Discussion 12 – Hydrogenic Atom : Radial Wavefunction

In Discussion 11 you separated the wavefunction and Schrödinger equation for any central potential $V(r)$ into a radial part $R(r)$ and an angular part $Y(\theta,\phi)$. You solved the angular part; that gave you the spherical harmonics $Y_l^m(\theta,\phi)$. In Homework 11, you solve the radial equation for the simple harmonic oscillator. Here, we will solve the radial equation for a very important system indeed: a **hydrogenic atom** , namely an atom with a **single electron** of charge e and a nucleus of charge Ze. The central potential seen by the electron is

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

in SI units. At right is the same strategy box as on homework; it is pretty much universal for solving the radial part of the spherically-separated Schrödinger equation. It greatly resembles the method you used to obtain the energy eigenfunctions of a harmonic oscillator in a Cartesian coordinate, but there are two important differences when the <u>radial coordinate r</u> is the independent variable .The differences are highlighted in red.

> <u>Radial SE : Strategy Box</u>
>
> 1. Use **dimensionless quantities** to simplify equation to solve (SE), and switch to $\boldsymbol{u(r) \equiv r\,R(r)}$
> 2. Find **asymptotic behaviour** of solutions as $r \to \pm\infty$ and $\boldsymbol{r \to 0}$ to ensure normalizability.
> 3. <u>Guess</u> ψ = asymptotic behaviour × **power series** … & <u>plug</u> in SE.
> 4. **Terminate power series** to again ensure normalizability.

Problem 1 : Separation of Variables & Step 1 *Checkpoints* [1]

Our goal is, as always, to "solve the Schrödinger equation", i.e. to find the eigenstates of the Hamiltonian, which are the energy eigenstates of the system. Last week you made huge progress: you found that for a central potential $V(r)$,

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(r) = -\frac{\hbar^2\nabla^2}{2m} + V(r) = \frac{1}{r^2}\left[-\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2m}\right] + V(r)$$

(a) Your separated form $\psi(\vec{r}) = R(r)Y(\theta,\phi)$ led to a class of solutions $Y_{lm}(\theta,\phi)$ for the angular part that are eigenfunctions of both L^2 and L_z , with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$ respectively. Plug this info into the SE,

$$\hat{H}\; R(r)\, Y_l^m(\theta,\phi) = E\; R(r)\, Y_l^m(\theta,\phi)\,,$$

to obtain the radial equation for $R(r)$.

(b) The new element in step 1 of the strategy box is to switch from $R(r)$ to $u(r) \equiv r\,R(r)$. (This reduces the number of terms and makes the resulting equation more similar in form to the 1D SE.) It's just algebra:

in terms of $\boxed{u(r) \equiv r\,R(r)}$, the **radial SE** is $\boxed{-\frac{\hbar^2}{2m}u'' + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = E\,u}$

Next, we switch to **dimensionless variables** as much as possible. This is still step 1 and will *enormously*

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[1] (a) $\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]R = l(l+1)R$ (b) remember: $\hbar$ has units of *angular momentum* … answer: 1/distance^2.

(c) $\frac{d^2u}{dr^2}r^2 = u\left[-\frac{2mE}{\hbar^2}r^2 + l(l+1) - \frac{Ze^2}{4\pi\varepsilon_0}\frac{2mr}{\hbar^2}\right]$ (d) Hint: think of the force and/or potential energy between two charges …

answ: energy · distance (e) energy · distance (f) 197 eV·nm (g,h) checked by later parts (i) $\lambda = Z\alpha\sqrt{-2mc^2/E}$ (j) 0.53×10^{-10} m simplify our work. It seems clear that we should multiply the radial SE by $-2m/\hbar^2$. That will give $2mE/\hbar^2$ on the right-hand side. What are the units of $2mE/\hbar^2$?

(c) To make all the coefficients in front of $u(r)$ dimensionless, we should therefore multiply the entire radial SE by $-2m/\hbar^2 \times$ distance^2 … so by $-2mr^2/\hbar^2$. Multiply the radial SE in the box by $-2mr^2/\hbar^2$ and rearrange the terms a bit so that the term with u'' is on its own on the left-hand side.

(d) Next let's work on the potential the electron sees from the singly-charged nucleus,

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

First, here are some REALLY BIG THINGS TO KNOW. What are the units of $e^2/4\pi\varepsilon_0$? Tactic: think of a *familiar formula* (look up …) that is *close* to the combination you are analyzing; that is usually the fastest way to figure out the units of a term with a quantity like ε_0 in it that has highly non-trivial units.

