Physics 40—Quantum Physics of Matter

HW 3—Due April 18, 2024

1. The Unsöld theorem states that for any value of the orbital quantum number l, the probability densities summed over all possible states from $m = -l$ to $m = +l$ yield a constant; *i.e.*, the sum is independent of the angles θ and φ. This means that every closed (filled) atomic subshell has a spherically symmetric distribution of electric charge. Verify Unsöld's theorem for $l = 2$, *i.e.*, show that

$$\sum_{m=-2}^{+2} Y_2^{m\,*}\, Y_2^m = \frac{2l+1}{4\pi} = \frac{5}{4\pi}$$

which is manifestly independent of θ and φ.

2. As the quantum numbers n and l become large, the hydrogen atom orbitals should somehow approach classical orbits. This problem (adapted from Griffiths Problem 4.55) explores that idea. A useful integral can be found on the last page.

Let's took at the hydrogenic radial wave function for the nth shell with the largest possbile angular momentum $l = n - 1$. The wave function is given by

$$R_{n,n-1} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{1}{(2n)!}}\, \left(\frac{2r}{na_0}\right)^{n-1} e^{-r/na_0}$$

where a_0 is the Bohr radius.

(a) Recalling that the probability density for $R_{n,n-1}$ is given by $\mathcal{P}_{n,n-1} = r^2 R_{n,n-1}^2$, show that the expectation value $\langle r \rangle$

$$\langle r \rangle = \int_0^\infty r\, \mathcal{P}_{n,n-1}\, dr$$

is given by

$$\langle r \rangle = (2n+1)\frac{na_0}{2}.$$

(b) Similarly, show that the expectation value $\langle r^2 \rangle$ is given by

$$\langle r^2 \rangle = (2n+2)(2n+1)\left(\frac{na_0}{2}\right)^2.$$

(c) Finally, use the definition $(\Delta r)^2 = \langle r^2 \rangle - (\langle r \rangle)^2$ of the uncertainty Δr to show that the *relative* uncertainty in r is given by

$$\frac{\Delta r}{\langle r \rangle} = \frac{1}{\sqrt{2n+1}}.$$

What does this result mean *physically* mean for large values of n?

(d) **Extra Credit:** Show that the angle θ between $\mathbf{L}$ and the z-axis given by

$$\cos\theta = \frac{L_z}{L}$$

is given approximately by

$$\theta \approx \frac{1}{\sqrt{n}}$$

for large n. What does this result mean physically? *Hint:* Use Taylor series expansions for small θ and large n (*i.e.* small $1/n$).

3. Find the expectation value $\langle r\rangle$ in the states $R_{10}(r)$, $R_{20}(r)$ and $R_{21}(r)$, and compare your results to Eq. 7-29 in E&R (here $Z = 1$). (You can find the wave functions in either of the tables from Beiser and Griffiths on the Canvas page.) Compare the difference between $\langle r\rangle$ in states $R_{10}(r)$ and $R_{20}(r)$ versus the difference for $R_{20}(r)$ and $R_{21}(r)$, and interpret your results in terms of the notion of subshells.

4. As discussed in class, the probability of the electron being found close to the nucleus is larger for smaller values of l. The net probability $P_{20}(r)$ of being within one Bohr radius of the origin in the state R_{20} is given by

$$P_{20} = \int_0^{a_0} \mathcal{P}_{20}\, dr = 1 - \frac{21}{8e} \approx 0.034.$$

Calculate the corresponding probabilities P_{10} and P_{21} for the R_{10} and R_{21}; compare to P_{20} and explain your results in terms of the behavior of the wave functions for small r. (Note: you'll have to integrate by parts for P_{10}, but you'll find a useful integral on the last page for P_{21}.)

Useful Integrals

$$\int_0^\infty u^n e^{-u}\, du = n!$$

$$\int u^4 e^{-u}\, du = -(u^4 + 4u^3 + 12u^2 + 24u + 24)e^{-u}$$