

This is a 3-hour test.

Please answer all 8 questions in the spaces provided.

Allow about 3 minutes per point.

A calculator and the equation sheets provided can be used.

No books or notes are allowed.

|     |   |
|-----|---|
| Q1. | 7 |
| Q2. | 7 |
| Q3. | 7 |
| Q4. | 7 |
| Q5. | 8 |
| Q6. | 8 |
| Q7. | 9 |
| Q8. | 7 |
| 60  |   |

Q1. This question refers to a ground state hydrogen-like atom described by the wave function

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi}} \frac{Z^{3/2}}{a_0^{3/2}} e^{-Zr/a_0} \quad (a_0 \text{ is the Bohr radius, } 0.0529177 \text{ nm})$$

a) What is a hydrogen-like atom? What is Z?

He<sup>+</sup>, Li<sup>2+</sup>, Be<sup>3+</sup>, ... one-electron atoms  
Two particles (nucleus, electron) ⇒ Schrodinger eq.  
Can be solved exactly

Z (number of protons) = atomic number

b) Chemists define the radius of an atom as the value of r that maximizes the radial probability distribution function P(r) for the outermost electrons. Use

$$P(r) = \int_0^{2\pi} \int_0^{\pi} \psi^* \psi r^2 \sin \theta d\theta d\phi$$

to prove the radius of a ground state hydrogen-like atom is  $a_0/Z$ .

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

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

constant

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

$$0 = 2re^{-2Zr/a_0} \left( 1 - \frac{Zr}{a_0} \right) \quad 1 - \frac{Zr}{a_0} = 0 \quad r = \frac{a_0}{Z}$$

c) The electric potential energy for an electron at distance r from the nucleus of a hydrogen-like atom is Z times larger than that for a hydrogen atom. Why?

$$V(r) = \frac{q_+ q_-}{4\pi \epsilon_0 r} = \frac{(+Ze)(-e)}{4\pi \epsilon_0 r} = -Z \left( \frac{e^2}{4\pi \epsilon_0 r} \right) \quad \text{for H}$$

d) Use the results from b and c to explain why the energy of a hydrogen-like atom is Z<sup>2</sup> larger than that of a hydrogen atom.

electron Z times closer to nucleus (b)  
in an electric field Z times stronger (c)

$$Z \times Z = Z^2$$

Q2. Are gravitational effects important for atoms? From Newton's law, the gravitational potential energy of a proton and an electron in a hydrogen atom is

$$V_{\text{grav}} = -\frac{Gm_p m_e}{r} \quad G = 6.674 \times 10^{-11} \text{ J m kg}^{-2}$$

$m_p$  and  $m_e$  are the proton and electron masses.  $G$  is the gravitational constant.

a) Use perturbation theory to calculate  $\Delta E$  for the change in energy of a ground-state hydrogen atom caused by the gravitational attraction of the electron and proton. *Hints:*

$$\hat{H}^{(1)} = -\frac{Gm_p m_e}{r} \quad \Delta E = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau \quad \psi^{(0)}(r) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0}$$

$$(d\tau = r^2 \sin\theta dr d\theta d\phi) \quad \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\Delta E = \int \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0} \left( -\frac{Gm_p m_e}{r} \right) \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/a_0} d\tau$$

$$= \left( -\frac{Gm_p m_e}{\pi a_0^3} \right) \int \frac{1}{r} e^{-2r/a_0} d\tau \quad (= -Gm_p m_e \langle \frac{1}{r} \rangle)$$

$$= -\frac{Gm_p m_e}{\pi a_0^3} \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \int_0^\infty \frac{1}{r} e^{-2r/a_0} r^2 dr \quad \left( r = \frac{r}{a_0} \right)$$

$$= -\frac{Gm_p m_e}{\pi a_0^3} [2\pi] [-\cos\theta]_0^\pi \left[ a_0^2 \int_0^\infty \frac{r}{a_0} e^{-2r/a_0} d\left(\frac{r}{a_0}\right) \right]$$

$$= -\frac{Gm_p m_e}{\pi a_0^3} 2\pi [-(-1) - (-1)] a_0^2 \int_0^\infty r e^{-2r} dr \quad \left( \text{note } \langle \frac{1}{r} \rangle = \frac{1}{a_0} \right)$$

$$= -\frac{Gm_p m_e}{\pi a_0^3} \frac{2\pi(2) a_0^2}{2^2} = -\frac{Gm_p m_e}{a_0}$$

$$= -\left( 6.674 \times 10^{-11} \right) \left( 1.673 \times 10^{-27} \right) \left( 9.109 \times 10^{-31} \right) = -1.922 \times 10^{-57} \text{ J}$$

b) The gravitational energy of an excited-state hydrogen atom ( $n = 2, 3, 4, \dots$ ) is smaller than that for a ground-state hydrogen atom. Why?

