Chemistry 332 **Problem Set #1** (due Thursday 18 January, in class)

1. High-resolution electronic spectroscopy gives the following frequencies for atomic hydrogen:

15,233.00 cm^{-1} 20,564.55 cm^{-1} 23,032.29 cm^{-1} 24,372.80 cm^{-1} (Balmer series)

[4] Assign initial and final values of quantum number n for each frequency.

2. For each of the frequencies measured for atomic hydrogen in Question 1, a very weak nearby transition is observed at the respective frequencies:

15,237.14 cm^{-1} 20,570.14 cm^{-1} 23,038.56 cm^{-1} 24,379.43 cm^{-1}

[2] Explain the origin of these slightly-shifted transitions. The scientist who first did this won a Nobel Prize!

3. Chemistry students are told atoms and ions get smaller if the nuclear charge is increased because the stronger electrical forces pull the electrons closer to the nucleu. To give a quantitative description of this effect, use the wave function for a ground state hydrogen-like atom

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)$$

[4] to derive an expression for the average value of r in terms of the Bohr radius a_0 and the atomic number Z.

$$<r> = \iiint \psi_{100}{}^* r \psi_{100} r^2 \sin\theta \mathrm{d}r \mathrm{d}\theta \mathrm{d}\phi$$

How does $<r>$ depend on Z?

Useful definite integral: $\int_0^\infty y^n e^{-ay} \mathrm{d}y = n!/a^{n+1}$

4. The ground-state energy of the hydrogen atom is

$$E_1 = -\frac{e^4\mu}{8\varepsilon_0^2 h^2} = -13.598 \text{ eV} = -2.1786\times10^{-18} \text{ J}$$

a) Use the virial theorem to calculate the average electric potential energy $< V_1 >$ and the average kinetic energy $< T_1 >$ of a ground-state hydrogen atom.

[4]

b) How fast is the electrons moving? Calculate the root-mean-square speed $\sqrt{< v^2 >}$ of an electron in a ground-state hydrogen atom. You should find $\sqrt{< v^2 >}/c \approx 1/137$, the "famous" fine structure constant.

To simplify the calculations, assume the reduced mass (μ) equals the electron mass.

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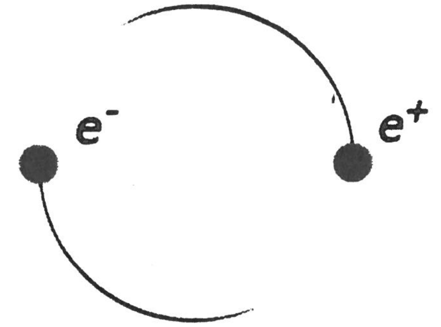
4. A **positron** (anti-electron) has the same mass as an electron, but opposite charge: $e = +1.602 \times 10^{-19}$ C. **Positronium** is an "exotic atom" consisting of a positron and an electron.



a) Show that the energy levels of positronium, to a good approximation, are one-half as large as the energy levels of the hydrogen atom:

[4] $$E_n(\text{positronium}) = E_n(\text{hydrogen atom})/2$$

b) Is a positronium "atom" larger than a hydrogen atom with the same quantum numbers n, l and m? Or smaller? Justify your answer.

5. A **random number generator** provides random numbers ε between 0 and 1. In this range, any value of ε is equally likely, so the probability distribution of the random numbers is

$$P(\varepsilon < 0) = 0 \qquad P(0 \le \varepsilon \le 1) = 1 \qquad P(\varepsilon > 1) = 0$$

[4]

Prove the following:

a) $P(\varepsilon)$ is normalized.

b) The average value of ε is $<\varepsilon> = 1/2$

c) The average value of ε^2 is $<\varepsilon^2> = 1/3$

d) The variance of ε is $\sigma_\varepsilon^2 = 1/12$.

As a result, ε_{random} defined by $\varepsilon_{random} = \sqrt{12}(\varepsilon - 1/2)\sigma$ has average value 0 and variance σ^2. Random number generators can therefore be used to simulate statistical errors of a specified standard deviation in the design of scientific experiments and in error analysis.

