Chem 332 **Assignment #3** (due Monday 08 February, in class)

Q1. For the hydrogen atom, <*r*> and <1/*r*> give the average values of *r* and 1/*r* for the electron. Does 1/<*r*> equal <1/*r*>? Justify your answer.
[1]

Q2. **a)** **Atomic sizes** are important in many chemical applications. Why?

b) A literature search gives 0.0529 nm for the radius of the carbon atom. *But wait*! Radius implies a sphere. Are carbon atoms spherical? Explain briefly.
[2]

Q3. **a)** Give a brief explanation of **shielding** (*aka* screening) in atomic structure calculations.

[2] **b)** Does shielding increase or decrease the sizes of atoms? Justify your answer.

Q4. 0.031 nm is reported for the **radius of the helium atom**. *But wait*! Because the electron probability density gradually decreases moving away from the nucleus, there is no sharp cut off marking a radius. *So have you ever wondered how atomic radii are defined*?

The radius of a free atom is usually defined as the value of *r* that gives the maximum radial electron probability density. Use this definition and the wave function for helium

$$\chi(r_1, r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} \exp(-Z'r_1/a_0)\frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} \exp(-Z'r_2/a_0)$$

[3] derived in class to calculate the radius of the ground-state helium atom. Is this estimate of the helium radius in acceptable agreement with the literature value 0.031 nm?

Data: $Z' = 1.6875$ and $a_0 = 0.0529$ nm (the Bohr radius of the hydrogen atom)
Suggestion: refer to Q1 from Assignment #1 (answers posted) for calculation details

Q5. **a)** Simple *first-order perturbation calculations* for the **Zeeman effect** give the energies of atoms in magnetic fields in exact agreement with measured values. For the energy of the helium atom, however, complicated *13th-order (!) perturbation calculations* are needed to get agreement with experiment. Why are perturbation calculations for helium much more difficult than those for the Zeeman effect?
[2]

b) Variational calculations are generally much more useful than perturbation calculations for quantum chemistry. Why?

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Q5. **a)** The electron-electron potential energy of the **helium atom** is $\dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{r}_1|}$.

b) What is $|\vec{r}_2-\vec{r}_1|$ in this equation?

c) Ignoring electron-electron interactions, the calculated energy of the helium atom is -1.744×10^{-17} J. The measured energy is -1.266×10^{-17} J. Use this data to estimate:

[4] **i)** $\left\langle \dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_2-\vec{r}_1|} \right\rangle$ (the average electron-electron potential energy)

ii) $\left\langle \dfrac{1}{|\vec{r}_2-\vec{r}_1|} \right\rangle$

d) Is the answer to **ii** "reasonable" given the diameter of the helium atom is 0.062 nm?

Q6. Show the **electron spin functions** α and β (Dirac theory) are normalized and orthogonal.

[1]

$$\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

Q7. Using the **trial wave function** $\varphi(r) = \exp(-cr)$ for the ground-state hydrogen atom, the
[1] variational method gives the *exact energy* of the atom! Why is the agreement so good?

Q8. **Gaussian functions** are easier to integrate numerically than exponential decays. For this reason, basis sets of Gaussian functions are frequently used for variational calculations.

[4] Using the Gaussian trial wave function $\varphi(r) = \exp(-cr^2)$ for the hydrogen atom gives

$$E' = \frac{3h^2}{8\pi^2\mu}c - \frac{e^2}{\sqrt{2}\pi^{3/2}\varepsilon_0}\sqrt{c}$$

a) Calculate the optimal values of c and the variational energy.

b) Compare the variational energy to the exact energy $\mu e^4/8\epsilon_0^2h^2$ for the ground-state hydrogen atom.

Chem 332

Assignment #3

(Q1) Are the average values of r and 1/r related as $\frac{1}{\langle r\rangle} = \langle \frac{1}{r} \rangle$?

