**Chemistry 332** **Assignment #1** (due* Monday 25 January, in class)

*Assignments handwritten on paper are welcome. If you prefer to submit your work electronically, please upload the finished assignment to the CHEM 332 Moodle page as a single pdf file.

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**Q1.** *How big are hydrogen atoms and hydrogen-like atoms?*

*Background*: The probability the electron lies between $r$, $\phi$, $\theta$ and $r + \mathrm{d}r$, $\phi + \mathrm{d}\phi$ and $\theta + \mathrm{d}\theta$ is

$$\psi_{n\ell m}{}^*(r,\phi,\theta)\,\psi_{n\ell m}(r,\phi,\theta)r^2\sin\theta\mathrm{d}r\mathrm{d}\phi\mathrm{d}\theta$$

Recall the wave function $\psi_{n\ell m}(r,\phi,\theta)$ is the product of the radial factor $R_{n\ell}(r)$ and the spherical harmonic $Y_{\ell m}(\phi,\theta)$. Integrating over all values of angles $\phi$ and $\theta$, the probability the electron is located radially between $r$ and $r + \mathrm{d}r$ is

$$P_{n\ell}(r)\mathrm{d}r = R^*_{n\ell}(r)\,R_{n\ell}(r)r^2\mathrm{d}r\int_0^{\pi}\int_0^{2\pi} Y^*_{\ell m}(\phi,\theta)Y_{\ell m}(\phi,\theta)\sin\theta\mathrm{d}\theta\mathrm{d}\phi$$

For ground-state 1s atom ($n = 1$, $\ell = 0$, $m = 0$), this gives the radial probability distribution function

$$P_{10}(r) = 4\frac{Z^3}{a_0^3}r^2\mathrm{e}^{-2Zr/a_0}$$

For ground-state $He^+$, use $P_{10}(r)$ to calculate:

**a)** the most probable value of $r$

[6] **b)** $<r>$ (the average value of $r$)

**c)** $<1/r>$ (the average value of $1/r$)

*Hints*: $a_0$ is the Bohr radius (0.05292 nm) and

$$<r> = \int_0^{\infty} rP_{10}(r)\mathrm{d}r \qquad <1/r> = \int_0^{\infty}\frac{1}{r}P_{10}(r)\mathrm{d}r \qquad \int_0^{\infty}x^n\mathrm{e}^{-ax}\mathrm{d}x = \frac{n!}{a^{n+1}}$$

**Q2.** The energy levels of hydrogen atoms are conveniently expressed as $E_n = -(13.60/n^2)$ eV. For $He^+$ ($Z = 2$), $Li^{2+}$ ($Z = 3$), $Be^{3+}$ ($Z = 4$), the corresponding energy levels are $E_n = -(Z^2 13.60/n^2)$ eV. *Why are the energy levels proportional to $Z^2$?*

[2] Question **1c** shows $<1/r>$ is proportional to atomic number $Z$. Use this result to prove the average electrical potential energy of a hydrogen-like atom

$$<V> = <-\frac{Ze^2}{4\pi\varepsilon_0 r}>$$

is proportional to $Z^2$. (The virial theorem gives $E_n = <V>/2$. If $<V>$ is proportional to $Z^2$, then so is $E_n$.)

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**Q4.** [1] For heavy atoms, show it is an excellent approximation to assume the reduced mass $\mu$ equals the electron mass.

**Q5.** [4]

**a)** Our treatment of hydrogen-like atoms is **nonrelativistic**. What does this mean?

**b)** The virial theorem gives $\langle T \rangle = -E_n$ for the average kinetic energy of a hydrogen-like atom. Estimate the speed of the electron in a ground-state $Au^{78+}$ ion ($Z = 79$). Assume $\mu$ equals the electron mass.

**c)** Part **b** suggests relativistic corrections are needed to accurately describe the quantum mechanics of heavy atoms. Explain.

**d)** The beautiful yellow color of gold is a relativistic effect! Provide a literature reference citation for this observation.

**Q6** [2]

**a)** Why are He, Li, Be, … *not* hydrogen-like atoms?

**b)** Why is the quantum mechanical treatment of He, Li, Be, … atoms much more complicated than that for hydrogen-like atoms?

**Q7.** [2] What is a **muon**? How are muons produced? For an interesting article on muons, see:

https://www.nature.com/articles/d41586-018-05254-2

**Q8.** [1] **Muonium** is an exotic hydrogen-like atom prepared by replacing the electron in a hydrogen atom with a muon (a "heavy" electron). The energy levels of hydrogen atoms are given by $E_n = -(13.60/n^2)$ eV. Give the corresponding energy equation for muonium atoms.
*Data*: a muon is 206.8 times heavier than an electron.

