

HW 14 for General Physics II

Answer Keys by SJ

1. (Adapted from Griffiths P 5.1, for the general treatment of two-particle system, where electron in H atom belongs)

For the potential only depends on relative position between the two particles: $V(r)$, $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$, and the mass are m_1, m_2 respectively;

$\vec{r}_1 = (x_1, y_1, z_1)$ for position of particle 1; and $\vec{r}_2 = (x_2, y_2, z_2)$ for particle 2. The S-equation in terms of $(x_1, y_1, z_1), (x_2, y_2, z_2)$ is:

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V(r)\psi = E\psi ; \text{ where:}$$

$$\nabla_1^2 = \nabla_1 \cdot \nabla_1 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \text{ and } \nabla_2^2 = \nabla_2 \cdot \nabla_2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}$$

In this case the S-equation can be separated into center of mass and

reduced mass part, with CM defined: $\vec{R} \equiv \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$, and reduced

mass: $\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$.

- (a) Show that $\vec{r}_1 = \vec{R} + (\mu/m_1)\vec{r}$, $\vec{r}_2 = \vec{R} - (\mu/m_2)\vec{r}$ and $\nabla_1 =$

$$(\mu/m_2)\nabla_R + \nabla_r, \nabla_2 = (\mu/m_1)\nabla_R - \nabla_r$$

- (b) Show that the time-independent S-equation then becomes:

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 \psi - \frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(r)\psi = E\psi$$

- (c) Separate the variables, letting $\psi(\vec{R}, \vec{r}) = \psi_R(\vec{R})\psi_r(\vec{r})$. The S-equation will be separated into two parts. One is a free particle with mass $M = m_1 + m_2$ and energy E_R ; the other is particle with reduced mass in central field with energy E_r , with $E_{\text{total}} = E_R + E_r$. Like in classical

mechanics, the M part is translation of the whole system and we seldom focus on it. The relative motion represented by $\psi_r(\vec{r})$ and E_r are what we concerned in such problems (as we did in H atom)

Answers:

(a) From $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$ (1), $\vec{R} \equiv \frac{m_1\vec{r}_1+m_2\vec{r}_2}{m_1+m_2}$ (2) and $\mu \equiv \frac{m_1m_2}{m_1+m_2}$
 $m_1\vec{r}_1 + m_2\vec{r}_2 = (m_1 + m_2)\vec{R}$, $m_2\vec{r} \equiv m_2\vec{r}_1 - m_2\vec{r}_2$, add the two and divide (m_1+m_2) then:

$$\vec{r}_1 = \vec{R} + (\mu/m_1)\vec{r}.$$

Similarly:

$$\vec{r}_2 = \vec{R} - (\mu/m_2)\vec{r}$$

Or write above in component:

$$x_1 = X + (\mu/m_1)x$$

$$x_2 = X - (\mu/m_2)x$$

$$X = \frac{m_1x_1+m_2x_2}{m_1+m_2}, x = x_1 - x_2 \text{ (similar for y, z parts)}$$

For the x component of the gradient:

$$\nabla_{1x} = \frac{\partial}{\partial x_1} = \frac{\partial}{\partial X} \frac{\partial X}{\partial x_1} + \frac{\partial}{\partial x} \frac{\partial x}{\partial x_1} = \frac{m_1}{m_1+m_2} \frac{\partial}{\partial X} + \frac{\partial}{\partial x} = \frac{\mu}{m_2} \frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

$$\nabla_{2x} = \frac{\partial}{\partial x_2} = \frac{\mu}{m_1} \frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

Similar relations for the y, z parts, so we have overall:

$$\nabla_1 = (\mu/m_2)\nabla_R + \nabla_r, \nabla_2 = (\mu/m_1)\nabla_R - \nabla_r$$

$$(b) H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r)$$

$$\begin{aligned}
\nabla_1^2 &= \nabla_1 \cdot \nabla_1 = [(\mu/m_2)\nabla_R + \nabla_r] \cdot [(\mu/m_2)\nabla_R + \nabla_r] \\
&= (\mu/m_2)^2 \nabla_R^2 + \nabla_r^2 + (\mu/m_2)\nabla_R \cdot \nabla_r + \nabla_r \cdot (\mu/m_2)\nabla_R \\
\nabla_2^2 &= [(\mu/m_1)\nabla_R - \nabla_r] \cdot [(\mu/m_1)\nabla_R - \nabla_r] \\
&= (\mu/m_1)^2 \nabla_R^2 + \nabla_r^2 - (\mu/m_1)\nabla_R \cdot \nabla_r - \nabla_r \cdot (\mu/m_1)\nabla_R
\end{aligned}$$

