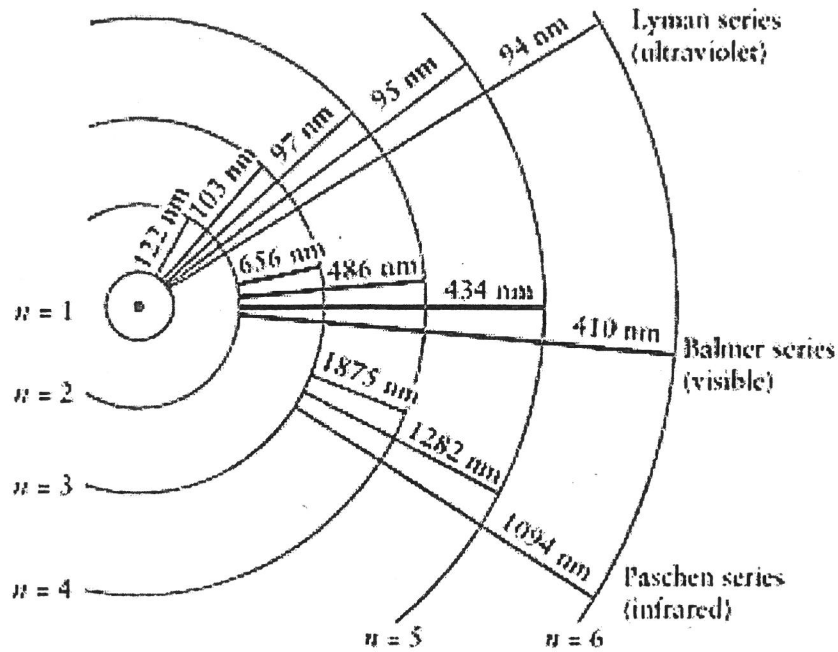
# Chemistry 332 Tutorial #1

**1. a)** The following diagram gives the first few **Lyman, Balmer, and Paschen lines** in the electronic spectra of hydrogen atoms. Calculate the corresponding lines for $He^+$. (*Hint:* These calculations can be performed quickly and efficiently by applying a simple scaling factor to hydrogen wavelengths.)




**b)** Emission nebulas are vast clouds of glowing dust and gas that surround stars. Many of these nebulas are vivid crimson in color as a result of radiation from atomic hydrogen. Identify the transition responsible for this color.

**2.** The average distance between the nucleus and the electron in a hydrogen-like atom (also called the **expectation value of *r***) is given by

$$< r_{n\ell m} > = \iiint (\psi_{n\ell m})^* r \psi_{n\ell m} r^2 \sin\theta dr d\theta d\phi$$

Calculate $< r_{n\ell m} >$ in terms of $a_0/Z$ for:

**a)** $n = 1, \ell = 0, m = 0$ $\qquad \psi_{100} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)$

**b)** $n = 2, \ell = 0, m = 0$ $\qquad \psi_{200} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2 - \dfrac{Zr}{a_0}\right)\exp(-Zr/2a_0)$ Also calculate the **radial node.**

**c)** $n = 2, \ell = 1, m = 0$ $\qquad \psi_{210} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \dfrac{Zr}{a_0} \cos\theta \exp(-Zr/2a_0)$

Notice that $n = 2$ electrons are considerably farther from the nucleus that $n = 1$ electrons.

**3. a)** Show that the answers to question #2 are consistent with the general formula

$$< r_{n\ell} > \;= \frac{a_0}{2Z}\left[3n^2 - \ell(\ell+1)\right]$$

**b)** In the laboratory, there is a limit on the number of lines that can be observed in the spectrum of hydrogen-like atoms because of "**pressure broadening**". Atoms in highly excited states are "big". As a result of the atoms bumping into each other, the energy levels are no longer sharply defined. In interstellar space, however, emissio from hydrogen atoms at very low pressures with very high quantum numbers can be detected. Radio astronomer have detected radiation from hydrogen atoms undergoing transitions from $n_i = 253$ to $n_f = 252$ states. Calculate frequency and wavelength of this radiation and identify the region of the electromagnetic spectrum. Also, calcul $2< r_{n\ell} >$ for $n = 253$ and $\ell = 0$ to indicate an effective diameter of a highly excited hydrogen atom.