Excited - state atoms are larger

Electron and proton are further apart on average  
less gravitational energy

c) High-resolution spectroscopy can detect atomic energy differences as small as  $10^{-32}$  J. Based on a and b, are gravitational energy effects measurable for atoms? Discuss briefly.

No,  $\Delta E$  far too small.

Q3. a) The Schrodinger equation is exact, but approximate numerical methods are essential for quantum chemistry. Why?  
 Schrodinger's equation can't be solved exactly for multi-electron atoms and molecules.

b) Why are variational methods generally much more useful for quantum chemistry than perturbation methods?

Perturbation methods require an exact solution of Schrodinger's equation for a closely related system — not available for multi-electron systems. Accurate variational calculations can be made with computers and trial functions with large basis sets of functions.

[7]

c) The trial wave function  $\varphi(r) = e^{-\alpha r}$  for the hydrogen atom with adjustable parameter  $\alpha$  gives

$$E' = \frac{\hbar^2 \alpha^2}{8\pi^2 \mu} - \frac{e^2 \alpha}{4\pi \epsilon_0}$$

optimize  $E'$  and  $\alpha$  by minimizing  $E'$

Calculate the optimum values of  $\alpha$  and the energy.

$$\frac{dE'}{d\alpha} = \frac{d}{d\alpha} \left( \frac{\hbar^2 \alpha^2}{8\pi^2 \mu} - \frac{e^2 \alpha}{4\pi \epsilon_0} \right) = \frac{\hbar^2}{8\pi^2 \mu} 2\alpha - \frac{e^2}{4\pi \epsilon_0} = 0$$

$$\alpha (\text{optimized}) = \frac{e^2}{4\pi \epsilon_0} \frac{1}{\hbar^2} = \frac{\pi e^2 \mu}{\epsilon_0 \hbar^2}$$

$$\begin{aligned} E(\text{minimized}) &= \frac{\hbar^2}{8\pi^2 \mu} \alpha_{\text{opt}}^2 - \frac{e^2}{4\pi \epsilon_0} \alpha_{\text{opt}} \\ &= \frac{\hbar^2}{8\pi^2 \mu} \frac{\pi^2 e^4 \mu^2}{\epsilon_0^2 \hbar^4} - \frac{e^2}{4\pi \epsilon_0} \frac{\pi e^2 \mu}{\epsilon_0 \hbar^2} \\ &= \frac{\mu e^4}{8 \epsilon_0^2 \hbar^2} - \frac{\mu e^4}{4 \epsilon_0 \hbar^2} = \left( \frac{1}{8} - \frac{1}{4} \right) \frac{\mu e^4}{8 \epsilon_0^2 \hbar^2} \\ &= - \frac{\mu e^4}{8 \epsilon_0^2 \hbar^2} \end{aligned}$$

d) Is the energy calculated in part c consistent with the variational theorem? Justify your answer. Hint: the ground state energy of a hydrogen atom is

$$E_1 = - \frac{\mu e^4}{8 \epsilon_0^2 \hbar^2} \quad (\text{true energy})$$

variational energy  $\geq$  true energy

here, variational energy = true energy

Q4. a) Solving the Schrodinger equation for the hydrogen atom gives the frequencies

$$\tilde{\nu} = 109,677.583 \text{ cm}^{-1} \left[ \frac{1}{(n_{\text{final}})^2} - \frac{1}{(n_{\text{initial}})^2} \right]$$

$$\frac{1}{1} - \frac{1}{4} = \frac{3}{4}$$

for the  $n_{\text{initial}} \rightarrow n_{\text{final}}$  transitions in the emission spectrum of atomic hydrogen. Calculate the frequency for the  $2p^1 \rightarrow 1s^1$  transition in units of  $\text{cm}^{-1}$ .  $n_{\text{init}} = 2$   $n_{\text{final}} = 1$