$\boxed{\text{No!}}$ recall for the ground state (1s) hydrogen atom $\langle r\rangle = \frac{3}{2}a_0$, $\langle \frac{1}{r}\rangle = \frac{1}{a_0}$

$$\frac{1}{\langle r\rangle} = \frac{2}{3a_0} \neq \langle \frac{1}{r}\rangle = \frac{1}{a_0}$$

Why? larger r values contribute more to $\langle r\rangle$, less to $\langle \frac{1}{r}\rangle$

Consider the arbitrary example

$$r_1 = 1, \quad r_2 = 2, \quad r_3 = 12$$

$$\langle r\rangle = \frac{1+2+12}{3} = 5$$

$$\langle \frac{1}{r}\rangle = \frac{\frac{1}{1}+\frac{1}{2}+\frac{1}{12}}{3} = 0.527\dot{7}$$

$\frac{1}{\langle r\rangle} = \frac{1}{5} = 0.2$ is less than $\langle \frac{1}{r}\rangle = 0.527\dot{7}$

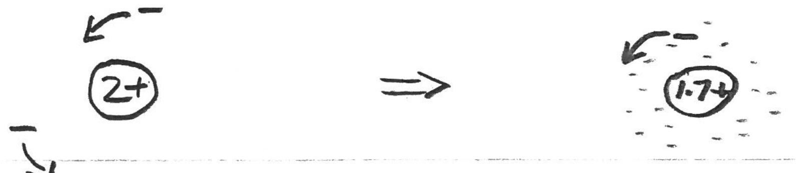
because $\langle r\rangle$ is most heavily weighted for $r_3 = 12$

(Q2) a) atomic sizes are useful for deciding bond lengths, intermolecular forces, steric hindrance effects, crystal structures, ... on and on!

b) No, carbon atoms are not spherical! (due to $2p^2$ electrons)

[See electron probability density diagrams for p orbitals]

The reported "radius" of the C atom is radially averaged



(Q3) a) In atomic structure calculations, "shielding" refers to inner electrons partially cancelling the effective nuclear charge experienced by the outer electrons

b) Shielding increases the size of atoms because the electrons are not held as closely to nucleus (the effective nuclear charge Z' is less than the actual nuclear charge Z,

so $$r_{\text{most probable}} = \underset{\text{(shielded)}}{\frac{a_0}{Z'}} > \underset{\text{(not shielded)}}{\frac{a_0}{Z}}$$ (also, see Q4)

$d\tau_1 = r_1^2 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1$ $\quad d\tau_2 = r_2^2 \sin\theta_2\, dr_2\, d\theta_2\, d\phi_2$

(Q4) electron probability distribution function $= \chi^*(r_1,r_2)\,\chi(r_1,r_2)\, d\tau_1\, d\tau_2$

(= probability of finding e_1 and e_2 in volume elements $d\tau_1, d\tau_2$)

(χ is real)

$$\chi^2(r_1,r_2)\, d\tau_1\, d\tau_2 = \left[\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\prime\,3/2} e^{-Z'r_1/a_0}\, \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} e^{-Z'r_2/a_0}\right]^2 d\tau_1\, d\tau_2$$

$$= \left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 e^{-2Z'r_1/a_0}\, d\tau_1\right]\left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 e^{-2Z'r_2/a_0}\, d\tau_2\right]$$

$$= \left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 e^{-2Z'r/a_0}\, r_1^2 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1\right]\left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 e^{-2Z'r/a_0}\, r_2^2 \sin\theta_2\, dr_2\, d\theta_2\, d\phi_2\right]$$

integrate the probability distribution over the angular variables to get the radial probability distribution function

$$P(r_1, r_2) = \left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 e^{-2Z'r_1/a_0}\, r_1^2 \overbrace{\int_0^{\pi} \sin\theta_1 \, d\theta_1 \int_0^{2\pi} d\phi_1}^{=\boxed{4\pi}}\right]$$

$$\times \left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 e^{-2Z'r_2/a_0}\, r_2^2 \overbrace{\int_0^{\pi} \sin\theta_2 \, d\theta_2 \int_0^{2\pi} d\phi_2}^{=\boxed{4\pi}}\right]$$