Thus: let $M=m_1+m_2$

$$\begin{aligned}
-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 &= -\frac{\hbar^2}{2} \left[\frac{m_1}{M^2} \nabla_R^2 + \frac{1}{m_1} \nabla_r^2 + \frac{m_2}{M^2} \nabla_R^2 + \frac{1}{m_2} \nabla_r^2 \right] \\
&= -\frac{\hbar^2}{2} \left[\frac{1}{M} \nabla_R^2 + \frac{1}{\mu} \nabla_r^2 \right]
\end{aligned}$$

The H and the time-independent S-equation becomes:

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_R^2 \psi - \frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(r)\psi = E\psi$$

(c) $H = H_{CM} + H_r$

$$H_{CM} = -\frac{1}{2M} \nabla_R^2; H_r = -\frac{1}{2\mu} \nabla_r^2 + V(r)$$

Letting: $\psi(\vec{R}, \vec{r}) = \psi_R(\vec{R})\psi_r(\vec{r})$ and divide the S-equation by it:

$$\frac{H_{CM}\psi_R}{\psi_R} + \frac{H_r\psi_r}{\psi_r} = E$$

The left two terms are function of R only and r only, so the requirement that they add up to some constant is the two terms equal to some constant each:

$$\frac{H_{CM}\psi_R}{\psi_R} = E_R \rightarrow H_{CM}\psi_R = E_R\psi_R$$

$$\frac{H_r\psi_r}{\psi_r} = E_r \rightarrow H_r\psi_r = E_r\psi_r$$

With $E = E_R + E_r$

2. Griffiths P 4.10

Work out the **radial** wave functions R_{30} , R_{31} and R_{32} for Hydrogen atom, using the recursion formula and don't bother to normalize them.

Answer:

The formulas we may use are:

$$R(r) = u(r)/r \quad u(r) = v(\rho)\rho^{l+1}e^{-\rho}$$

$$\rho \equiv kr, \quad k = \sqrt{2m(-E)}/\hbar$$

$$E = -\frac{1}{n^2} \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -\frac{\hbar^2}{2n^2 m_e a_0^2}; \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

$$\text{Then } \rho = \frac{r}{na_0}$$

$$v(\rho) = c_0 + c_1\rho + \dots = \sum_{j=0}^{\infty} c_j \rho^j$$

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

$n \equiv j_0 + l + 1$ (j_0 is the highest power in polynomial)

For the R_{30} , $n = 3, l = 0$, then $j_0 = 2$, $\rho = r/3a_0$

$$v_{30}(\rho) = c_0 + c_1\rho + c_2\rho^2$$

$$c_1 = c_0 \left[\frac{2(0+0+1) - 6}{(0+1)(0+0+2)} \right] = -2c_0$$

$$c_2 = c_1 \left[\frac{2(1+0+1) - 6}{(1+1)(1+0+2)} \right] = -\frac{1}{3}c_1 = \frac{2}{3}c_0$$

$$R_{30}(r) = c_0 \left(1 - 2\rho + \frac{2}{3}\rho^2 \right) \frac{\rho}{r} e^{-\rho}, \quad \rho = r/3a_0$$

For R_{31} , $n = 3, l = 1$. Then $j_0 = 1, \rho_0 = 6$ and $\rho = r/3a_0$

$$v_{31}(\rho) = c_0 + c_1\rho$$

$$c_1 = c_0 \left[\frac{2(0+1+1) - 6}{(0+1)(0+2+2)} \right] = -\frac{1}{2}c_0$$

$$R_{31}(r) = c_0 \left(1 - \frac{1}{2}\rho\right) \frac{\rho^2}{r} e^{-\rho}$$

For R_{32} , $n = 3, l = 2 \rightarrow j_0 = 0, \rho_0 = 6, \rho = r/3a_0$

$$R_{32}(r) = c_0 \frac{\rho^3}{r} e^{-\rho}$$

3. Combined Griffiths P 4.13 and P 4.14 and more

(a) Find $\langle r \rangle$ and $\langle r^2 \rangle$ for an electron in the ground state of hydrogen. Express the answer in terms of Bohr radius.