**4.** The probability that an electron in a hydrogen-like atom lies between $r$ and $r + dr$ is obtained by integrating $\psi_{n\ell m}(r,\theta,\phi)^* \psi_{n\ell m}(r,\theta,\phi)$ over all values of $\theta$ and $\phi$ according to

$$\text{prob} = \left[\int_0^{2\pi}\int_0^{\pi} \psi(r,\theta,\phi)^* \psi(r,\theta,\phi) r^2 \sin\theta \, d\theta \, d\phi \right] dr$$

Show that the most probable value of r for the 1s state is $a_0/Z$.

**5. a)** A muon is an elementary particle with a negative charge equal to that of the electron and a mass approximately 200 times larger than the electron mass. The **muonium atom** is formed by a proton and a muon. Calculate the reduced mass and the Rydberg constant $\Re$ for this atom. Once again, a simple scaling factor can simplify the calculations.

**b)** Give the equation for the muonium energy levels.

**c)** Evaluate $<r_{00}>$ for the atom. Compare this value to $<r_{00}>$ for the hydrogen atom.

**6.** Last term, the first Schrödinger equation we solved was for the celebrated **particle in a box**. The potential e inside the box was assumed to be zero. What happens if a potential is applied? To illustrate an application of perturbation theory, consider a particle in a box with a "slanted bottom"

$$V(x) = \frac{x}{a}\Delta V \qquad V = 0 \text{ at } x = 0 \text{ and } V = \Delta V \text{ at } x = a, \text{ the other edge of the box.}$$

Use **first-order perturbation theory** $\Delta E = \int \psi^{(0)} * \hat{H}^{(1)} \psi^{(0)} \, dx$ to calculate the energy levels for a partic box with a slanted bottom. Recall that the unperturbed wave functions and energies are

$$\psi^0(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \qquad E^0 = \frac{n^2 h^2}{8ma^2}$$

7. To illustrate the **variational method**, use the trial function $\exp(-Ar)$ with $A$ as a variational parameter to culate the ground state energy of hydrogen-like atoms. Compare your answer with the exact result

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

The agreement is very good! Why?

**8.** Gaussian functions can be more convenient than exponential decays for numerical computer calculations involving integrals. For this reason, quantum chemistry computer software packages frequently use basis sets of Gaussian functions. Use the trial function $\exp(-Ar^2)$ with $A$ as a variational parameter to calculate the ground state energy of hydrogen-like atoms. What is the magnitude of the error in the calculated energy?

**9. a)** Calculate the difference in energy between two spin angular momentum states for electrons in the 1s orbital of a hydrogen atom in a magnetic field of 5 Tesla. What is the wavelength of the radiation emitted when the spin is "flipped"? Identify the region of the electromagnetic spectrum (*i.e.*, … , microwave, IR, visible, ultraviolet, …).

**b)** Just as electrons have intrinsic moments, so do nuclei. The magnitude of a nuclear magnetic moment is given by

$$\vec{\mu} = g\frac{e}{2m_N}\vec{S}$$

where $g$ is a factor characteristic of the particular nucleus, $m_N$ is the mass of the nucleus, and $\vec{S}$ is the spin angular momentum of the nucleus. For example, a proton has spin ½ and $g = 5.5849$. In a nuclear magnetic resonance experiment with protons, the protons undergo transitions between states with $s_z = -1/2$ and $s_z = +1/2$. Calculate the wavelength of the corresponding radiation in a magnetic field of 5 Tesla. Identify the region of the electromagnetic spectrum.

**10.** For a hydrogen-like atom, what is the magnitude of the orbital angular momentum and what are the possible values of $L_z$ for electrons in the 2p and 3d orbitals?

**11.** The antisymmetric spin function for two electrons is $N[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. Evaluate the normalization constant $N$.