$$\tilde{\nu} = 109,677.583 \text{ cm}^{-1} \left[ \frac{1}{1^2} - \frac{1}{2^2} \right]$$

$$= 82,258.187 \text{ cm}^{-1}$$

[7]

b) But wait! Spectroscopy shows the  $2p^1 \rightarrow 1s^1$  transition for hydrogen is actually a doublet with frequencies  $82,258.917 \text{ cm}^{-1}$  and  $82,259.272 \text{ cm}^{-1}$ . Why is a doublet not predicted by the Schrodinger equation, which is solved exactly for the hydrogen atom?

Schrodinger's equation does not include terms for spin angular momentum (a relativistic effect)

c) i) Give the complete term symbol (or symbols) for the  $1s^1$  hydrogen configuration.

$$M=0 \quad M \quad M_S \quad M_J \quad \Rightarrow L=0 \text{ only}$$

$$\uparrow \quad 0 \quad 1/2 \quad 1/2 \quad \Rightarrow S=1/2$$

$$\downarrow \quad 0 \quad -1/2 \quad -1/2 \quad \Rightarrow J=1/2$$

$$2S+1 = 2 \quad 2S_{1/2}$$

ii) Give the complete term symbol (or symbols) for the  $2p^1$  hydrogen configuration.

| $M$          | $M_S$        | $M_J$  |
|--------------|--------------|--------|
| $M=0$        | $M=1$        | $M_J$  |
| $\uparrow$   | $\uparrow$   | $1/2$  |
| $\downarrow$ | $\downarrow$ | $-1/2$ |
| $\uparrow$   | $\uparrow$   | $3/2$  |
| $\downarrow$ | $\downarrow$ | $1/2$  |

max  $M=1$  (twice)  
 $\therefore$  two P states

max  $M_S=1/2$  (thrice)

$\therefore S=1/2$  states

$$M_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$$

and  $-1/2, 1/2$

$$\therefore J = \frac{3}{2} \text{ or } \frac{1}{2}$$

Spin multiplicity  $2S+1 = 2$

$2P_{3/2}$  and  $2P_{1/2}$

iii) Assign initial and final term symbols for the  $82,258.917 \text{ cm}^{-1}$  transition.

Comparing the  $2P_{3/2}$  and  $2P_{1/2}$  energies, use Hund's rule,  $2P^1$  subshell  $< 1/2$  full  $E_{2P_{1/2}} < E_{2P_{3/2}}$

$$2P_{1/2} \rightarrow 2S_{1/2}$$

iv) Assign initial and final term symbols for the  $82,259.272 \text{ cm}^{-1}$  transition.



$2S_{1/2}$

Q5. a) Use the term symbols for ground-state atoms from  $Z = 1$  to  $Z = 10$  given below to decide which of these atoms are paramagnetic (generates a magnetic field). Justify your answers.

| atom      | term symbol | yes                                 | no                                  | $L$ | $S$ |
|-----------|-------------|-------------------------------------|-------------------------------------|-----|-----|
| hydrogen  | $2S_{1/2}$  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | 0   | 1/2 |
| helium    | $1S_0$      | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | 0   | 0   |
| lithium   | $2S_{1/2}$  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | 0   | 1/2 |
| beryllium | $1S_0$      | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | 0   | 0   |
| boron     | $2P_{1/2}$  | <input type="checkbox"/>            | <input type="checkbox"/>            | 1   | 1/2 |
| carbon    | $3P_0$      | <input type="checkbox"/>            | <input type="checkbox"/>            | 1   | 1   |
| nitrogen  | $4S_{3/2}$  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | 0   | 3/2 |
| oxygen    | $3P_2$      | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | 1   | 1   |
| fluorine  | $2P_{3/2}$  | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | 1   | 1/2 |
| neon      | $1S_0$      | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | 0   | 0   |

paramagnetic

if there is angular momentum

$$L > 0$$

and/or there is

spin angular momentum

$$S > 0$$

b) Use data given from part a to decide which of the first ten elements has the largest number of unpaired electrons in its ground atomic state. Justify your answer.

$$N \quad S = 3/2$$

[8]

c) The atomic radii given below show atomic sizes decrease significantly as the 2p subshell is filled. Account for this trend.

