Hydrogen atom in 3D: Nonrelativistic QM

We all know the hamiltonian

$$\boxed{\frac{\vec{\mathbb{P}}_n^2}{2M_n} + \frac{\vec{\mathbb{P}}_e^2}{2M_e} - \frac{Ze^2}{|\vec{x}_e - \vec{x}_n|}} \quad (1)$$

$\vec{x}_e$ is the position of the electron, $\vec{x}_n$ the position of the nucleon and $\vec{\mathbb{P}}_e$, $\vec{\mathbb{P}}_n$ their corresponding momenta.

We go, as usual, to the CM and relative coordinates.

$$\boxed{\vec{\mathbb{R}}_{CM} = \frac{M_n \vec{x}_n + M_e \vec{x}_e}{M_n + M_e} \qquad \vec{x} = \vec{x}_e - \vec{x}_n} \quad (2)$$

with the corresponding canonically conjugate momenta

$$\boxed{\vec{\mathbb{P}}_{CM} = \vec{\mathbb{P}}_e + \vec{\mathbb{P}}_n \qquad \vec{\mathbb{P}} = \frac{M_n \vec{\mathbb{P}}_e - M_e \vec{\mathbb{P}}_n}{M_e + M_n}} \quad (3)$$

The Hamiltonian becomes

$$\boxed{\mathcal{H} = \frac{\vec{\mathbb{P}}_{CM}^2}{2(M_e+M_n)} + \frac{\vec{\mathbb{P}}^2}{2M} - \frac{Ze^2}{|\vec{x}|}} \quad (4)$$

$$\boxed{M = \text{reduced mass} = \frac{M_e M_n}{M_e + M_n}} \quad (5)$$

The CM motion decouples and we will ignore it in the following.

$$\boxed{\mathcal{H}_H = \frac{\vec{\mathbb{P}}^2}{2M} - \frac{Ze^2}{|\vec{x}|}} \quad 6$$

Before we actually solve it let's do an order-of-magnitude estimate for the ground state energy.

Say the size of the wave f^n is $a \approx \Delta x$

Now by de Broglie's relation $p = \frac{h}{\lambda} \simeq \frac{h}{a}$

$$E \approx \frac{h^2}{2Ma^2} - \frac{Ze^2}{a}$$

What is the "best" value of a? The one that minimizes E

$$\frac{dE}{da} = 0 \Rightarrow -\frac{h^2}{Ma^3} + \frac{Ze^2}{a^2} = 0 \qquad a \simeq \frac{h^2}{MZe^2}$$

This defines a quantum length scale arising from this problem.

$$\boxed{a_0 = \frac{\hbar^2}{ZMe^2} \qquad \left(= \frac{4\pi\epsilon_0 \hbar^2}{ZMe^2} \text{ in MKS} \right)} \quad 7$$

This is the natural unit of length. The natural energy unit is $$\boxed{\frac{Ze^2}{a_0} = E_0 = \frac{\hbar^2}{Ma_0^2}} \quad (8)$$

Now we are ready to solve the problem. First let us identify all the symmetries we know about.

Clearly $\mathbb{H}_H$ is rotationally invariant, so $\vec{\mathbb{L}}^2$ and $\mathbb{L}_z$ are conserved.

$$\boxed{[\vec{\mathbb{L}}^2, \mathbb{H}_H] = [\mathbb{L}_z, \mathbb{H}_H] = [\vec{\mathbb{L}}^2, \mathbb{L}_z] = 0} \quad (9)$$

So we can simultaneously diagonalize $\mathbb{H}_H$, $\vec{\mathbb{L}}^2$ and $\mathbb{L}_z$.

We will choose to work in real space. The problem can also be solved completely algebraically, but that solution is not transparent.

The algebraic approach is based on the conserved Runge-Lenz vector

$$\boxed{\mathbb{A}_i = \epsilon_{ijk}(\mathbb{P}_j \mathbb{L}_k + \mathbb{L}_k \mathbb{P}_j) - \alpha \frac{\mathbb{X}_i}{|\mathbb{X}|}} \quad (10)$$

but we will not pursue this here.