Chemistry 332    Tutorial #1

① a) For H atoms ($Z = 1$), the energy levels, in wavenumbers, are

$$\tilde{E}_{Hn} = \frac{-\mu_H e^4}{4\varepsilon_0^2 h^3 c} \frac{1}{n^2} = -R_H \frac{1}{n^2}$$

with the reduced mass

$$\mu_H = \frac{m_p m_e}{m_p + m_e}$$

For hydrogen-like $He^+$ ions ($Z = 2$)

$$\tilde{E}_{He^+ n} = \frac{-\mu_{He^+} 4 e^4}{4\varepsilon_0^2 h^3 c} \frac{1}{n^2} = -R_{He^+} \frac{1}{n^2}$$

for the transition $n_i \rightarrow n_f$

$$\Delta\tilde{E}_H = -R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad \Delta\tilde{E}_{He^+} = -R_{He^+}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\Delta\tilde{E} \propto \frac{1}{\lambda} \qquad \frac{\lambda_{He^+}}{\lambda_H} = \frac{\Delta\tilde{E}_H}{\Delta\tilde{E}_{He^+}} = \frac{R_H}{R_{He^+}} = \frac{\mu_H}{4\mu_{He^+}}$$

mass of He nucleus $\approx 4 m_p$

$$\frac{\lambda_{He^+}}{\lambda_H} = \frac{1}{4} \frac{\frac{m_e m_p}{m_p + m_e}}{\frac{m_e m_{He}}{m_{He} + m_e}} = \frac{1}{4} \frac{m_p}{m_p + m_e} \frac{m_{He} + m_e}{m_{He}}$$

$$= \frac{1}{4} \frac{1.67265}{1.67265 + 0.000910953} \frac{4.0026(1.67265) + 0.00091}{4.0026(1.67265)}$$

$$= \frac{1}{4}\, 0.999456 \;\; 1.000136 = 0.249898$$

multiply each H wavelength by 0.249898 ($\approx \frac{1}{4}$)

(1 cont.)

b) crimson ~ red 656 nm
Balmer $n = 3$ to $n = 2$ emission

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(2) a) 1s orbital:

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$$

$$\langle r_{100} \rangle = \int \psi_{100}^* \, r \, \psi_{100}\, d\tau$$

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

$$\langle r_{100} \rangle \; \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^\infty r^3 e^{-2Zr/a_0}\, dr$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 2\pi\,(-\cos\theta)\Big|_0^{\pi} \left(\frac{a_0}{2Z}\right)^4 \int_0^\infty \left(\frac{2Zr}{a_0}\right)^3 e^{-2Zr/a_0}\, d\!\left(\frac{2Zr}{a_0}\right)$$

$$= \frac{1}{\cancel{\pi}}\left(\frac{Z}{a_0}\right)^3 4\cancel{\pi} \left(\frac{a_0}{2Z}\right)^4 \int_0^{x} x^3 e^{-x}\, dx = \frac{1}{4}\frac{a_0}{Z}\, 3! = \frac{6a_0}{4Z}$$

$$\boxed{\langle r_{100} \rangle = \frac{3}{2}\frac{a_0}{Z}}$$

for H $(Z=1)$
$\langle r_{100} \rangle = 1.5$ Bohr radius

b) 2s orbital:

$\langle r_{200} \rangle =$ assignment #2!

(2 b cont.)

c) $\langle r_{210} \rangle = \iiint \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3 r \frac{Z^2 r^2}{a_0^2}\cos^2\theta\, e^{-Zr/a_0} r^2 \sin\theta\, dr\, d\theta\, d\phi$

$$= \frac{1}{32\pi}\left(\frac{Z}{a_0}\right)^3 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \cos^2\theta\, d\theta \int_0^{\infty} r^3 \frac{Z^2 r^2}{a_0^2} e^{-Zr/a_0}$$

$$= \frac{1}{16}\left(\frac{Z}{a_0}\right)^3 \left(-\frac{\cos^3\theta}{3}\right)\Big|_0^{\pi} \left(\frac{a_0}{Z}\right)^4 \int_0^{\infty} \left(\frac{Zr}{a_0}\right)^3 \frac{Z^2 r^2}{a_0^2} e^{-Zr/a_0} d\left(\frac{Zr}{a_0}\right)$$

$$= \frac{1}{16}\frac{a_0}{Z}\frac{2}{3}\int_0^{\infty} x^5 e^{-x} dx = \frac{1}{8}\frac{a_0}{Z}\frac{5!}{3} = \boxed{5\frac{a_0}{Z}}$$