As the 2p subshell is filled, the nuclear charge increases but shielding from the nucleus by 1s and 2s electrons remains the same, so the electrons are pulled closer to the nucleus

|          |                  |         |
|----------|------------------|---------|
| boron    | $1s^2 2s^2 2p^1$ | 77.6 pm |
| carbon   | $1s^2 2s^2 2p^2$ | 62.0 pm |
| nitrogen | $1s^2 2s^2 2p^3$ | 52.1 pm |
| oxygen   | $1s^2 2s^2 2p^4$ | 45.0 pm |
| fluorine | $1s^2 2s^2 2p^5$ | 39.6 pm |
| neon     | $1s^2 2s^2 2p^6$ | 35.4 pm |

d) For the manganese atom ( $1s^2 2s^2 3p^6 3s^2 4s^2 3d^5$ ), there are  $10!/5!5! = 252$  different ways to place the five 3d electrons in the ten spin orbitals. So you won't be asked to give the term symbols for manganese! But what about the term symbol for the ground-state?

i) The following 3d electron arrangement contributes to manganese ground state. Why?

$$\uparrow_{m=-2} \quad \uparrow_{m=-1} \quad \uparrow_{m=0} \quad \uparrow_{m=1} \quad \uparrow_{m=2}$$

Hund's Rule #1: Highest spin possible gives the lowest energy state

ii) For this arrangement, show  $M = 0$  and  $M_s = 5/2$ .

$$M = -2 - 1 + 0 + 1 + 2 = 0 \Rightarrow L = 0 \text{ (S state)}$$

$$M_s = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{5}{2} \Rightarrow S = \frac{5}{2}$$

$$M_j = -\frac{3}{2} + -\frac{1}{2} + \frac{1}{2} + \frac{3}{2} + \frac{5}{2} = \frac{5}{2} \Rightarrow J = 5/2$$

iii) Show the term symbol for ground-state manganese is  ${}^6S_{5/2}$ .

$$\text{Spin multiplicity } 2\left(\frac{5}{2}\right) + 1 = 6$$

$$\therefore {}^6S_{5/2}$$

Q6. Use the Hartree-Fock orbital energies on the graph provided to answer this question.

- a) The energies of the 2s and 2p orbitals for hydrogen are identical. Why?  
 $E_n = -\frac{m_e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}$  depends only on principle quantum number  $n$  for the H atom

- b) As  $Z$  increases from 1, the 2s energy drops below the 2p energy. Why?  
2p electrons are more effectively shielded from the nucleus by the inner 2s and 1s electrons, feel a weaker nuclear charge

[8]

- c) Why does the 4s subshell fill before the 3d subshell?  
3d electrons more effectively shielded

- d) Orbital energies can be measured by photoelectric spectroscopy. Calculate the wavelength of radiation required to eject a 1s electron from neon ( $Z = 10$ ).

for  $Z = 10$ , read  $\sqrt{\frac{E_{1s}}{E_H}} = 7.6$

$$E_{1s} = (7.6)^2 E_H = 57.8 E_H = 57.8(-13.6 \text{ eV})$$

$$E_{1s} = -785 \text{ eV} = -1.26 \times 10^{-16} \text{ J}$$

$$h\nu = \Delta E = \frac{hc}{\lambda} \quad \lambda = \frac{hc}{\Delta E} = 1.58 \times 10^{-9} \text{ m}$$

- e) Calculate the ionization energy of calcium ( $Z = 20$ ,  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ ).

read from graph

$$\sqrt{\frac{E_{4s}}{E_H}} = 0.56 \quad E_{4s} = (0.56)^2 (-13.6 \text{ eV}) = -4.26 \text{ eV}$$

Ionization energy 4.26 eV

Q7. a) Indicate whether each of the following functions is symmetric, antisymmetric, or neither with respect to the interchange of electrons 1 and 2.

i)  $f(1)g(1)$  neither

iii)  $f(1)g(2) + g(1)f(2)$  symmetric

ii)  $f(1)g(2)$  neither

iv)  $[1s(1)2s(2) + 2s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$   
Anti-Symmetric

v)  $\exp[-b(r_1 - r_2)]$   
neither

b) i)  $[1s(1)2s(2) - 2s(1)1s(2)] [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$   
Anti-Symmetric

ii)  $r_1^2 - 2r_1r_2 + r_2^2$   
symmetric

[9]

b) Why the type of symmetry described in part a important for quantum chemistry?