(b) What is the most probable value of r , in the ground state of hydrogen? Hint: First you must find the probability density that the electron would be found between r and $r+dr$.

c) For the ground state 1S orbit (same ψ_{100} as above), we are trying to calculate the radius of the sphere R , of which the electron in 1S orbit has 90% probability found inside this sphere. Express R in terms of Bohr radius. (This is the sphere I draw in my PPT of the 1S, and the size of it give us a rough idea to the distance between H atoms in ground state in order to have significant interaction, such as forming H₂ molecule).

During the calculation you may need software (or graphical tool) to get the numerical value. I recommend <https://www.wolframalpha.com/>; you

can do the numerical computation online there. (That is a famous website for numerical computation and really easy to use; and also you can access it in Mainland, at least for now)

d) For the 2S orbit (ψ_{200} , the 1st excited state), find the position of local extremes along the radial r ; i.e. finding the local extremes of $P(r)$, the probability density along r . (be warned $P(r)$ is not same as $R_{nl}(r)^2$, and also you may need wolframalpha). Express the location of extremes in terms of Bohr radius. (you shall find 3 local extremes, corresponding to local max.; local mini. And another local max.)

Answers:

(a) The ground state of H atom is:

$$\begin{aligned}\psi_{100} &= R_{10}(r)Y_0^0(\theta, \varphi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \\ \langle r \rangle &= \iiint r |\psi|^2 r^2 \sin \theta \, dr d\theta d\varphi = \frac{1}{\pi a_0^3} 4\pi \int_0^\infty r e^{-2r/a_0} r^2 dr \\ &= \frac{3}{2} a_0 \\ \langle r^2 \rangle &= \frac{1}{\pi a_0^3} 4\pi \int_0^\infty r^2 e^{-2r/a_0} r^2 dr = 3a_0^2\end{aligned}$$

(b) The probability find the electron between r and $r+dr$, is just the probability of electron in a spherical shell with radius r , and that of $r+dr$. Volume of the shell is $4\pi r^2 dr$, the probability for electron in

this shell is then:

$$P_{r \rightarrow r+dr} = |\psi_{100}|^2 4\pi r^2 dr = \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr$$

(or you may use $P(r) = R_{nl}(r)^2 r^2$, $R_{10} = 2a_0^{-3/2} e^{-r/a_0}$)

The probability density along r is then:

$$\rho = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

It is largest when:

$$\frac{d\rho}{dr} = 0 = \frac{4}{a_0^3} [2r e^{-2r/a_0} - \frac{2r^2}{a_0} e^{-2r/a_0}] \rightarrow r = a_0$$

The probability density along r is largest when $r=a_0$

c) Let the radius of the sphere be R, the 90% chance to find e inside the sphere is:

$$\int_0^R P(r) dr = 0.9, \text{ where } P(r) = R_{nl}(r)^2 r^2, R_{10} = 2a_0^{-3/2} e^{-r/a_0}$$

So the integration will be:

$$\frac{4}{a_0^3} \int_0^R r^2 e^{-2r/a_0} dr = 0.9$$

Check the table (or integration by part):