**Q9.** Show that muonium atoms are much smaller than hydrogen atoms. [1]

**Q10.** [1] An externally-applied magnetic field has no effect on the 1s, 2s, 3s, … energy levels of hydrogen-like atoms. Why? Explain briefly, in words.

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Q1 a) What is the most probable value of r for a ground-state hydrogen-like atom?

The probability the electron lies between r and r+dr is proportional to $P_{10}(r)$. To find the most probable r value: maximize $P_{10}(r)$ where $\frac{dP_{10}}{dr} = 0$

$$0 = \frac{dP_{10}}{dr} = \frac{d}{dr}\left(4\frac{Z^3}{a_0^3} r^2 e^{-2Zr/a_0}\right)$$

$$0 = 4\frac{Z^3}{a_0^3}\frac{d}{dr}\left(r^2 e^{-2Zr/a_0}\right)$$

$$0 = \frac{d}{dr}\left(r^2 e^{-2Zr/a_0}\right) = r^2\frac{d}{dr}e^{-2Zr/a_0} + e^{-2Zr/a_0}\frac{dr^2}{dr}$$

$$0 = r^2\left(\frac{-2Z}{a_0}\right)e^{-2Zr/a_0} + 2re^{-2Zr/a_0}$$

$$0 = \left(-\frac{2Z}{a_0}r^2 + 2r\right)e^{-2Zr/a_0}$$

$$0 = -\frac{\cancel{2}Z}{a_0}r^{\cancel{2}} + \cancel{2}\cancel{r} \qquad 0 = -\frac{Z}{a_0}r + 1$$

most probable r value $\boxed{r_{mp} = \frac{a_0}{Z}}$

for $He^+ (Z=2)$ $\quad r_{mp} = \frac{a_0}{2} = \frac{0.05292\text{ nm}}{2} = \boxed{0.02646\text{ nm}}$

(Q1 cont.)

b) average value of $r$?

$$\langle r \rangle = \int_0^\infty r P_{10}(r)\, dr = \int_0^\infty r\, 4 \frac{Z^3}{a_0^3} r^2 e^{-2Zr/a_0} dr$$

$$= 4 \frac{Z^3}{a_0^3} \int_0^\infty r^3 e^{-2Zr/a_0} dr = 4 \frac{Z^3}{a_0^3} \left( \frac{3!}{\left(\frac{2Z}{a_0}\right)^4} \right)$$

$$\boxed{\langle r \rangle = \frac{3}{2} \frac{a_0}{Z}}$$

for $He^+$ ($Z = 2$) $\quad \langle r \rangle = \frac{3}{2} \frac{0.05292 \text{ nm}}{2} = \boxed{0.03969 \text{ nm}}$

c) average value of $\frac{1}{r}$?

$$\langle \tfrac{1}{r} \rangle = \int_0^\infty \frac{1}{r} P_{10}(r)\, dr = \int_0^\infty \frac{1}{r} \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0} dr$$

$$= \frac{4Z^3}{a_0^3} \int_0^\infty r e^{-2Zr/a_0} dr$$

$$= \frac{4Z^3}{a_0^3} \left( \frac{1!}{\left(\frac{2Z}{a_0}\right)^2} \right)$$

$$\boxed{\frac{1}{r} = \frac{Z}{a_0}}$$

for $He^+$ ($Z=2$):

$$\frac{1}{r} = \frac{2}{0.05292 \text{ nm}} = 37.79 \text{ nm}^{-1}$$

$$\boxed{\langle \tfrac{1}{r} \rangle = 3.779 \times 10^{10} \text{ m}^{-1}}$$

Q2 The energies of hydrogen-like atoms

[e.g., $H (Z=1)$, $He^{+} (Z=2)$, $Li^{2+} (Z=3)$ ...]

are proportional to the square of the atomic number $Z$.

$$E_n = -\frac{13.60\, Z^2}{n^2}\ \text{eV} \qquad n = 1, 2, 3, \ldots$$

Why $Z^2$?

Q1c shows $\langle \frac{1}{r} \rangle = \frac{Z}{a_0}$ is proportional to $Z$

this means the electron is $Z$ times closer to the nucleus

the electric potential energy of the nucleus (charge $Ze$) and the electron (charge $-e$) from Coulomb's Law is

$$\langle V \rangle = \left\langle \frac{(Ze)(-e)}{4\pi\varepsilon_0 r} \right\rangle = -\left\langle \frac{Ze^2}{4\pi\varepsilon_0 r} \right\rangle$$

$$= -\frac{Ze^2}{4\pi\varepsilon_0} \langle \frac{1}{r} \rangle$$

$$= -\frac{Ze^2}{4\pi\varepsilon_0} \frac{Z}{a_0} = -Z^2 \frac{e^2}{4\pi\varepsilon_0 a_0}$$