(e) What are the units of the EXTREMELY USEFUL combination $\hbar c$?

(f) Calculate $\hbar c$ in units of eV · nm, where 1 eV = 1.6×10^{-19} J of energy and 1 nm = 10^{-9} m of distance. Totally equivalent units are MeV · fm, where 1 MeV = 10^6 eV and 1 fm = 10^{-6} nm.

(g) 197 is so close to 200 that EVERYONE in nuclear / particle physics knows that $\boxed{\hbar c = 200 \text{ MeV}\cdot\text{fm}}$, and EVERYONE in atomic / optical physics knows that $\boxed{\hbar c = 200 \text{ eV}\cdot\text{nm}}$. This is accurate to 1.5%, perfect! Super! OK, now take the ratio of the combinations in parts (d) and (e). This ratio is universally called α:

$$\boxed{\alpha \equiv \frac{e^2}{4\pi\varepsilon_0 \hbar c}}$$

It is dimensionless by construction, so it is a **dimensionless measure** of the **strength of the electromagnetic interaction**. It is often called the **electromagnetic coupling constant**. Using some consistent set of units, calculate the inverse of this number, $1/\alpha$.

(h) $\boxed{\alpha = 1/137}$ to 4 significant digits! This is also a BIG THING TO KNOW.
The particle whose wavefunction we are calculating is an atomic electron. Its mass *m* appears in our equations. Well, everyone in atomic or subatomic physics knows not the *mass m* of elementary particles exactly, but instead their *rest energy* mc^2. That comes out in units of energy, and for atomic or subatomic particles, the perfect energy unit is the electron-volt, eV = 1.6×10^{-19} J. In atomic physics, the **electron mass** is universally known as $\boxed{mc^2 = 0.5 \text{ MeV}}$, which is another BIG THING TO KNOW. Now back to the radial equation. We found the dimensionless combination $2mEr^2/\hbar^2$ in an earlier part, so let's introduce variables to exploit that:

$$\boxed{K \equiv \frac{\sqrt{-2mE}}{\hbar} = \frac{\sqrt{-2mc^2E}}{\hbar c}}$$ has distance units, $\therefore$ $\boxed{\rho \equiv Kr}$ is dimensionless.

$\rho \equiv Kr$ will serve as our **dimensionless distance**. From part (c), our radial equation is :

$$\frac{d^2u}{dr^2} r^2 = u\left[-\frac{2mE}{\hbar^2} r^2 + l(l+1) - \frac{Ze^2}{4\pi\varepsilon_0}\frac{2mr}{\hbar^2}\right]$$

Rewrite this, replacing all incidences of r with ρ/K, so that we are solving for $u(\rho)$ now instead of $u(r)$, and so that u'' now means $d^2u/d\rho^2$ instead of d^2u/dr^2.

(i) To the right of the *obviously* dimensionless term $l(l+1)$ is the electric potential term. It should now look like <dimensionless_prefactor> · ρ. What is this <dimensionless_prefactor>? We'll henceforth label it λ.

CHECKPOINT: At this point your radial SE should have this form :

$$\boxed{u''(\rho) = u(\rho)\left[1 - \frac{\lambda}{\rho} + \frac{l(l+1)}{\rho^2}\right]} \qquad \text{where} \qquad \boxed{\lambda \equiv Z\alpha\sqrt{\frac{2mc^2}{-E}}}$$

(j) There's one more important quantity to introduce: the **Bohr radius, a_0** = $\hbar c / (\alpha m_e c^2)$. Calculate its value using the fabulous numbers from the boxes on the previous page. It will turn out to be the average radius of the hydrogen ground state (in the somewhat unusual manner shown below).

That was the last BIG THING TO KNOW, i.e. the last of the numerical quantities that every physicist knows by heart (at least, those related to atoms).

$$\boxed{a_0 = \frac{\hbar c}{\alpha\, m_e c^2} = 0.5\,\text{Å}} = \begin{matrix}\text{Bohr}\\ \text{radius}\end{matrix}$$; we will find that the hydrogen ground state has $$\boxed{\left\langle \frac{1}{r} \right\rangle_{\substack{\text{ground}\\ \text{state}}} = \frac{1}{a_0}}$$

Problem 2 : Step 2 = Asymptotic Behaviour *Checkpoints* [2]

Next step: find the asymptotic behaviour of $u(\rho)$. As you see in the strategy box, you have to consider not only the behaviour as $\rho = K r \to \infty$ but also the behaviour as $\rho \to 0$. The spherical coordinate system has "coordinate singularities" at the origin $r = 0$ and at the poles $\theta = 0$ and π. We must always check these spots for unphysical behaviour like functions going to ∞ (which a physical wavefunction cannot do!)

