"The Ising Model is the Hydrogen Atom' of understanding ~~of~~ phase transitions"

The Hydrogen atom is the most important problem in QM.

The radial eqn, like that of the infinite spherical well, is not trivial to solve. Griffiths, because of its importance, goes through in great detail. As my stat mech told me "The serious ~~stat~~ student of stat mech will go through Onsager's sol-n of 2D Ising model" ~ 20 pages of very hairy algebra. So too here → the serious student of QM will go through H atom problem in detail.

Here we will not do all the algebra at the board

$\boxed{\text{START WITH ANSWER PAGE HA-6}}$

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2mr^2}\frac{l(l+1)}{}\right]u = Eu$$

"Tidy up notation" as before $\hbar^2k^2/2m = -E$

bound states $E<0$

$$\frac{1}{k^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2k}\frac{1}{kr} + \frac{l(l+1)}{(kr)^2}\right]u$$

$$\rho = kr \qquad \rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2k}$$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

$$\frac{d^2u}{dr^2} = \left[-k^2 + \frac{l(l+1)}{r^2}\right]u \quad \leftarrow \text{SQUARE WELL}$$

HA-2

$\rho = kr$ so $r \to \infty$

Consider $\rho \to \infty$ $\quad \left[1 - \rho_0/\rho + \ell(\ell+1)/\rho^2\right] \to 1$

$$d^2u/d\rho^2 = u \qquad u(\rho) = Ae^{-\rho} + Be^{\rho}$$

diverges / not normalizable

Similarly for $\rho \to 0$

$$d^2u/d\rho^2 = \frac{\ell(\ell+1)}{\rho^2}u \qquad u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

diverges / not normalizable

Actually not true for $\ell = 0$ but all we are doing is motivating a change of variables so okay.

Factoring out asymptotic behavior

$$u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho)$$

So now Griffiths computes $du/d\rho$ and $d^2u/d\rho^2$ for substitution in radial eqn and ends up with (Griffiths p147)

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + (\rho_0 - 2(\ell+1))v = 0$$

Just as for SHO and Hermite polys, at this point look for power series soln $\quad v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$

Again, considerable intervening algebra (Griffiths p 148) yields recursion reln

$$c_{j+1} = \left[\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right]c_j$$

HA-3

For large j one gets $c_{j+1} = \frac{2}{j+1} c_j$ ← why not drop the 1 if one is dropping l and ρ_0?! see Griffiths footnote p148

and, if this were always true $a_j = \frac{2^j}{j!} c_0$

with then $v(\rho) = c_0 \sum_j \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$

This overwhelms the $e^{-\rho}$ in $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$

so the series <u>must</u> <u>terminate</u>

$$c_{j_{max}+1} = 0 \implies 2(j_{max} + l + 1) - \rho_0 = 0$$

smallest n is n=1 since $j_{max}, l \geq 0$

Define $n = j_{max} + l + 1$ we get $\rho_0 = 2n$ and

$$E = \frac{-\hbar^2 k^2}{2m} = -\frac{m e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2} = \boxed{-\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = E_n}$$

Recall $k = \frac{m e^2}{2\pi\epsilon_0 \hbar^2 \rho_0}$

Energy indep of l

The value of this is $-13.6\,eV$

<u>1 Rydberg</u>

Meanwhile $k_n = \frac{m e^2}{4\pi\epsilon_0 \hbar^2} \frac{1}{n} = \frac{1}{a_0 n}$ $\boxed{\rho = k_n r = \frac{r}{a_0 n}}$

$$\boxed{a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \cdot 10^{-10}\ m}$$ <u>Bohr</u> <u>radius</u>

<u>Check #1s</u> $\frac{4\pi\epsilon_0 \hbar^2}{m e^2} = \frac{1}{9\cdot 10^9}\left(\frac{6.63 \cdot 10^{-34}}{2\pi}\right)^2 \frac{1}{9.11 \cdot 10^{-31}} \frac{1}{(1.6\cdot 10^{-19})^2}$

$$= \left(\frac{6.63}{2\pi}\right)^2 \frac{1}{9} \frac{1}{9.11} \frac{1}{(1.6)^2} \underbrace{10^{-68-9+31+38}}_{10^{-8}}$$

$$= \underbrace{\left(\frac{6.63}{2\pi}\right)^2 \frac{10}{9} \frac{10}{9.11} \frac{1}{(1.6)^2}}_{o(1)} \cdot 10^{-10}\ m$$

✓✓

Put everything together

These we know about already

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi)$$ ← Even though E is indep of ℓ, the wave function $R_{n\ell}$ is <u>not</u>

note u has ℓ dependence

$$R_{n\ell}(r) = \frac{u(\rho)}{\rho} = \frac{u(k_n r)}{\rho} = \frac{u(r/a_0 n)}{\rho}$$

ρ or r irrelevant here (just normalization)

$$j_{max} = n-\ell-1 \quad \text{with} \quad c_{j_{max}+1} = 0$$

$$u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho) \qquad v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \qquad \rho = r/a_0 n$$