$\langle V \rangle$ (and therefore $E = \frac{\langle V \rangle}{2}$) is proportional to $Z^2$

because the electron is $Z$ times closer to the nucleus with electric charge $Z$ times larger

Q4 The quantum mechanics of "two-body" systems, such as hydrogen-like atoms (electron + nucleus), is reduced to a much simpler one-body problem by using the reduced mass

$$\boxed{\mu = \frac{m_e m_N}{m_e + m_N} = m_e \frac{1}{1+\frac{m_e}{m_N}}}$$

$m_e$ is the electron mass ($9.11 \times 10^{-31}$ kg)

$m_N$ is the mass of the nucleus

for hydrogen ($Z=1$) atoms, $m_N = m_{proton}$ and

$$\mu = m_e \frac{1}{1+\frac{9.11\times10^{-31}\,kg}{1.67\times10^{-27}\,kg}} = 0.99945\, m_e$$

$m_e$ and $\mu$ differ by only 0.05%

for a "heavy" gold $Au^{78+}$ ion $\left(m_N \approx \frac{M_{Au}}{N_{Avogadro}} = 3.3\times10^{-25}\,kg\right)$

$$\mu = m_e \frac{1}{1+\frac{9.11\times10^{-31}}{3.3\times10^{-25}}} = 0.9999972$$

$m_e$ and $m_N$ differ by only 0.0003% $\approx 0$!

in the limit $m_N \to \infty$

$$\lim_{m_N\to\infty} \mu = m_e \frac{1}{1+\frac{m_e}{\infty}} = m_e$$

Why? In this limit the nucleus is at the center of mass, and the electron is "doing all the moving"

$(\hat{H}\psi = E\psi)$

Q5 a) The Shrodinger equation (nonrelativistic)

uses
$$E = \underbrace{\frac{\langle p_x^2 \rangle}{2m} + \frac{\langle p_y^2 \rangle}{2m} + \frac{\langle p_z^2 \rangle}{2m}}_{\text{kinetic energy}} + \underbrace{V}_{\text{potential energy}}$$

for the energy. This is correct for particles (e.g., electrons) moving at speeds much smaller than the speed of light (c).

In atoms, however, especially heavy atoms, electrons are moving at high speeds, 0.6% of c for 1s H atoms.

For relativistic systems (particles moving at speeds significant compared to the speed of light) the energy (from Einstein's theory of special relativity) is different:

$$E = \pm\sqrt{p_x^2 c^2 + p_y^2 c^2 + p_z^2 c^2 + m^2 c^4}$$

requiring a "relativistic Shrodinger equation"

$\Rightarrow$ the Dira Equation

( Q5 cont. )

b) for a hydrogen-like atom of atomic number Z :

$$E_n = -Z^2 \frac{13.60\ eV}{n^2}$$

for ground-state ($n=1$) $Au^{78+}$ ($Z=79$) :

$$E_1 = -79^2 \frac{13.60\ eV}{1^2} = -84,880\ eV \quad \text{(wow!)}$$

$$= (-84,880\ eV)(1.602 \times 10^{-19}\ J\ eV^{-1})$$

$$E_1 = -1.359 \times 10^{-14} J = -\langle T \rangle \qquad \left(\begin{array}{c}\text{assume} \\ \text{(see Q4)} \\ \mu = m_e\end{array}\right)$$

kinetic energy $T = 1.359 \times 10^{-14} J = \frac{1}{2}\mu v^2 \cong \frac{1}{2} m_e v^2$

$$v = \sqrt{\frac{2T}{m_e}} = \sqrt{\frac{2(1.359 \times 10^{-14} J)}{9.11 \times 10^{-31} kg}} = \boxed{1.73 \times 10^{8}\ m\ s^{-1}}$$

(high speed!)
($\approx 60\%$ of c)

c) part b shows the electron in a ground-state $Au^{78+}$ ion is moving at $\frac{1.78 \times 10^8 ms^{-1}}{2.99 \times 10^8 ms^{-1}} 100\% = 59.5\%$ of the speed of light!

at this high speed, a significant fraction of the speed of light, relativistic effects are important

d) according to the empirical periodic table of the elements, gold should have the color of silver!
the golden color of Au (heavier than silver, larger Z) is relativistic

3 particles — 4 particles — 5 particles

Q6 a) He (2 electrons), Li (3 electrons), Be (4 electrons), ...
are not hydrogen-like atoms because
they are not "two-body" systems and
can't be reduced to one-body systems using
reduced masses Important consequence:

b) $\Rightarrow$ $\hat{H}\psi = E\psi$ (Shrodinger's equation)
can't be solved exactly (analytically)
for 3-, 4-, 5-, ... n-body systems