Wave functions of multi-electron atoms are asymmetric with respect to interchanging any two electrons.

c) In the course notes, an external magnetic field was shown to split the energy of a 2p electron in a hydrogen atom into three different energy levels. Why does a magnetic field cause this splitting?

2p electron ( $l=1$ )

$m = -1, 0, 1$



magnetic moment of the electron due to orbital angular momentum provides magnetic potential energy  $m\beta_0 B_z$

d) Oops! Spectroscopy shows a magnetic field produces six different energy levels for a hydrogen 2p electron. Explain briefly.

Spin angular momentum ( $m_s = -\frac{1}{2}, 0, +\frac{1}{2}$ ) splits each of the three levels in part c into two levels



e) For an excited-state helium atom with electronic configuration  $1s^1 2s^1$ , give two reasons why the wave function  $\psi = 1s(1)2s(2)$  is physically unrealistic.

$\psi(1,2) \neq \psi(2,1)$

Can't say electron 1 is in the 1s orbital, electron 2 is in the 2s orbital (electrons are not distinguishable)

no spin terms



Q8. The trial wave function  $\chi = c_1 1s_A(1) + c_2 1s_B(1)$  for the  $H_2^+$  molecule ion leads to the determinant equation.

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{AA} - E \end{vmatrix} = 0$$

a) Show the predicted energies of  $H_2^+$  are

$$E_+ = \frac{H_{AA} + H_{AB}}{1 + S}$$

$$E_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

$$(H_{AA} - E)(H_{AA} - E) - (H_{AB} - SE)(H_{AB} - SE) = 0$$

$$\underbrace{(H_{AA} - E)^2}_{\text{+ve root}} = (H_{AB} - SE)^2 \quad H_{AA} - E = \pm (H_{AB} - SE)$$

$$[7] \quad H_{AA} - E = \underbrace{H_{AB} - SE}_{\text{-ve root}} \quad H_{AA} - E = -H_{AB} + SE$$

$$H_{AA} - H_{AB} = E - SE \quad H_{AA} + H_{AB} = E + SE$$

$$E = \frac{H_{AA} - H_{AB}}{1 - S} \quad E = \frac{H_{AA} + H_{AB}}{1 + S}$$

b) Prove the wave function for energy  $E_+$  is spatially symmetric:  $c_1 = c_2$

$$(H_{AA} - E)c_1 + (H_{AB} - SE)c_2 = 0$$

$$E = E_+ = \frac{H_{AA} + H_{AB}}{1 + S}$$

$$(H_{AA} - E)c_1 = (SE - H_{AB})c_2$$

$$\left( H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S} \right) c_1 = \left( S \frac{H_{AA} + H_{AB}}{1 + S} - H_{AB} \right) c_2$$

*multiply by 1+S*

$$(H_{AA} + SH_{AA} - H_{AA} - H_{AB})c_1 = (SH_{AA} + SH_{AB} - H_{AB} - SH_{AB})c_2$$

$$(SH_{AA} - H_{AB})c_1 = (SH_{AA} - H_{AB})c_2$$

$$c_1 = c_2$$

c) Prove the wave function for energy  $E_-$  is spatially antisymmetric:  $c_1 = -c_2$

$$(H_{AA} - E)c_1 = (SE - H_{AB})c_2 \quad E = E_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

$$\left( H_{AA} - \frac{H_{AA} - H_{AB}}{1 - S} \right) c_1 = \left( S \frac{H_{AA} - H_{AB}}{1 - S} - H_{AB} \right) c_2$$

*multiply by 1-S*

$$(H_{AA} - SH_{AA} + H_{AA} + H_{AB})c_1 = (SH_{AA} - SH_{AB} - H_{AB} + SH_{AB})c_2$$

$$(H_{AB} - SH_{AA})c_1 = (-H_{AB} + SH_{AA})c_2$$

$$c_1 = -c_2$$

Q2 7  
Q3 7  
Q4 7  
Q5 8  
Q6 8  
Q7 9  
Q8 7