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3 a) $\langle r_{100} \rangle = \frac{a_0}{2Z}\left[3(1)^2 - 0\right] = \frac{3a_0}{2}$

$$\langle r_{200} \rangle = \frac{a_0}{2Z}\left[3(2^2) - 0\right] = \frac{6a_0}{Z}$$

$$\langle r_{210} \rangle = \frac{a_0}{2Z}\left[3(2^2) - (1)(1+1)\right] = \frac{a_0}{2Z}(12-2) = \frac{5a_0}{Z}$$

3 cont.

3b) $\Delta\tilde{E} = \mathcal{R}_H\left(\frac{-1}{n_f^2} - \frac{-1}{n_i^2}\right) = \mathcal{R}_H\left(\frac{-1}{252^2} + \frac{1}{253^2}\right)$

$= -1.24236 \times 10^{-7}\, \mathcal{R}_H$

$\frac{1}{\lambda} = 1.24236\times10^{-7}\left(1.096776\times10^{7}\ m^{-1}\right) = 1.362596\ m^{-1}$

$\lambda = 0.733893\ m$ $\qquad \nu = \frac{c}{\lambda} = \frac{2.997925\times10^{8}\ m\ s^{-1}}{0.733893\ m}$

$\nu = 4.08496\times10^{8}\ Hz$

radio waves $\qquad (\simeq 408\ MHz)$

size of a hydrogen atom with $n = 253,\ l = 0$

$\langle r_{253,0}\rangle = \frac{a_0}{2}\,3n^2 = \frac{a_0}{2}\,3(253)^2 = 96013\,a_0$

$= 96013\left(5.292\times10^{-11}\right)m = 5.081\times10^{-6}\ m = 5081\ nm!$

$\simeq 0.51$ microns!

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(4) radial probability distribution function for the 1s state

$$R(r) = \int_0^{2\pi}\int_0^{\pi} \psi_{100}^{*}\,\psi_{100}\, r^2 \sin\theta\, d\theta\, d\phi$$

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

(4 cont.)

$$R(r) = 4\left(\frac{Z}{a_0}\right)^3 \left(\frac{a_0}{Z}\right)^2 \left(\frac{Z}{a_0}\right)^2 r^2 e^{-2rZ/a_0}$$

$$= 4\frac{Z}{a_0}\left(\frac{Zr}{a_0}\right)^2 e^{-2rZ/a_0} \qquad x \equiv \frac{2Zr}{a_0}$$

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

$$R(x) = \frac{Z}{a_0} x^2 e^{-x}$$

the most probable value of $r$ occurs at $\frac{dR}{dr} = 0 \left(\text{or } \frac{dR}{dx} = 0\right)$

$$\frac{dR}{dx} = \frac{Z}{a_0}\left(-x^2 e^{-x} + 2xe^{-x}\right) = xe^{-x}(2-x)$$

$$\frac{dR}{dx} = 0 \text{ at } x' = 2 = \frac{2Zr'}{a_0} \qquad \frac{Zr'}{a_0} = 1$$

$$r' = \frac{a_0}{Z}$$ most probable value of $r$ ($a_0$ for H atom)

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(5.) a) $$R_H = \frac{\mu_H e^4}{4\varepsilon_0^2 h^3 c} \qquad \mu_H = \frac{m_e m_p}{m_e + m_p}$$

H energy levels $-\frac{R_H}{n^2}$ $\quad n = 1, 2, 3, \ldots$

muonium

same electrical charge

$$R_{Mu} = \frac{\mu_{Mu} e^4}{4\varepsilon_0^2 h^3 c} \qquad \mu_{Mu} = \frac{m_e m_{Mu}}{m_e + m_{Mu}}$$

(5 cont.)