Chem 332 <u>Assignment #1</u>

Q1 Balmer series: $n=3 \rightarrow n=2$, $n=4 \rightarrow n=2$, etc.
(for emission)

$n=2 \rightarrow n=3$, $n=2 \rightarrow n=4$, $n=2 \rightarrow n=5$, etc
(for absorption)

Balmer frequencies (in wavenumbers):

$$\tilde{\nu}_n = \tilde{E}_n - \tilde{E}_2 = \tilde{R}_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \qquad n=3,4,5,\ldots$$

Rydberg constant for the H atom $\tilde{R}_H = 109{,}677.58\ cm^{-1}$
(from course notes)

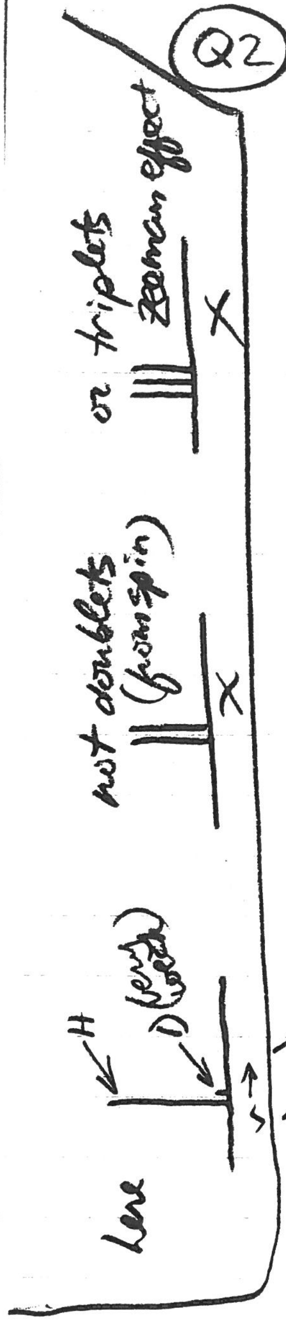
$n=3 \rightarrow n=2$ $\quad \tilde{\nu}_2 = 109{,}677.58\left(\frac{1}{4} - \frac{1}{9}\right) = 15{,}233.00\ cm^{-1}$

$n=4 \rightarrow n=2$ $\quad \tilde{\nu}_3 = 109{,}677.58\left(\frac{1}{4} - \frac{1}{16}\right) = 20{,}564.55\ cm^{-1}$

$n=5 \rightarrow n=2$ $\quad \tilde{\nu}_4 = 109{,}677.58\left(\frac{1}{4} - \frac{1}{25}\right) = 23{,}032.29\ cm^{-1}$

$n=6 \rightarrow n=2$ $\quad \tilde{\nu}_5 = 109{,}677.58\left(\frac{1}{4} - \frac{1}{36}\right) = 24{,}372.80\ cm^{-1}$

(The Rydberg constant for H-like atoms is proportional to the reduced mass : $\tilde{R} = \dfrac{\mu e^4}{8\varepsilon_0^2 c h^3}$)



Q2 For every line in the spectrum of atomic hydrogen, a very weak "satellite" line is observed, shifted to a slightly higher frequency.

Why? Deuterium! An isotope effect.

For every H atom in a sample of hydrogen, only about 0.00016 D atoms exist.

$\Rightarrow$ very weak satellite line for each H line

The mass of a D nucleus, due to the neutron, is approximately twice as large as the mass of the H nucleus (a proton).