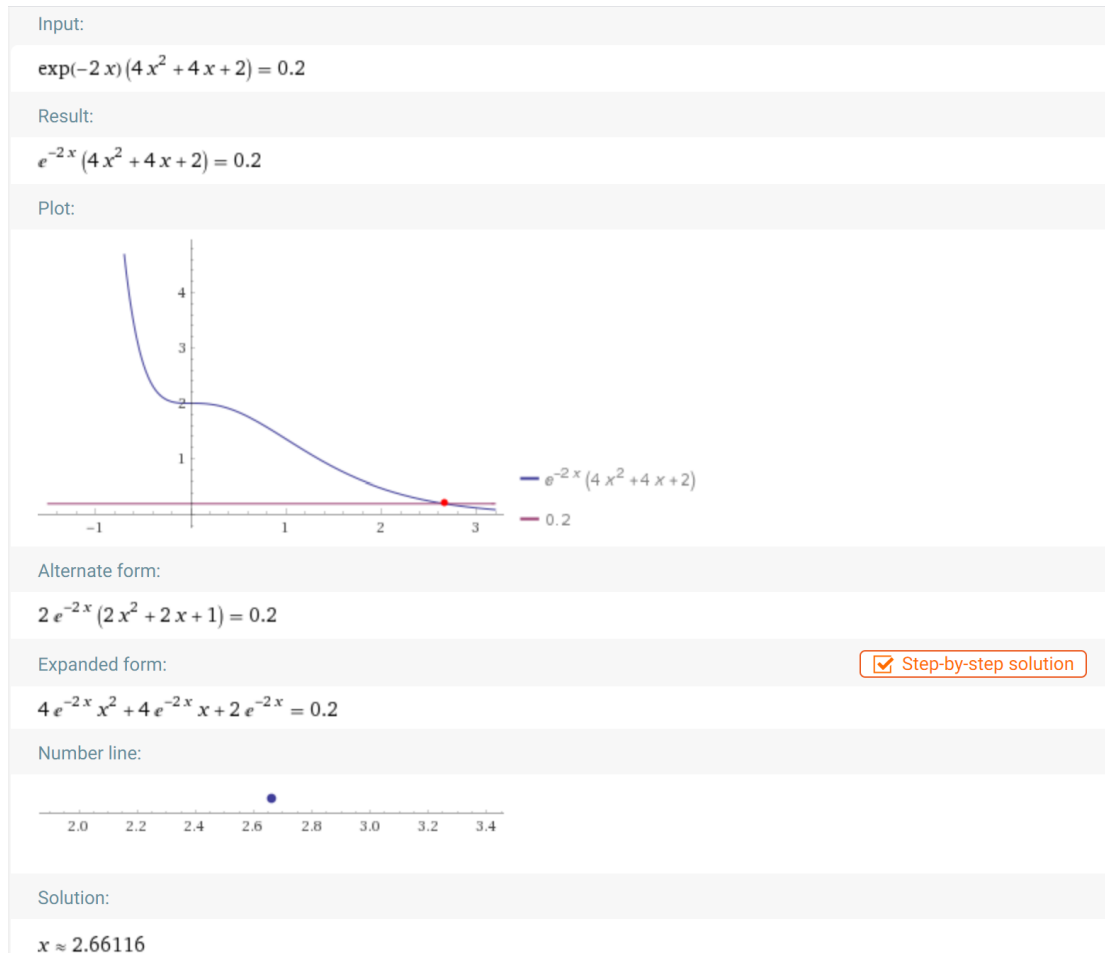
$$\int x^2 e^{-Ax} dx = -\frac{e^{-Ax}}{A^3} ((Ax)^2 + 2Ax + 2)$$

Here out $A = \frac{2}{a_0}$, using above formula, our integration is:

$$1 - \frac{1}{2} e^{-2x} (4x^2 + 4x + 2) = 0.9; \quad x = r/a_0$$

$$\text{Or: } e^{-2x} (4x^2 + 4x + 2) = 0.2$$

I used wolfram:



So $R=2.66a_0$

d) For the 2s orbit $\psi_{200} = \frac{1}{\sqrt{2}}a_0^{-\frac{3}{2}}\left(1 - \frac{1}{2}\frac{r}{a_0}\right)e^{-r/2a_0}\frac{1}{\sqrt{4\pi}}$

(I purposely write the R and Y part apart)

The probability density along r P(r):

$$P(r) = R_{20}^2 r^2 = \frac{1}{2a_0^3} e^{-x} \left(1 - x + \frac{x^2}{4}\right) r^2, \text{ where } x = r/a_0$$