We already know the eigenfunctions of $\vec{\mathbb{L}}^2$ & $\mathbb{L}_z$. They are the spherical Harmonics.

$$\boxed{\begin{aligned} \vec{\mathbb{L}}^2 Y_{\ell m}(\theta,\varphi) &= \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta,\varphi) \\ \mathbb{L}_z Y_{\ell m}(\theta,\varphi) &= \hbar m Y_{\ell m}(\theta,\varphi) \end{aligned}} \quad (11)$$

In 3D.

$$\boxed{\vec{p}^{\,2} = -\hbar^2 \vec{\nabla}^2 = -\hbar^2 \quad \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \quad + \frac{1}{r^2}\vec{\mathbb{L}}^2} \quad (12)$$

So our eigenstate is

$$\boxed{\psi_{\alpha l m}(r,\theta,\varphi) = R_{\alpha l m}(r)\, Y_{lm}(\theta,\varphi)} \quad (13)$$

where α is some (set) of other labels needed to completely characterize the quantum state.

$$\mathcal{H}_H \psi_{\alpha l m} = E_\alpha \psi_{\alpha l m}$$

$$\frac{-\hbar^2}{2Mr^2}\frac{d}{dr} r^2 \frac{dR_{\alpha l m}}{dr} + \frac{\hbar^2 l(l+1)}{2Mr^2} R_{\alpha l m} - \frac{Ze^2}{r} R_{\alpha l m} = E_\alpha R_{\alpha l m} \quad (14)$$

The eq^n is independent of m, so $\boxed{R_{\alpha l m} \equiv R_{\alpha l}}$ (15)

Let us work with dimensionless variables $\boxed{\rho = \beta r}$ (16) such that the E_α term becomes exactly $1/4$. This has the advantage that the large ρ asymptotics of R are uniform

$$\Rightarrow \frac{\hbar^2}{2M\rho^2}\beta^2 \left[-\frac{d}{d\rho} \rho^2 \frac{dR_{\alpha l}}{d\rho} + l(l+1) R_{\alpha l} \right] - \frac{Ze^2}{\rho}\beta R_{\alpha l} = E_\alpha R_{\alpha l}$$

$$\Rightarrow \text{ want } \boxed{\frac{2ME_\alpha}{\hbar^2\beta^2} = -\frac{1}{4} \qquad \beta = \sqrt{\frac{8M|E_\alpha|}{\hbar^2}}} \quad (17)$$

Remember, we want bound states so $E_\alpha < 0$

Define $\boxed{g = \frac{2MZe^2}{\hbar^2 \beta}}$ (18) which is dimensionless.

So $\frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{d}{d\rho}R_{\alpha\ell} + \left(\frac{g}{\rho} - \frac{\ell(\ell+1)}{\rho^2} + \frac{1}{4}\right)R_{\alpha\ell} = 0$

$$\Rightarrow \boxed{R''_{\alpha\ell} + \frac{2}{\rho}R'_{\alpha\ell} + \left(-\frac{1}{4} + \frac{g}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)R_{\alpha\ell} = 0} \quad (19)$$

The first thing to do is to look at the large-ρ behavior. The eq^n reduces to

$$\boxed{R''_{\alpha\ell} - \frac{1}{4}R_{\alpha\ell} = 0 \Rightarrow R_{\alpha\ell} \sim e^{-\rho/2}} \quad (20)$$

So let us define

$$\boxed{R_{\alpha\ell} = e^{-\rho/2} S_{\alpha\ell}(\rho)} \quad (21)$$

$$R'_{\alpha\ell} = e^{-\rho/2}\left(S'_{\alpha\ell} - \frac{1}{2}S_{\alpha\ell}\right)$$

$$R''_{\alpha\ell} = e^{-\rho/2}\left(S''_{\alpha\ell} - S'_{\alpha\ell} + \frac{1}{4}S_{\alpha\ell}\right)$$

The differential eq^n for $S_{\alpha\ell}$ is

$$S''_{\alpha\ell} - S'_{\alpha\ell} + \frac{1}{4}S_{\alpha\ell} + \frac{2}{\rho}S'_{\alpha\ell} - \frac{S_{\alpha\ell}}{\rho} - \frac{1}{4}S_{\alpha\ell} + \frac{g}{\rho}S_{\alpha\ell} - \frac{\ell(\ell+1)}{\rho^2}S_{\alpha\ell} = 0$$

$$\boxed{S''_{\alpha\ell} + \left(\frac{2}{\rho} - 1\right)S'_{\alpha\ell} + \frac{g-1}{\rho}S_{\alpha\ell} - \frac{\ell(\ell+1)}{\rho^2}S_{\alpha\ell} = 0} \quad (22)$$

Now we use the method of Frobenius. We assume a power series of the form

$$\boxed{S_{\alpha l}(\rho) = \rho^{\nu} \sum_{n=0}^{\infty} c_n \rho^n} \quad (23)$$

Where the power ν is known as the index.