As a result, the reduced mass of the D atom is slightly larger than that of the H atom :

$$\frac{\mu_D}{\mu_H} = \frac{\dfrac{m_e m_D}{m_e + m_D}}{\dfrac{m_e m_H}{m_e + m_H}} = \frac{1 + \dfrac{m_e}{m_H}}{1 + \dfrac{m_e}{m_D}} \approx \frac{1 + \dfrac{m_e}{m_H}}{1 + \dfrac{m_e}{2m_H}}$$

$$\approx \left(1 + \frac{m_e}{m_H}\right)\left(1 - \frac{m_e}{2m_H}\right) \approx 1 + \frac{1}{2}\frac{m_e}{m_H} > 1$$

$$\frac{\mu_D}{\mu_H} \approx 1 + \frac{1}{2}\,\frac{9.11 \times 10^{-31}\,\text{kg}}{1.67 \times 10^{-27}\,\text{kg}} = 1.00027$$

SO WHAT?

The Rydberg constant for D is 0.027 % larger than $\tilde{R}_H$, shifting the D lines to slightly higher frequencies.

$\tilde{R}_H = 109677.58\ \text{cm}^{-1}$

$\tilde{R}_D = 109707.43\ \text{cm}^{-1}$

(Q3) How does the size of a hydrogen-like atom depend on the nuclear charge?

Calculate the average electron-nucleus distance as a function of nuclear charge Z.

$$\langle r \rangle = \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} \psi_{100}^{*}\, r\, \psi_{100}\, r^2 \sin\theta\, d\theta\, d\phi\, dr$$

$$= \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}\, r\, \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}\, r^2 \sin\theta\, d\theta\, d\phi\, dr$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \underbrace{\int_0^{2\pi} d\phi}_{2\pi}\ \underbrace{\int_0^{\pi} \sin\theta\, d\theta}_{2} \int_0^{\infty} r^3 e^{-2Zr/a_0}\, dr$$

(variable change from r to $y = \frac{Zr}{a_0}$)

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 4\pi \int_0^{\infty} r^3 e^{-2Zr/a_0}\, dr = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 4\pi \left(\frac{a_0}{Z}\right)^4 \int_0^{\infty} \left(\frac{Zr}{a_0}\right)^3 e^{-\frac{2Zr}{a_0}}\, d\left(\frac{Zr}{a_0}\right)$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 4\pi \left(\frac{a_0}{Z}\right)^4 \int_0^{\infty} y^3 e^{-2y}\, dy$$

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

H-like atom size inversely proportional to Z

Q4 a) Virial Theorem

The average potential energy is twice as large as the total energy: $\langle V \rangle = 2E$

The average kinetic energy (always positive) is equal to the magnitude of the total energy (negative):

$$\langle T \rangle = -E$$

for a ground state H atom ($n = 1$), $E_1 = -13.598\ eV$

$$\langle T_1 \rangle = 13.598\ eV$$

$$\langle V_1 \rangle = 2E_1 = 2(-13.598\ eV) = -27.196\ eV$$

b) how fast is the electron moving in a ground-state H atom?

$$\langle T \rangle = \langle \tfrac{1}{2} m_e v^2 \rangle = \tfrac{1}{2} m_e \langle v^2 \rangle$$

$$\langle v^2 \rangle = \frac{2\langle T \rangle}{m_e} = \text{average squared velocity}$$

$$\text{rms velocity} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2\langle T \rangle}{m_e}} = \sqrt{\frac{2(13.598\,eV)\, 1.602 \times 10^{-19} \frac{J}{eV}}{9.110 \times 10^{-31}\ kg}}$$

$$= 2.186 \times 10^{6}\ \frac{m}{s}$$ (0.729% of the speed of light)

(Q4) a) For H-like atoms, including positronium, the energies are

$$E_n = -\frac{\mu e^4 Z^2}{8\varepsilon_0^2 h^2}\frac{1}{n^2}$$

(E_n is proportional to the reduced mass)

for positronium $Z = 1$ (an anti-electron has the same electrical charge as a proton)

positronium reduced mass $\mu_{Pos.} = \dfrac{m_{e+}\, m_{e-}}{m_{e+} + m_{e-}} = \dfrac{m_e m_e}{m_e + m_e} = \dfrac{m_e}{2}$

H-atom reduced mass $\mu_H = \dfrac{m_p\, m_{e-}}{m_p + m_{e-}} = \dfrac{m_{e^-}}{1 + \frac{m_{e-}}{m_p}}$