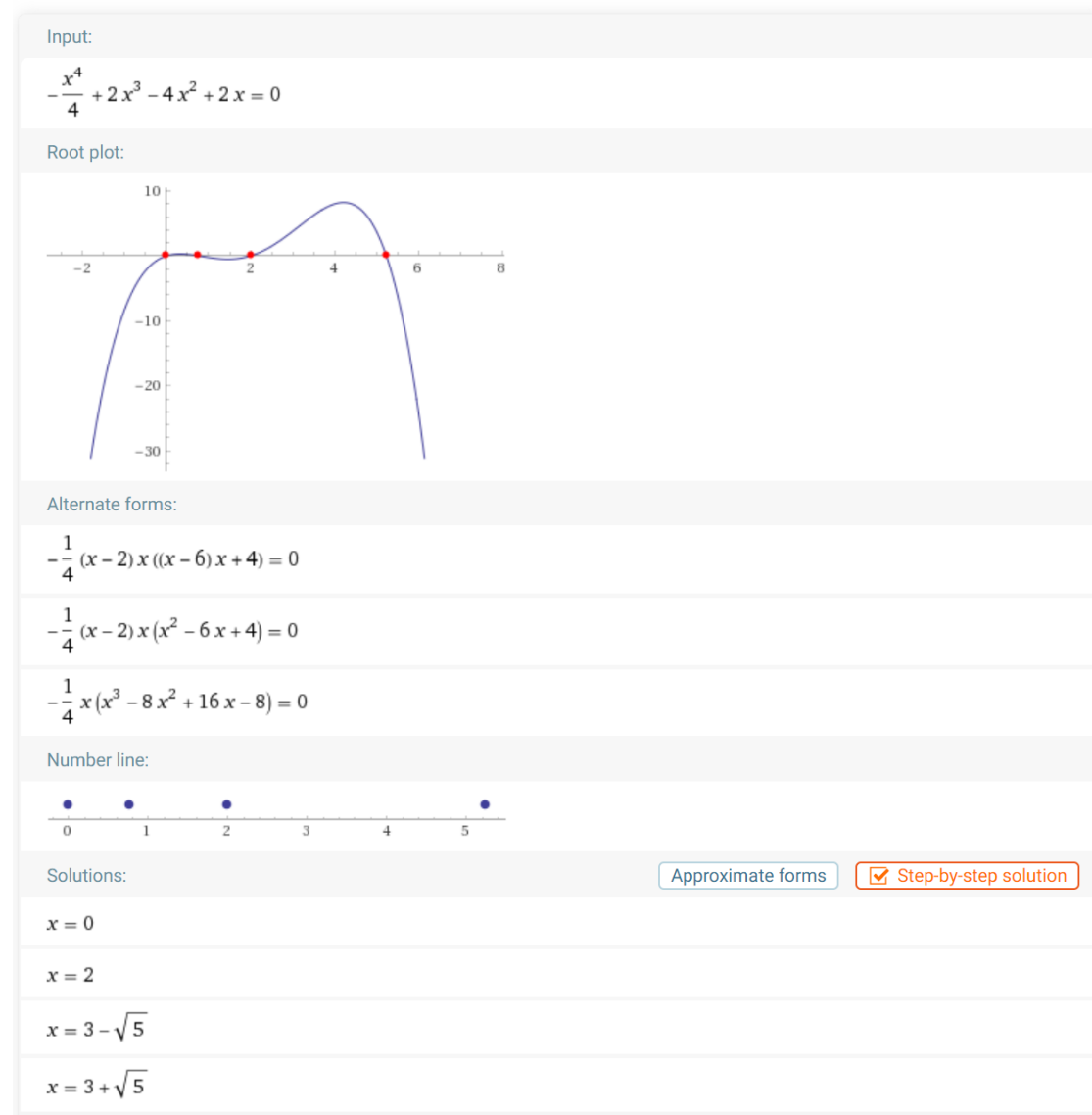
I should put all in terms of x:

$$P(x) = \frac{1}{2a_0} e^{-x} \left(x^2 - x^3 + \frac{x^4}{4}\right)$$

To find extremes: (in terms of x, neglect $\frac{1}{2a_0}$ factor)

$$\frac{dP(x)}{dx} = 0 = -e^{-x} \left(x^2 - x^3 + \frac{x^4}{4}\right) + e^{-x} (x^3 - 3x^2 + 2x)$$

$$-\frac{x^4}{4} + 2x^3 - 4x^2 + 2x = 0$$



At $x=0$, the $P(x)=0$, it is a minimum but we usually neglect this because electron hardly get into the nuclei. (of course you may include this $x=0$, but it is not very useful in application, such as forming bond between atoms)

So the extremes are:

$x = 3 - \sqrt{5}$; $x = 2$ and $x = 3 + \sqrt{5}$ (in terms of a_0), the first will be a local maximum (I will not compute 2nd derivative to confirm), and $x=2$

is a local minimum (this is quite obvious that $R(r=2a_0)=0$); and $= 3 + \sqrt{5}$ is another local maximum (make sense between local maximum lies a local minimum)

So we see that for 2s electron, it does has one local maximum further outside, it is this part make the excited state H more active in reaction.