$$S'_{\alpha l} = \sum_{0}^{\infty} (\nu+n)\, c_n \rho^{\nu+n-1}$$

$$S''_{\alpha l} = \sum_{0}^{\infty} (\nu+n)(\nu+n-1)\, c_n \rho^{\nu+n-2}$$

$$\Rightarrow \boxed{\begin{aligned} &\sum_{n=0}^{\infty} \left\{ c_n \rho^{\nu+n-2} \left[(\nu+n)(\nu+n-1) + 2(\nu+n) - l(l+1) \right] \right\} \\ &+ \sum_{n=0}^{\infty} c_n \rho^{\nu+n-1} \left[-(\nu+n) + g - 1 \right] = 0 \end{aligned}} \quad (24)$$

Let us look at the smallest power of ρ which is $\nu-2$. The coefficient must vanish

$$\Rightarrow \boxed{\nu(\nu-1) + 2\nu - l(l+1) = 0 \quad \text{or} \quad \nu(\nu+1) = l(l+1)} \quad (25)$$

This is the indicial equation. The solutions are

$$\boxed{\nu = l \quad \text{or} \quad \nu = -l-1} \quad (26)$$

For $l > 0$ any function that goes like $\rho^{-(l+1)}$ is not normalizable.

Even for $l=0$ one can show that choosing $\nu=-1$ does not give a different solution.

So in general $\boxed{\nu = l}$. (27) Putting this in we get

$$\sum_{j=0}^{\infty} \left\{ \rho^{l+j-2} c_j \left[\underbrace{(l+j)(l+j+1) - l(l+1)}_{j^2 + l(2j+1)} \right] + \rho^{l+j-1} c_j \left[g-1-l-j \right] \right\} = 0$$

The coeff of ρ^{l+j-1} is

$$\boxed{\begin{aligned} & c_j (g-1-l-n) + c_{j+1}\left[(j+1)^2 + l(2j+3)\right] = 0 \\ \Rightarrow \quad & c_{j+1} = c_j \frac{j+l+1-g}{(j+1)^2 + l(2j+3)} \end{aligned}} \quad (28)$$

For non-integer values of g this series will not terminate. Suppose this occurs. Then for large values of n we get

$$\boxed{c_{j+1} \approx \frac{c_j}{j+1} \quad \Rightarrow \quad c_j \approx \frac{1}{j!}} \quad (29)$$

$$\Rightarrow \quad \boxed{S_{\alpha l} \sim \rho^l e^{\rho}} \quad (30)$$

However, if this happens $R_{\alpha l} \sim \rho^l e^{\rho/2}$ diverges as $\rho \to \infty$, and is un-normalizable.

So we conclude that the series has to terminate.

This means $\boxed{g = \tilde{j} + \ell + 1}$ (31) for some $\tilde{j}$

Define $\boxed{n = \tilde{j} + \ell + 1 \Rightarrow g = n}$ (32)

This n is the principal quantum number.

Clearly, since $j \geq 0$ $\boxed{n - \ell - 1 \geq 0}$ (33)

Recall $g = \dfrac{2MZe^2}{\hbar^2 \beta}$ $\beta = \dfrac{\sqrt{8M|E_\alpha|}}{\hbar}$

$$g = n = \frac{Ze^2\sqrt{M}}{\hbar\sqrt{2|E_n|}}$$

$\Rightarrow$ $n^2 = \dfrac{Z^2e^4 M}{2\hbar^2|E_n|}$ $\boxed{E_n = -\dfrac{Ze^2}{2n^2 a_0}}$ (34)

Where $\boxed{a_0 = \dfrac{\hbar^2}{ZMe^2}}$ (7) is the length-scale we found earlier.

Since the series for $S_{\alpha\ell} \equiv S_{n\ell}$ terminates it is a polynomial. This polynomial belongs to a class called the (associated) Laguerre polynomials.

Let us define $\boxed{S_{n\ell}(\rho) = \rho^\ell L_{n\ell}(\rho)}$ (35)

$$S_{n\ell}' = \ell \rho^{\ell-1} L_{n\ell} + \rho^{\ell} L_{n\ell}'$$

$$S_{n\ell}'' = \ell(\ell-1)\rho^{\ell-2} L_{n\ell} + 2\ell\rho^{\ell-1} L_{n\ell}' + \rho^{\ell} L_{n\ell}''$$

$$\boxed{S_{\alpha\ell}'' + \left(\frac{2}{\rho} - 1\right) S_{\alpha\ell}' + \frac{g-1}{\rho} S_{\alpha\ell} - \frac{\ell(\ell+1)}{\rho^2} S_{\alpha\ell} = 0} \quad (22)$$

$$\Rightarrow \ell(\ell-1)\rho^{\ell-2} L_{n\ell} + 2\ell\rho^{\ell-1} L_{n\ell}' + \rho^{\ell} L_{n\ell}'' + 2\ell\rho^{\ell-2} L_{n\ell} + 2\rho^{\ell-1} L_{n\ell}'$$

$$- \ell\rho^{\ell-1} L_{n\ell} - \rho^{\ell} L_{n\ell}' + (g-1)\rho^{\ell-1} L_{n\ell} - \ell(\ell+1)\rho^{\ell-2} L_{n\ell} = 0$$