$n =$ $\quad j_{max} = 0$

So for $n=1$ $\ell=0$ $\quad C_1 = 0 = c_2 = c_3 = \cdots$ so only $c_0 \neq 0$

$$u(\rho) = \rho^{\ell+1}e^{-\rho}c_0 = \rho e^{-\rho}c_0$$

$$R_1(r) = c_0 e^{-\rho} = c_0 e^{-r/a_0}$$

__Finally__ $\quad \psi_{100}(r,\theta,\phi) = c_0 e^{-r/a_0}\frac{1}{\sqrt{4\pi}} \rightarrow \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$

normalized

~~Normalized~~

Similarly get $\psi_{2lm} = R_{2l}(r)\, Y_{lm}(\theta,\phi)$

$$J_{max} = n - l - 1 \nearrow 0 \quad n=2 \; l=1$$
$$\searrow 1 \quad n=2 \; l=0$$

$c_{J_{max}+1} = 0$

For $n=2\; l=1$ $\quad c_1 = 0$ again and $v(\rho) = c_0$

$u \;\cancel{R_{21}} = \rho^{l+1} e^{-\rho} c_0$

$R_{21} \sim u/\rho \sim \rho e^{-\rho} c_0$

$$\psi_{21m}(r,\theta,\phi) = c_0 \rho e^{-\rho} \;\cancel{e^{-r/2a}}\; Y_{1m}(\theta,\phi)$$
$$\Rightarrow A\, r\, e^{-r/2a} Y_{1m}(\theta,\phi)$$
$$m = \pm 1, 0$$

On the other hand if $n=2\; l=0$ then $c_2 = 0$ and c_1 and c_0

terms both survive with (going back to recursion rel'n)

$$c_{J+1} = \frac{2(J+l+1-n)}{(J+1)(J+2l+2)} c_J$$

$n=2$
$J=0$
$l=0$

$$c_1 = \frac{2(-1)}{+2} c_0 = -c_0 \qquad v(\rho) = c_0(1-\rho)$$

$$u(\rho) \sim \rho^{(l+1)} e^{-\rho} c_0 (1-\rho)$$

$$R_{20} \sim u/\rho \sim c_0 e^{-\rho}(1-\rho) \qquad R_{20} \sim e^{-r/2a}\left(1 - \frac{r}{2a}\right)$$

In general, this procedure results in the "associated Laguerre polynomials"

$$V(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho)$$

Griffiths
pp 152-153

$$L^{p}_{q-p}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

$$\psi_{n\ell m}(r,\theta,\phi) = \left\{\begin{matrix}\text{normalization}\\ \text{constant}\end{matrix}\right\} e^{-r/na_0}\, r^\ell\, L^{2\ell+1}_{n-1-\ell}\left(\frac{2r}{na_0}\right) Y_{\ell m}(\theta,\phi)$$

$$a_0 = 4\pi\varepsilon_0\hbar^2/me^2 = 0.529 \cdot 10^{-10}\,\text{m}$$

this is $\rho^{\ell+1}$

$$E_{n\ell m} \to E_n = -\underbrace{\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2}_{13.6\,\text{eV}} \frac{1}{n^2}$$

conversion from u to V
and $1/r$ from u to R

Check out a few examples: ψ_{100} involves L^1_0 $\leftarrow p=1$, $\leftarrow q-p=0$ so $q=1$ also

$n=1$ $\ell=m=0$

$$L_1(x) = e^x \frac{d}{dx}(e^{-x}x) = e^x\left(e^{-x} - e^{-x}x\right) = 1-x$$

$$L^1_0(x) = (-1)^1 \frac{d}{dx}(1-x) = 1$$

so indeed no r dependence

Check also $n = 2$ cases

$$n = 2 \quad l = 1 \qquad L_{n-1-l}^{2l+1} \to L_0^3 \begin{array}{l} \leftarrow p = 3 \\ \leftarrow q - p = 0 \Rightarrow q = 3 \end{array}$$

$$L_3(x) = e^x \frac{d^3}{dx^3}\left(e^{-x} x^3\right)$$

$$\cancel{\frac{d}{}\left(e^{-x} x^3\right)} = e^x \frac{d^2}{dx^2}\left(e^{-x} 3x^2 - e^{-x} x^3\right)$$

$$= e^x \frac{d^2}{dx^2} e^{-x}(3x^2 - x^3)$$

$$= e^x \frac{d}{dx}\left[-e^{-x}(3x^2 - x^3) + e^{-x}(6x - 3x^2)\right]$$

$$= e^x \frac{d}{dx}\left[e^{-x}(6x - 6x^2 + x^3)\right]$$

$$= e^x \left[-e^{-x}(6x - 6x^2 + x^3) + e^{-x}(6 - 12x + 3x^2)\right]$$

$$= \left[-6x + 6x^2 - x^3 + 6 - 12x + 3x^2\right]$$

$$L_3(x) = (6 - 18x + 9x^2 - x^3)$$

$$L_0^3(x) = (-1)^3 \left(\frac{d}{dx}\right)^3 L_3(x) = 6$$ no r dependence here!

$$\psi_{21m} \sim e^{-r/2a_0} r^1 Y_{lm}(\theta, \phi) \quad \checkmark\checkmark$$

$$n = 2 \quad l = 0 \qquad L_{n-1-0}^{2l+1} \to L_1^1 \begin{array}{l} \leftarrow p = 3 \\ \leftarrow q - p = 1 \quad q = 4 \end{array}$$

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