4. Griffiths P 4.55. (modified, no addition of angular momentum part)

The electron in a hydrogen atom occupies the combined spin and position state:

$$R_{21}(\sqrt{1/3}Y_1^0\alpha_+ + \sqrt{2/3}Y_1^1\alpha_-)$$

- (a) If you measure the orbital angular momentum squared L^2 , what values might you get, and what is the probability of each?
- (b) Same for the z component of orbital angular momentum L_z
- (c) Same for the spin angular momentum S^2 .
- (d) Same for the z component of spin S_z .
- (e) If you measure the position of the particle, what is the probability density for finding it at (r, θ, ϕ)
- (f) If you measure both the S_z and the distance from the origin (these are commute operators and thus compatible observables), what is the probability density for finding the particle with spin up and at radius r ?

Answers:

The state is a superposition of:

$$|\psi\rangle = \sqrt{1/3}|2,1,0\rangle |S_+\rangle + \sqrt{2/3}|2,1,1\rangle |S_-\rangle$$

(a) This state is an eigenstate with $l=1$ (superposition of two degenerate eigenstates is the eigenstate with same eigenvalue), with L^2 measurement gives value of $l(l+1)\hbar^2 = 2\hbar^2$, with probability 1.

(b) For L_z measurement, it can be:

$$m = 0, P = 1/3$$

$$m = 1, P = 2/3$$

(c) For S^2 measurement:

We get $S(S+1)\hbar^2 = \frac{3}{2}\hbar^2 = \frac{3}{4}\hbar^2$, with probability 1.

(d) For S_z , we have:

$$S_z = \frac{1}{2}\hbar, P = 1/3$$

$$S_z = -\frac{1}{2}\hbar, P = 2/3$$

(e) The probability density of particle at (r, θ, ϕ) is:

$$\langle \psi | \psi \rangle = \frac{1}{3} \langle 2,1,0 | 2,1,0 \rangle + \frac{2}{3} \langle 2,1,1 | 2,1,1 \rangle$$

Above I used that the "integral" over spin-space gives: $\langle S_+ | S_- \rangle =$

$$0, \langle S_+ | S_+ \rangle = 1$$

$$P = \langle \psi | \psi \rangle = \frac{1}{3} |R_{21}|^2 |Y_1^0|^2 + \frac{2}{3} |R_{21}|^2 |Y_1^1|^2$$

Of course you shall get same result by directly using 3rd postulate:

The total probability of finding an electron at position (x,y,z) (or (r, θ, ϕ) if expressed in spherical coordinate) with spin up **OR** down is just:

$$\begin{aligned} P &= | \langle x, y, z, S_+ | \psi \rangle |^2 + | \langle x, y, z, S_- | \psi \rangle |^2 \\ &= \frac{1}{3} | \langle x, y, z | 2, 1, 0 \rangle |^2 + \frac{2}{3} | \langle x, y, z | 2, 1, 1 \rangle |^2 \\ &= \frac{1}{3} |R_{21}|^2 |Y_1^0|^2 + \frac{2}{3} |R_{21}|^2 |Y_1^1|^2 \end{aligned}$$

(f) The probability finding electron at r distance AND spin up is:

According to Griffiths manual:

$$\begin{aligned} P &= | \langle r, S_+ | \psi \rangle |^2 = \frac{1}{3} | \langle r | 2, 1, 0 \rangle |^2 \\ | \langle r | 2, 1, 0 \rangle |^2 &= |R_{21}|^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |Y_1^0|^2 \sin \theta d\theta d\phi = |R_{21}|^2 \end{aligned}$$

Above is integral over angular part at distance r.

$$P = |R_{21}(r)|^2 / 3$$

You may throw in the explicit expressions for $R_{21}(r), Y_l^m(\theta, \phi)$ to have detailed dependence on (r, θ, ϕ) in (e) and (f).