$m_{Mu} \simeq 200 m_e$

$$\frac{R_{Mu}}{R_H} = \frac{\mu_{Mu}}{\mu_H} = \frac{m_e\, m_{Mu}}{m_e + m_{Mu}} \frac{m_e + m_p}{m_e\, m_p} = \frac{\cancel{m_e}\,\cancel{m_e}\,200}{\cancel{m_e} + 200\cancel{m_e}} \frac{m_e + m_p}{\cancel{m_e}\, m_p}$$

$$= \frac{200}{201} \frac{0.00091095 + 1.67265}{1.67265} = 0.995567$$

$$R_{Mu} = (0.995567)\, 1.096776 \times 10^7\ m^{-1} = 1.091914 \times 10^7\ m^{-1}$$

b) Muonium energy levels $\quad E_n = -\dfrac{R_{Mu}}{n^2} \qquad n = 1, 2, 3, \ldots$

c) $a_0 = \dfrac{\varepsilon_0 h^2}{\pi \mu e^2} = 5.29177 \times 10^{-11}\ m$ for $H$

$$\frac{\langle r_{nl} \rangle_{Mu}}{\langle r_{nl} \rangle_H} = \frac{\mu_H}{\mu_{Mu}} = \frac{1}{0.995567} = 1.0445$$

$$\langle r_{00} \rangle_H = \frac{3}{2} a_0 = 7.93765 \times 10^{-11}\ m$$

$$\langle r_{00} \rangle_{Mu} = 1.0445 \left(7.93765 \times 10^{-11}\ m\right) = 8.2908 \times 10^{-11}\ m$$

$\simeq$ 4.5% larger than for $H$

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6

assignments # 1!

7. trial wave function : $\chi(r) = e^{-Ar}$ (not normalized)

variational energy $E' = \dfrac{\int \chi(r)^* \hat{H} \chi(r)\, d\tau}{\int \chi(r)^* \chi(r)\, d\tau}$

notice that $\chi(r)$ is independent of $\theta, \phi$

$\Longrightarrow$ ignore $\theta, \phi$ terms in $\nabla^2$

$$\hat{H} = V(r) - \frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \cancel{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)} + \cancel{\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}\right]$$

ignore

(7 cont.)

$$\hat{H}\chi(r) = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial e^{-Ar}}{\partial r}\right) - \frac{e^2}{4\pi\varepsilon_0 r}e^{-Ar}$$

$$= A\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2e^{-Ar} - \frac{e^2}{4\pi\varepsilon_0 r}e^{-Ar}$$

$$= \frac{A\hbar^2}{2\mu}\frac{1}{r^2}\left(-Ar^2e^{-Ar} + 2re^{-Ar}\right) - \frac{e^2}{4\pi\varepsilon_0 r}e^{-Ar}$$

$$= \left(-\frac{A^2\hbar^2}{2\mu} + \frac{A\hbar^2}{\mu r} - \frac{e^2}{4\pi\varepsilon_0 r}\right)e^{-Ar}$$

$$\int \chi(r)\hat{H}\chi(r)\,d\tau = \int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int e^{-Ar}\left(-\frac{A^2\hbar^2}{2\mu} + \frac{A\hbar^2}{\mu r} - \frac{e^2}{4\pi\varepsilon_0 r}\right)e^{-Ar}r^2dr$$

$$= (2\pi)(2)\left[-\frac{A^2\hbar^2}{2\mu}\int_0^\infty r^2e^{-2Ar}dr + \left(\frac{A\hbar^2}{\mu} - \frac{e^2}{4\pi\varepsilon_0}\right)\int_0^\infty re^{-2Ar}dr\right]$$

