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 $q \to \infty$

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

so c_q looks like

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

which means that the full series looks like

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

$$\sim e^{2\lambda_{nl}\rho} \tag{61}$$

which would leave us with

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

which is not normalizable.

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

$$q = 1, 2, 3 \quad \text{etc} \tag{63}$$

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

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

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

That is,

$$\lambda_{n\ell} = \frac{1}{\ell+k} \qquad (66)$$

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

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

or

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

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

$$n = \ell + k \qquad (69)$$

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

$$n = \ell + k \qquad (70)$$

and

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

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

$$E_n = -\frac{1}{2}\mu c^2 \alpha^2 \simeq -13.6\ \mathrm{eV}. \qquad (72)$$

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

$$\ell = n - k \qquad (73)$$

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 $k=1$

$$0 \le \ell \le n-1 \qquad (74)$$

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

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

One may show that c_q is

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

in which c_0 is determined by the normalization condition

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

The first three R's are

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

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

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

The historical jargon is s for $\ell=0$, p for $\ell=1$, d for $\ell=2$, f for $\ell=3$, g for $\ell=4$, etc., 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

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

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.