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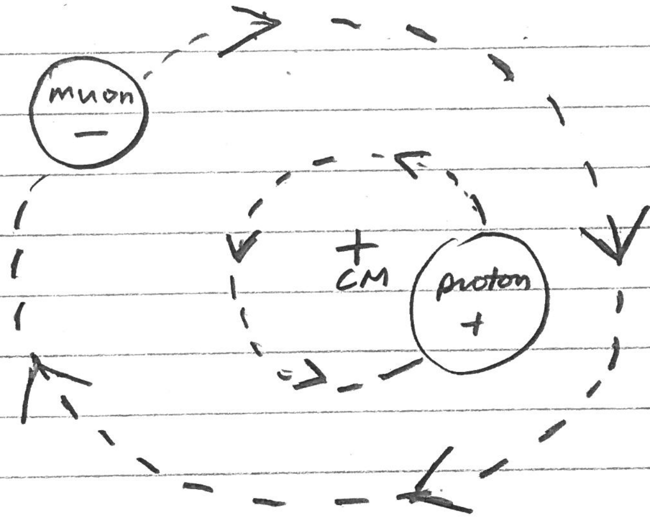
Q7 A "muon" is an elementary subatomic particle, similar to the electron (a muon has the same charge as an electron and the same $\frac{1}{2}$ spin), but 206.8 times more massive.

Muons are unstable and decay to electrons and neutrinos (other elementary particles) with a half-life of about $2 \times 10^{-6}$ s.

Discovered in 1936 by noticing some of the nuclear reactions of cosmic rays (such as high-energy protons) with air produced particles with same charge as electrons, but much heavier (less curvature of trajectories in an applied magnetic fields)

Q8




"muonium": hydrogen-like atom with a muon (−) and a proton (+) orbitting about the center of mass (CM)

This is a hydrogen-like atom with $Z = 1$ (proton nucleus) and reduced mass

$$\mu_{muonium} = \frac{m_{muon}\, m_{proton}}{m_{muon} + m_{proton}}$$

$$= \frac{206.8\, m_{electron}\, m_{proton}}{206.8\, m_{electron} + m_{proton}}$$

$$\mu_{muonium} = \frac{206.8\,(9.109\times10^{-31})(1.673\times10^{-27})}{(206.8)(9.109\times10^{-31}) + 1.673\times10^{-27}} = 1.693\times10^{-28}\ kg$$

$$\mu_{H\,atom} = \frac{m_{electron}\, m_{proton}}{m_{electron} + m_{proton}} = 9.104\times10^{-31}\ kg$$

$$\frac{E_{muonium}(n)}{E_{H\,atom}(n)} = \frac{-\dfrac{\mu_{muonium}\, e^4}{8\varepsilon_0 h^2 n^2}}{-\dfrac{\mu_{H\,atom}\, e^4}{8\varepsilon_0 h^2 n^2}} = \frac{\mu_{muonium}}{\mu_{H\,atom}} = 186.0$$

$$E_{muonium} = 186.0\, E_{H\,atom} = 186.0\left(-\frac{13.60}{n^2}\, eV\right) = \boxed{-\frac{2529\, eV}{n^2}}$$

(Q8 cont.)

Why is the energy of an n-state muonium atom 186.0 time larger than that of an n-state hydrogen atom?

Recall the orbital angular momentum takes discrete values
$\hbar, 2\hbar, 3\hbar, \ldots$

Because the electron is much lighter than a muon, the electron in a hydrogen atom must orbit the proton at a larger radius to generate the same angular momentum.

This means the electron and proton in hydrogen atoms are much farther apart than the electron and muon in muonium.

The larger electron-proton distance means the electric potential energy (proportional to $1/r$) is much smaller for hydrogen atoms, and so is the total energy ($\langle E \rangle = \langle V \rangle / 2$).

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Q9

$$\frac{\text{Bohr radius muonium}}{\text{Bohr radius hydrogen atom}} = \frac{\dfrac{4\pi\varepsilon_0 \hbar^2}{\mu_{muonium} e^2}}{\dfrac{4\pi\varepsilon_0 \hbar^2}{\mu_{H atom} e^2}}$$

$$= \frac{\mu_{H atom}}{\mu_{muonium}} = \frac{9.104 \times 10^{-31}\text{ kg}}{1.693 \times 10^{-28}\text{ kg}} = 0.005378$$
$(\ll 1)$

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Q10 The energy levels of s-states ($l = 0$, $L = 0$) are not affected by externally-applied magnetic field because s states have no angular momentum $\Rightarrow$ no magnetic dipole moment