$$= 4\pi\left[-\frac{A^2\hbar^2}{2\mu}\frac{1}{8A^3}\int_0^\infty (2Ar)^2e^{-2Ar}d(2Ar) + \left(\frac{A\hbar^2}{\mu} - \frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{4A^2}\int_0^\infty 2Are^{-2Ar}d(2Ar)\right]$$

$$= 4\pi\left[-\frac{A^2\hbar^2}{2\mu}\frac{1}{8A^3}\int_0^\infty \varphi^2e^{-\varphi}d\varphi + \left(\frac{A\hbar^2}{\mu} - \frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{4A^2}\int_0^\infty \varphi e^{-\varphi}d\varphi\right]$$

$$= 4\pi\left[-\frac{A^2\hbar^2}{2\mu}\frac{1}{8A^3}\,2 + \left(\frac{A\hbar^2}{\mu} - \frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{4A^2}\right]$$

$$= \pi\left[-\frac{\hbar^2}{2\mu A} + \frac{\hbar^2}{A\mu} - \frac{e^2}{4\pi\varepsilon_0 A^2}\right] = \pi\left(\frac{\hbar^2}{2A\mu} - \frac{e^2}{4\pi\varepsilon_0 A^2}\right)$$

7 cont.

normalization factor $\int \chi^* \chi \, d\tau$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} e^{-Ar} e^{-Ar} r^2 \, dr$$

$$= (2\pi)(2) \int_0^{\infty} e^{-2Ar} r^2 \, dr$$

$$= 4\pi \frac{1}{8A^3} \int_0^{\infty} e^{-2Ar} (2Ar)^2 \, d(2Ar)$$

$$= \frac{4\pi}{8A^3} \int_0^{\infty} \varphi^2 e^{-\varphi} \, d\varphi = \frac{4\pi}{8A^3} 2 = \frac{\pi}{A^3}$$

$$E' = \frac{\int \chi^* \hat{H} \chi \, d\tau}{\int \chi^* \chi \, d\tau}$$ variational energy (to be minimized)

$$E' = \frac{\pi \left( \frac{\hbar^2}{2A\mu} - \frac{e^2}{4\pi\varepsilon_0 A^2} \right)}{\frac{\pi}{A^3}} = \frac{\hbar^2}{2\mu} A^2 - \frac{e^2 A}{4\pi\varepsilon_0}$$

to minimize $E'$, set $\frac{dE'}{dA}$ equal to zero

$$\frac{dE'}{dA} = \frac{\hbar^2 A}{\mu} - \frac{e^2}{4\pi\varepsilon_0} = 0 \qquad A = \frac{e^2 \mu}{4\pi\varepsilon_0 \hbar^2}$$

$$E'_{min} = \frac{\hbar^2}{2\mu} \frac{e^4 \mu^2}{(4\pi\varepsilon_0)^2 \hbar^4} - \frac{e^2}{(4\pi\varepsilon_0)} \frac{e^2 \mu}{(4\pi\varepsilon_0)\hbar^2} =$$

$$= \frac{e^4 \mu}{(4\pi\varepsilon_0)^2 \hbar^2} \left( \frac{1}{2} - 1 \right) = -\frac{1}{2} \frac{e^4 \mu}{(4\pi\varepsilon_0)^2 \hbar^2} = -\frac{e^4 \mu}{8\varepsilon_0^2 h^2}$$

7 cont.

Solving Schrödinger's equation for the H atom gives the exact ground state energy $-\dfrac{e^4\mu}{8\varepsilon_0^2 h^2}$

in perfect agreement with our variational calculation!