(a) From the radial equation in the box at the top of the page, take the approximation $\rho \to \infty$ and see what *physically-reasonable* asymptotic solution $u_\infty(\rho)$ you obtain. REMEMBER from class: the asymptotic solution is an approximate solutions to an approximate equation, which takes a bit of getting used to.

(b) Now do the same for the limit $\rho \to 0$. What *physically reasonable* asymptotic solution $u_0(\rho)$ do you obtain in this region?

Problem 3 : Step 3 = Power Series Solution *Checkpoints* [3]

Now that we have the behaviour of $u(\rho)$ at large and small ρ, we can assume that the remaining behaviour in the "middle" region of finite ρ is a well-behaved function that we will call $h(\rho)$. Our proposed solution form is then $u(\rho) = u_\infty(\rho)\, u_0(\rho)\, h(\rho)$. We will try a power-series solution for $h(\rho)$ – the polynomial method :

$$u(\rho) = e^{-\rho}\, \rho^{l+1}\, h(\rho) \qquad \text{where} \qquad h(\rho) = \sum_{j=0}^{\infty} a_j\, \rho^j$$

We plug this $u(p)$ back into the radial SE and, after some tedious and completely uninstructive algebra we get an equation for $h(\rho)$:

$$h''[\rho] + h' 2\left[-\rho + (l+1)\right] + h\left[\lambda - 2(l+1)\right] = 0$$

Using this equation, find the **recursion relation** for the coefficients a_j in the power series.

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[2] **Q2 (a)** $u_\infty(\rho) \sim e^{-\rho}$ **(b)** $u_0(\rho) \sim \rho^{l+1}$

[3] **Q3** $a_{j+1} = a_j \dfrac{2(l+1+j) - \lambda}{(j+1)\left[2(l+1) + j\right]}$

Problem 4 : Step 4 = Truncation of Series → Energy Spectrum *Checkpoints* [4]

We must make sure that the power series $h(\rho)$ doesn't alter the asymptotic behaviour that we already took care of with $u_\infty(\rho)$. Let's leave off questions of convergence for the moment; we know that we will *for sure* leave the asymptotic behaviour unchanged if we **truncate** the power series for $h(\rho)$ at some finite index $j_{\max}$.

(a) Perform this truncation: restrict some parameter of our system so that $a_{j\,\max}$ is the last non-zero term in the series. You will obtain the **discrete energy spectrum** $\boldsymbol{E_n}$ for the hydrogen atom.
IMPORTANT: What is n, you ask? You define it! Pick something that makes the energy formula E_n as simple as possible, then see if your choice matches the standard one given in the checkpoint.

(b) For a given value of n, what is the allowed range of l ? You should find another very important constraint!

(c) Was this truncation *necessary*? Using what we learned in class, show that it was!

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[4] **Q3 (a)** $n \equiv j_{\max} + l + 1 \;\rightarrow\; E_n = -\dfrac{Z^2\alpha^2 mc^2}{2n^2}$ **(b)** $l < n$ because of $n \equiv j_{\max} + l + 1$ and the fact that $j_{\max}$ = max-of-index-$j \geq 0$

(c) Taylor-expand the asymptotic behaviour $e^{-\rho}$ as a power series $\sum_j b_j \rho^j$ … find $b_j = (-1)^j / j!$ … compare $\dfrac{a_{j+1}}{a_j}$ & $\dfrac{b_{j+1}}{b_j}$

… at very large j (the only terms that affect the $\rho \to \pm\infty$ behaviour of these series) you find $\dfrac{a_{j+1}}{a_j} \approx \dfrac{2}{j}$ & $\dfrac{b_{j+1}}{b_j} \approx -\dfrac{1}{j}$

… since the "b-series" is $e^{-\rho}$, you can conclude that the "a-series", $h(\rho)$, has asymptotic behaviour $e^{+2\rho}$

… $h(\rho) \rightarrow e^{+2\rho}$ as will *destroy* the $e^{-\rho}$ behaviour that we know we must get as $\rho \rightarrow \infty$, ∴ we MUST truncate the a-series