But I think the P defined (or calculated above is ambiguous), it is better to specify the P (r) is the probability density of finding the electron in a spherical shell between r, r+dr; in that case the answer should be:

$$P = |R_{21}(r)|^2 r^2 / 3$$

5. Consider the hydrogen like carbon ion C^{5+} , calculate its “Bohr” radius and energy E_n , and what is its transition relation (energy difference) from n_1 state to n_2 ?

Answer: The charge at nucleus is $6e$, and the potential becomes:

$$V = \frac{6e^2}{4\pi\epsilon_0}, \text{ we need to replace the } \frac{e^2}{4\pi\epsilon_0} \text{ in H atom with } \rightarrow \frac{6e^2}{4\pi\epsilon_0}$$

(Of course the reduced mass will be slightly different, but that is a smaller effect, so I neglect it here).

$$E_H = -\frac{1}{n^2} \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right], \text{ then:}$$

$$E_c = -\frac{1}{n^2} \left[\frac{m_e}{2\hbar^2} \left(\frac{6e^2}{4\pi\epsilon_0} \right)^2 \right] = 36E_H$$

$$\frac{\hbar c}{\lambda} = (E_{n_1} - E_{n_2}) = \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) E_{1c} = \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) 36 \times 13.6 eV$$

6. (Griffiths' 5.2, and you may use result from problem 1)

In view of P5.1 (problem 1 in our case), we can correct for the motion of the nucleus in hydrogen by simply replacing the electron mass with reduced mass. ($m_e=0.51100\text{MeV}$, $m_p \sim m_n=938.27\text{MeV}$)

(a) Find (to two significant digits) the percent error in the binding energy of hydrogen introduced by use of m instead of μ .

(b) Find the separation in wavelength between the Balmer lines ($n=3$ to $n=2$ transitions) for hydrogen and deuterium (proton+neutron for nucleus).

- (c) Finding the binding energy of positronium (in which the proton is replaced by positron, same mass as electron but opposite charge)
- (d) Suppose you want to confirm the existence of muonic hydrogen, in which the electron is replaced by muon (same $-e$ charge, but 206.77 times heavier). What wavelength would you look for the Lyman transition ($n=2$ to $n=1$)?

Answer: The m_e in formulas will be replaced by μ

(a) The reduced mass is:

$$\mu = \frac{m_e m_p}{m_e + m_p} = 0.51072 \text{ MeV} = 0.99945 m_e$$

$$E_\mu = -\frac{1}{n^2} \left[\frac{\mu_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right], E_m = -\frac{1}{n^2} \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right]$$

$$\frac{E_m - E_\mu}{E_m} = \frac{m_e - \mu}{m_e} = 0.00055 = 0.055\%$$

(b) $\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 13.6 \text{ eV}$

$$E_1 = \frac{\mu_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 0.99945 \times 13.6 = 13.59 \text{ eV}$$

$$\frac{\hbar c}{\lambda} = \left(\frac{1}{2^2} - \frac{1}{3^2} \right) E_1 = \frac{5}{36} E_1$$

$$\lambda_H = \frac{36 \hbar c}{5 E_1} = 657.8 \text{ nm}$$

For deuterium, $\mu = \frac{m_e 2m_p}{(m_e + 2m_p)} = 0.51086 \text{ MeV} = 0.99973 m_e$

$$E_1' = 0.99973 \times 13.6 = 13.596 \text{ eV}$$

$$\lambda_D = \frac{36}{5} \frac{\hbar c}{E_1} = 657.5 \text{ nm}$$

The separation is 0.3nm which can be easily resolved by a grating spectrometer.

(c) Here the reduced mass is:

$$\mu = \frac{1}{2} m_e$$

The energy will be:

$$E = \frac{1}{2} E_H$$

(d) The reduced mass is:

$$\mu_\mu = \frac{m_\mu m_p}{m_\mu + m_p} = 94.965 \text{ MeV} = 185.84 m_e$$

$$E_{1\mu} = \frac{\mu_\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 185.84 \times 13.6 = 2527.4 \text{ eV}$$

$$\frac{\hbar c}{\lambda} = \left(1 - \frac{1}{2^2} \right) E_{1\mu} \rightarrow \lambda = \frac{4}{3} \frac{\hbar c}{E_{1\mu}} = 6.5 \times 10^{-10} \text{ m}$$