$\dfrac{\text{electron mass}}{\text{proton mass}} = \dfrac{m_{e-}}{m_p} = \dfrac{9.10 \times 10^{-31}\,kg}{1.67 \times 10^{-27}\,kg} = 0.000545$

so the H reduced mass is

$$\mu_H = \frac{m_{e^-}}{1 + \frac{m_{e-}}{m_p}} = \frac{m_{e^-}}{1 + 0.000545} \simeq m_{e-}$$

$$\frac{\mu_{pos.}}{\mu_H} \simeq \frac{m_e/2}{m_e} = \frac{1}{2}$$

$$E_{n\,pos.} \simeq \frac{1}{2} E_{n\ H atom}$$

(Q4 cont.)

b) How does the size of a positronium "atom" compare with the size of a hydrogen atom?

As illustrated in Q3, the size of a hydrogen atom is proportional to the Bohr radius

$$a_{0(H)} = \frac{4\pi\varepsilon_0 \hbar^2}{\mu_H e^2}$$

Notice that $a_{0(H)}$ is inversely proportional to the reduced mass.

The reduced mass of positronium is half as large as that for H atoms.

Result: A positronium "atom" is twice as large as a hydrogen atom

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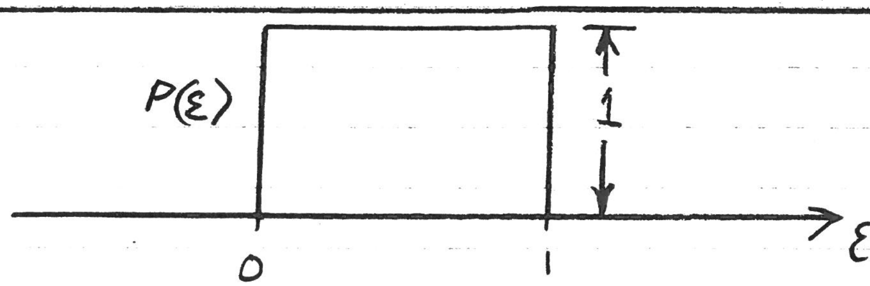
Q5



a) Is $P(\varepsilon)$ normalized?

$$\int_{-\infty}^{\infty} P(\varepsilon)\,d\varepsilon = \int_{-\infty}^{0} \overset{0}{P(\varepsilon)}\,d\varepsilon + \int_{0}^{1} \overset{1}{P(\varepsilon)}\,d\varepsilon + \int_{1}^{\infty} \overset{0}{P(\varepsilon)}\,d\varepsilon$$

$$= 0 + \int_{0}^{1} d\varepsilon + 0 = 1$$

(Q5 cont.)

b) $$\langle \varepsilon \rangle = \int_{-\infty}^{\infty} \varepsilon P(\varepsilon)\, d\varepsilon = \int_{0}^{1} \varepsilon P(\varepsilon)\, d\varepsilon$$

$$= \int_{0}^{1} \varepsilon (1)\, d\varepsilon = \frac{\varepsilon^2}{2}\Big|_0^1 = \frac{1}{2} - 0 = \frac{1}{2}$$

c) $$\langle \varepsilon^2 \rangle = \int_{-\infty}^{\infty} \varepsilon^2 P(\varepsilon)\, d\varepsilon = \int_{0}^{1} \varepsilon^2 P(\varepsilon)\, d\varepsilon$$

$$= \int_{0}^{1} \varepsilon^2 (1)\, d\varepsilon = \frac{\varepsilon^3}{3}\Big|_0^1 = \frac{1}{3} - 0 = \frac{1}{3}$$

d) variance $$\sigma_\varepsilon^2 = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$$

$$= \frac{1}{3} - \left(\frac{1}{2}\right)^2 = \frac{1}{3} - \frac{1}{4}$$

$$= \frac{4}{12} - \frac{3}{12}$$

$$= \frac{1}{12}$$