The $\rho^{\ell-2} L_{n\ell}$ terms cancel.

$$\rho^{\ell} L_{n\ell}'' + \rho^{\ell-1}(2\ell+2-\rho) L_{n\ell}' + \rho^{\ell-1}(g-1-\ell) L_{n\ell} = 0$$

or

$$\boxed{\rho L_{n\ell}'' + (2\ell+2-\rho) L_{n\ell}' + (n-1-\ell) L_{n\ell} = 0} \quad (36)$$

recall $g \equiv n$

Now we will make the connection with Laguerre polynomials.

The Laguerre polynomials $L_n(\rho)$ are defined by the generating function

$$\boxed{\frac{e^{-\frac{\rho s}{1-s}}}{1-s} = \sum_{0}^{\infty} \frac{L_n(\rho)}{n!} s^n} \quad (37)$$

They also have a Rodriguez formula

$$\boxed{L_n(\rho) = \frac{e^{\rho}}{n!}\frac{d^n}{d\rho^n}\left(e^{-\rho}\rho^n\right)} \quad (38)$$

(39)

In a power series $\boxed{L_n(\rho) = \sum_{k=0}^{n} (-1)^k \frac{\rho^k}{k!} \frac{n!}{k!(n-k)!}}$

The first few of them are

$$\boxed{L_0(\rho) = 1 \qquad L_1(\rho) = 1-\rho \qquad L_2(\rho) = 1 - 2\rho + \rho^2/2} \quad (40)$$

The associated Laguerre polynomials are

$$\boxed{\begin{aligned} L_m^p(\rho) &= \frac{x^{-p}e^{x}}{n!}\frac{d^m}{dx^m}\left(x^{m+p}e^{-x}\right) \\ &= \sum_{k=0}^{m} (-1)^k \frac{\rho^k}{k!} \frac{(m+p)!}{(m-k)!\,(p+k)!} \end{aligned}} \quad (41)$$

The differential eq^n satisfied by L_n^p is

$$\boxed{\rho\left(L_m^p(\rho)\right)'' + (p+1-\rho)\left(L_m^p(\rho)\right)' + m L_m^p(\rho) = 0} \quad (42)$$

Comparing to (35) we see that we need

$m = n-l-1 \qquad p = 2l+1$

The solution we want is

$$\boxed{R_{n\ell}(\rho) = \rho^{\ell}\, L^{2\ell+1}_{n-\ell-1}(\rho)\, e^{-\rho/2}} \quad (43)$$

The fully normalized wave f^n is

$$\psi_{n\ell m} = \left\{ \left(\frac{2}{n a_0}\right)^3 \frac{(n-\ell-1)!}{2n\,((n+\ell)!)} \right\}^{1/2} e^{-\rho/2} \rho^{\ell} L^{2\ell+1}_{n-\ell-1}(\rho)\, Y_{\ell m}(\theta,\varphi)$$

$$\rho = \frac{2r}{n a_0} \qquad a_0 = \frac{\hbar^2}{ZMe^2} \quad (44)$$

Recall that $n-\ell-1 \geq 0$.

So $n=1$ is the smallest possible value.

For any n we can have values of ℓ

$$\boxed{0 \leq \ell \leq n-1} \quad (45)$$

Each value of ℓ has a degeneracy of $2\ell+1$ so the orbital degeneracy of a given n (which determines the energy E_n) is

$$\boxed{\sum_0^{n-1} (2\ell+1) = n + 2 \cdot \frac{n(n-1)}{2} = n^2} \quad (46)$$

Including the spin of the electron we get $2n^2$ states with energy E_n

Normally, if a 3D Hamiltonian has only rotational invariance we expect the energy to be independent of m, but dependent on n and l.

The reason the H-Atom hamiltonian has extra degeneracies is due to the conservation of the Runge-Lenz vector of Eq 10.

Of course, what we have done is only the beginning of the story of atoms.

Atoms have many electrons that interact with each other. Also, we have assumed the nucleus to be a point particle, which is not true. Finally, the correct eq^n for the electron is the Dirac eq^n which, in the non-relativistic limit produces the Hamiltonian we have started with, but also many other correction terms.