$$P(r_1, r_2) = \overbrace{\left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 4\pi\right]^2}^{\boxed{\text{a constant}}} r_1^2 e^{-2Z'r_1/a_0}\, r_2^2 e^{-2Z'r_2/a_0}$$

maximize $P(r_1, r_2)$ to find the radius of the He atom by solving:

$$\frac{\partial P}{\partial r_1} = 0 \qquad\qquad \frac{\partial P}{\partial r_2} = 0$$

$$\frac{\partial P}{\partial r_1} = \left(\frac{\partial}{\partial r_1}\left[\overbrace{\left[\frac{1}{\pi}\left(\frac{Z'}{a_0}\right)^3 4\pi\right]^2}^{\text{const.}} r_1^2 e^{-2Z'r_1/a_0} \cdot \overbrace{r_2^2 e^{-2Z'r_2/a_0}}^{\text{const.}}\right]\right)_{r_2} = 0$$

$$0 = \frac{\partial}{\partial r_1}\left(r_1^2 e^{-2Z'r_1/a_0}\right) = \overbrace{\left[-r_1^2 \frac{2Z'}{a_0} + 2r_1\right]}^{(=0)} e^{-2Z'r_1/a_0}$$

$$r_1^2 \frac{2Z'}{a_0} = 2r_1 \implies r_1 = \frac{a_0}{Z'}$$

similarly, $\frac{\partial P}{\partial r_1} = 0$ gives $r_2 = \frac{a_0}{Z'} = r_1$

most probable r_1, r_2 values

find max. $P(r_1, r_2)$ at $r = r_1 = r_2 = \frac{a_0}{Z'} = \frac{0.0529\text{ nm}}{1.6875}$

$= 0.0313$ nm (in excellent agreement with the literature value 0.031 nm!)

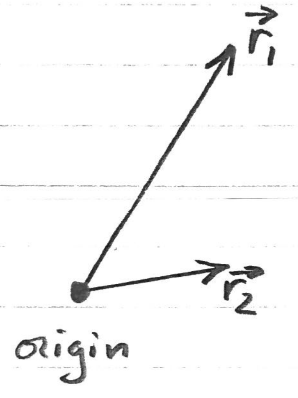
Ⓠ5 a) Perturbation calculations are well suited to studies of the Zeeman effect because the perturbation (the magnetic potential energy) is very weak and the energy change ΔE is therefore accurately calculated by considering first-order terms (no need for successive corrections)

But for the helium atom, the perturbation (the electron-electron repulsive energy) is large ($\approx$ 40% of the total energy) so successive approximations (1st order, 2nd order, ... 13th order) are required for accurate results

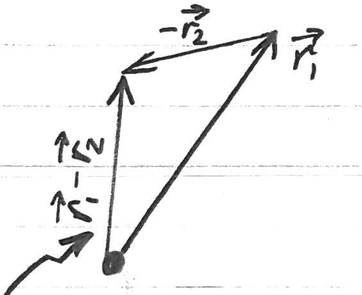
b) Variational calculations are more useful for quantum chemistry calculations because an exactly solved wavefunction ($\psi^{(0)}$, required for perturbation calculations) is rarely available for multi-electron atoms and molecules.

Also, variational calculations are easy to implement using digital computers (solve the secular determinant equation), flexible (wide range of basis-set fuctions can be used), and can be accurate, especially if a large number of fitting functions is used

Q5 a) $|\vec{r}_1 - \vec{r}_2|$ is the distance between electron 1 and electron 2



vector subtraction:



$|\vec{r}_1 - \vec{r}_2|$ is the magnitude of the vector $\vec{r}_1 - \vec{r}_2$

b) Ignoring electron-electron repulsive energy in the helium atom gives the energy -1.744×10^{-17} J

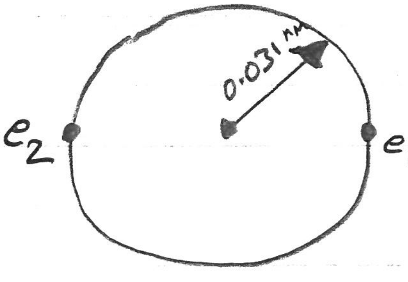
The actual energy of helium is -1.266×10^{-17} J.