Why? Because we "guessed" the correct functional form for $\chi(r)$. $\chi(r) \propto e^{-Ar}$

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(8) $\chi(r) = e^{-Ar^2}$ Gaussian trial function for the ground state of the H atom

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{e^2}{4\pi\varepsilon_0 r} \quad \text{(ignore angular parts)}$$

$$\text{variational energy} = \frac{\int \chi^*(r)\hat{H}\chi(r)\,d\tau}{\int \chi^*(r)\chi(r)\,d\tau}$$

$$E' = \frac{\int_0^\infty 4\pi r^2 e^{-Ar^2}\hat{H}e^{-Ar^2}\,dr}{\int_0^\infty 4\pi r^2 e^{-Ar^2}e^{-Ar^2}\,dr}$$

$$E' = \frac{-\frac{\hbar^2}{2\mu}\int_0^\infty (4A^2r^4 - 6Ar^2)e^{-2Ar^2}\,dr - \frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r e^{-2Ar^2}\,dr}{\int_0^\infty r^2 e^{-2Ar^2}\,dr}$$

$$E' = \frac{-\frac{\hbar^2}{2\mu}4A^2\int_0^\infty r^4 e^{-2Ar^2}\,dr + \frac{\hbar^2}{2\mu}6A\int_0^\infty r^2 e^{-2Ar^2}\,dr - \frac{e^2}{4\pi\varepsilon_0}\int_0^\infty r e^{-2Ar^2}\,dr}{\int_0^\infty r^2 e^{-2Ar^2}\,dr}$$

(8 cont.)

$$E' = \frac{-\frac{\hbar^2}{2\mu} 4\cancel{A^2} \frac{3}{8(2\cancel{A})^2}\sqrt{\frac{\pi}{2A}} + \frac{\hbar^2}{2\mu} 6\cancel{A} \frac{1}{4(2\cancel{A})}\sqrt{\frac{\pi}{2A}} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{4A}}{\frac{1}{8A}\sqrt{\frac{\pi}{2A}}}$$

$$= \frac{\frac{\hbar^2}{2\mu}\sqrt{\frac{\pi}{2A}}\left(\frac{-3}{8} + \frac{3}{4}\right) - \frac{e^2}{16\pi\varepsilon_0 A}}{\frac{1}{8A}\sqrt{\frac{\pi}{2A}}}$$

$$E' = \frac{\hbar^2}{2\mu} 8A \frac{3}{8} - \frac{8\cancel{A}\sqrt{2A}}{\sqrt{\pi}} \frac{e^2}{16\pi\varepsilon_0 \cancel{A}} = \frac{3\hbar^2 A}{2\mu} - \frac{e^2\sqrt{A}}{\sqrt{2}\,\varepsilon_0 \pi^{3/2}}$$

to minimize $E'$, find $E'$ where $dE'/dA = 0$

$$\frac{dE'}{dA} = \frac{3\hbar^2}{2\mu} - \frac{e^2}{2\sqrt{2}\,\varepsilon_0 \pi^{3/2}\sqrt{A}} \qquad 3\hbar^2\, 2\sqrt{2}\,\varepsilon_0 \pi^{3/2}\sqrt{A} = e^2\, 2\mu$$

$$\sqrt{A} = \frac{e^2 \cancel{2}\mu}{3\hbar^2 \cancel{2}\sqrt{2}\,\varepsilon_0 \pi^{3/2}} \qquad A = \frac{e^4 \mu^2}{9\hbar^4\, 2\, \varepsilon_0^2 \pi^3}$$

$$E'_{min} = \frac{3\hbar^2 e^4 \mu^2}{2\mu\; 18\hbar^4 \varepsilon_0^2 \pi^3} - \frac{e^2}{\sqrt{2}\,\varepsilon_0 \pi^{3/2}} \frac{e^2 \mu}{3\hbar^2\sqrt{2}\,\varepsilon_0 \pi^{3/2}}$$

$$= \frac{e^4\mu}{\hbar^2\varepsilon_0^2}\left(\frac{3}{2(18)\pi^3} - \frac{1}{2(3)\pi^3}\right) = -\frac{1}{12\pi^3}\frac{e^4\mu}{\hbar^2\varepsilon_0^2}$$