The difference is the average value of the repulsive energy

$$[-1.266 - (-1.744)] \times 10^{-17} \text{ J} = \left\langle \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \right\rangle$$

$$= 0.478 \times 10^{17} \text{ J} = \frac{e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right\rangle$$

c) $$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \left(\frac{4\pi\varepsilon_0}{e^2}\right)(4.78 \times 10^{17} \text{ J}) = 2.072 \times 10^{10} \text{ m}^{-1}$$



would give $\frac{1}{0.062 \text{ nm}} = 1.61 \times 10^{10} \text{ m}^{-1}$

so $\left\langle \frac{1}{\vec{r}_1 - \vec{r}_2} \right\rangle = 2.072 \times 10^{10}$ m seems "reasonable"

(Q6) $\alpha^*\alpha = \begin{bmatrix}1 & 0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = (1)(1)+(0)(0) = 1$

$\beta^*\beta = \begin{bmatrix}0 & 1\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix} = (0)(0)+(1)(1) = 1$

$\alpha^*\beta = \begin{bmatrix}1 & 0\end{bmatrix}\begin{bmatrix}0\\1\end{bmatrix} = (1)(0)+(0)(1) = 0$

$\beta^*\alpha = \begin{bmatrix}0 & 1\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = (0)(1)+(1)(0) = 0$

(Q7) Using the variational method and the trial wave function $\varphi(r) = e^{-cr}$ gives the exact energy of the ground-state H atom!

Why?

The exact wave function is $\Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

We were "lucky" to guess the trial wave function $\varphi(r)$ with the same functional form as Ψ_{100}.

So, in this case, the variational method gives Ψ_{100} when $\varphi(r) = e^{-cr}$ is optimized by minimizing the variational energy

Q8 a) Using the Gaussian trial wave function $\varphi(r) = e^{-cr^2}$ gives

$$E' = \frac{3h^2}{8\pi^2\mu}\,c - \frac{e^2}{\sqrt{2}\,\pi^{3/2}\varepsilon_0}\sqrt{c}$$

To optimize the trial wave function, minimize E' by solving

$$\frac{dE'}{dc} = 0 = \frac{3h^2}{8\pi^2\mu} - \frac{1}{2}\,\frac{e^2}{\sqrt{2}\,\pi^{3/2}\varepsilon_0}\,\frac{1}{\sqrt{c}}$$

$$\frac{3h^2}{8\pi^2\mu} = \frac{e^2}{2\sqrt{2}\,\pi^{3/2}\varepsilon_0}\,\frac{1}{\sqrt{c}}$$

$$\sqrt{c} = \frac{2\sqrt{2\pi}}{3}\,\frac{\mu e^2}{h^2\varepsilon_0} \qquad c = \frac{8\pi}{9}\,\frac{\mu^2e^4}{h^4\varepsilon_0^2}$$

b) $$E'_{opt} = \frac{3h^2}{8\pi^2\mu}\,\frac{8\pi}{9}\,\frac{\mu^2e^4}{h^4\varepsilon_0^2} - \frac{e^2}{\sqrt{2}\,\pi^{3/2}\varepsilon_0}\,\frac{2\sqrt{2\pi}}{3}\,\frac{\mu e^2}{h^2\varepsilon_0}$$

$$= \left(\frac{1}{3\pi} - \frac{2}{3\pi}\right)\frac{\mu e^2}{h^2\varepsilon_0^2} = -\frac{1}{3\pi}\,\frac{\mu e^2}{h^2\varepsilon_0^2}$$

$$= -\frac{8}{3\pi}\,\frac{\mu e^2}{8h^2\varepsilon_0^2} = -\frac{8}{3\pi}\,E_{exact}$$

$$= -(0.8488\ldots)\,E_{exact}$$