$$E'_{min} = -\frac{1}{3\pi}\frac{e^4\mu}{\varepsilon_0^2 h^2}$$

(9) a) energy of an electron "spin-up" magnetic dipole

$$E_+ = \mu_{sz} B_z = g\beta_0 \tfrac{1}{2} B_z$$

spin down energy $\quad E_- = g\beta_0\left(\frac{-1}{2}\right) B_z$

anomolous spin factor $= 2.0023$

Bohr magneton $9.274 \times 10^{-24}\ J\,T^{-1}$

z-component of the magnetic field

$$\Delta E = E_+ - E = g\beta_0 B_z$$

$$= 2.0023\left(9.274 \times 10^{-24}\ J\,T^{-1}\right) 5\,T$$

$$= 9.285 \times 10^{-23}\ J = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}(2.998 \times 10^{8})}{9.285 \times 10^{-23}} = 0.002139\ m$$

(microwave)

b) $\Delta E = g\beta_0 B_z = 5.5849\left(9.274 \times 10^{-24}\right) 5\ J = 2.590 \times 10^{-22}\ J$

$\lambda = 0.0007671\ m$ (microwave)

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(10) a) 2 p electrons $\ell = 1$ $\qquad |\vec{L}^2| = \ell(\ell+1)\hbar^2$

magnitude of $\vec{L}$ is $\sqrt{\ell(\ell+1)}\,\hbar = \sqrt{2}\,\hbar$

$|\vec{L}_z| = m\hbar \qquad m = -1, 0, 1 \qquad$ possible magnitudes of $\vec{L}_z$ are $= -\hbar, 0, \hbar$

b) 3d electrons $\qquad \ell = 2 \qquad |\vec{L}| = \sqrt{2(3)}\,\hbar = 6\,\hbar$

possible values of $L_z \qquad -2\hbar, -\hbar, 0, \hbar, 2\hbar$

$\psi(2,1) = -\psi(1,2)$

(11) Normalization factor $N$ for the two-electron antisymmetric wave function: $\psi = N[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

know $\alpha(i)$ and $\beta(i)$ are orthonormal:

$$\int \alpha(i)^* \alpha(i)\, d\sigma_i = 1$$
$$\int \alpha(i)^* \beta(i)\, d\sigma_i = 0$$
$$\int \beta(i)^* \alpha(i)\, d\sigma_i = 0$$
$$\int \beta(i)^* \beta(i)\, d\sigma_i = 1$$

require:

$$1 = \iint \psi^* \psi \, d\sigma_1\, d\sigma_2$$

$$= \iint N^* [\alpha(1)\beta(2) - \alpha(2)\beta(1)]^* N [\alpha(1)\beta(2) - \alpha(2)\beta(1)]\, d\sigma_1\, d\sigma_2$$

$$= N^*N \iint \alpha(1)^* \beta(2)^* \alpha(1)\beta(2) - \alpha^*(1)\beta^*(2)\alpha(2)\beta(1) - \alpha(2)^*\beta^*(1)\alpha(1)\beta(2) + \cdots$$
$$+ \alpha(2)^*\beta^*(1)\alpha(2)\beta(1)\, d\sigma_1\, d\sigma_2$$

$$= N^*N \int \alpha_1^* \alpha_1\, d\sigma_1 \int \beta^*(2)\beta(2)\, d\sigma_2 - N^*N \int \alpha^*(1)\beta(1)\, d\sigma_1 \int \beta^*(2)\alpha(2)\, d\sigma_2$$
$$- N^*N \int \beta^*(1)\alpha(1)\, d\sigma_1 \int \alpha^*(2)\beta(2)\, d\sigma_2 + N^*N \int \beta^*(1)\beta(1)\, d\sigma_1 \int \alpha^*(2)\alpha(2)\, d\sigma_2$$

$$= N^*N[(1)(1) - (0)(0) - (0)(0) + (1)(1)]$$

$$1 = N^*N\, 2 \qquad N^*N \text{ is real}$$

$$1 = N^2 2$$

$$N^2 = \frac{1}{2}$$

$$\boxed{N = \frac{1}{\sqrt{2}}}$$

for a $N$-electron antisymmetric spin function, the normalization factor is $\frac{1}{\sqrt{N}}$