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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.

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Q1. The Schrodinger equation gives $E_n = -\frac{13.60 \text{ eV}}{n^2}$

$$n = 1, 2, 3, \dots$$

for the energies of the hydrogen atom.

a) Calculate the ionization energy for one mole of ground-state hydrogen atoms.

13.60 eV to ionize one H atom

$$\begin{aligned} \text{per mole: } & (6.022 \times 10^{23} \text{ mol}^{-1})(13.60 \text{ eV}) = 8.190 \times 10^{24} \text{ eV} \\ & = (8.190 \times 10^{24} \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1}) \text{ mol}^{-1} \\ & = 1.312 \times 10^6 \text{ J mol}^{-1} = 1312 \text{ kJ mol}^{-1} \end{aligned}$$

b) Convert the equation for E_n to give E_n in wavenumbers.

$$\begin{aligned} \tilde{E}_n &= \frac{E_n}{hc} = -\frac{13.60 \text{ eV}}{hc n^2} = -\frac{(13.60 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})}{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{10} \text{ cm s}^{-1})n^2} \\ &= \boxed{-\frac{109,700 \text{ cm}^{-1}}{n^2}} \end{aligned}$$

c) Give the shortest wavelength in the spectrum of atomic hydrogen. \Rightarrow highest energy

$\Rightarrow n = \infty$ to $n = 1$ transition

$$h\nu_{\text{max}} = \Delta E_{\text{max}} = 13.60 \text{ eV} = 2.178 \times 10^{-18} \text{ J}$$

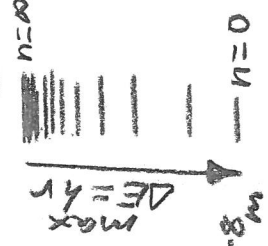
$$\nu_{\text{max}} = \frac{\Delta E_{\text{max}}}{h} = 3.288 \times 10^{15} \text{ s}^{-1} \text{ (UV)}$$

$$\lambda_{\text{min}} = c/\nu_{\text{max}} = \boxed{91.18 \text{ nm}}$$

d) Molecules such as HCl and H₂O have strong absorptions in the infrared (wavelengths from 700 nm to 1 mm) due to molecular vibrations. Do hydrogen atoms have infrared spectra? Justify your answer.

[6] **YES**

for the $n_i \rightarrow n_f$ emission $\tilde{\nu} = -109,700 \text{ cm}^{-1} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$
 $\tilde{\nu}$ ranged from $109,700 \text{ cm}^{-1}$ (for $n_i = \infty \rightarrow n_f = 0$)
 to zero cm^{-1} as $n_i, n_f \rightarrow \infty$



e) Molecules such as HCl and H₂O have strong microwave absorptions (wavelengths from 1 mm to 1 m) due to molecular rotations. Do hydrogen atoms have microwave spectra? Justify your answer.

YES

(see d)

f) High-resolution spectroscopy shows the equation for E_n is "not quite right". Explain.

The Schrodinger equation is non-relativistic, and there fore does not include spin angular momentum that produces doublets measured by high-resolution spectroscopy (see Q5 d)

- Q2. a) Protons and electrons have very small masses, but they are very close together in hydrogen atoms. Is the gravitational potential energy of the hydrogen atom (V_{grav}) significant?

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

Give two reasons why the perturbation calculations are well suited to answer this question.

- i) The perturbation $\Delta E^{(1)}$ should be very small and therefore an accurate correction to the energy
 ii) The wave function $\psi^{(0)} = \psi_{100}$ for the non-perturbed state is accurately known

- b) To calculate the gravitational potential energy of the ground-state hydrogen atom by the perturbation method, give the expressions for:

i) $\psi^{(0)} = \psi_{100}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ (see the next page)

ii) $E^{(0)} = E_1 = -13.60 \text{ eV} = -2.178 \times 10^{-18} \text{ J}$

iii) $\hat{H}^{(1)} = V_{\text{grav}} = -G \frac{m_e m_p}{r}$

- c) Calculate the perturbation energy $\Delta E^{(1)}$ for the ground-state hydrogen atom. Hint: $\langle 1/r \rangle = 1/a_0$

$$\begin{aligned} \Delta E^{(1)} &= \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} dr \\ &= \int \psi_{100}^* \left(-G \frac{m_e m_p}{r} \right) \psi_{100} dr \\ &= -G m_e m_p \int \psi_{100}^* \frac{1}{r} \psi_{100} dr \\ &= -G m_e m_p \langle \frac{1}{r} \rangle = -G m_e m_p \frac{1}{a_0} \\ &= - \frac{(6.674 \times 10^{-11}) (9.110 \times 10^{-31}) (1.673 \times 10^{-27})}{5.292 \times 10^{-11}} \quad \left(\frac{\text{all SI units}}{\text{units}} \right) \end{aligned}$$

$$\Delta E^{(1)} = -1.922 \times 10^{-57} \text{ J}$$

- d) Is gravitational potential energy significant for hydrogen atoms. Justify your answer.

No!

$$\begin{aligned} \frac{\Delta E^{(1)}}{E^{(0)}} &= \frac{-1.922 \times 10^{-57} \text{ J}}{-13.60 \text{ eV} (1.602 \times 10^{-19} \text{ J eV}^{-1})} \\ &= 8.822 \times 10^{-40} \end{aligned}$$

≈ 0

Q3. Use the wave functions for hydrogen-like atoms given below to answer this question.

a) The probability of finding electrons inside the nucleus of an atom can be non-zero. As a result, a nuclear reaction called **electron capture** can occur, converting an electron and a proton to a neutron, which reduces the atomic number by one. For example: $K \rightarrow Ar$. **Alchemy!**

Use the orbitals for hydrogen-like atoms given below to explain why electron capture is: $Z=1$

i) more probable for 1s electrons in He^+ than for 1s electrons in the hydrogen atom

at $r=0$, the probability distribution function Z^3 or 8 times larger for He

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

ii) more probable for 1s electrons than for 2s electrons

$$\frac{\psi_{200}^2}{\psi_{100}^2} = \frac{1}{32} \frac{e^{-2Zr/a_0}}{(2-0)e^{-2Zr/a_0}} = \frac{1}{64}$$

iii) negligible for 2p electrons.

ψ_{210} and $\psi_{21\pm 1}$ are proportional to r

so ψ_{210}^2 and $\psi_{21\pm 1}^2$ are zero at the nucleus

b) How do chemists define the size of an atom?

maximum in the radial probability distribution function $P(r)$

c) Show the radius of a hydrogen-like atom in the 1s state is a_0/Z .

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

$$P(r) = \psi_{100}^2 r^2 \left[\int_0^{2\pi} d\phi \right] \left[\int_0^\pi \sin\theta \, d\theta \right] = \frac{r^2}{\pi} \left(\frac{Z}{a_0}\right)^3 e^{-2Zr/a_0} \text{ (const.)}$$

to maximize $P(r)$, maximize $r e^{-2Zr/a_0}$

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

0 = $2r_{mp} \left[-\frac{2Z}{a_0} + 1 \right] = 2r_{mp} \left[-\frac{2Z}{a_0} + 1 \right] e^{-2Zr_{mp}/a_0}$

$$\Rightarrow r_{mp} = \frac{a_0}{Z}$$

d) High-Z hydrogen-like atoms, such as Kr^{35+} , have very small radii. Why?

Z is large (36), so $r_{mp} = \frac{a_0}{36}$ only 0.00147 nm

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

$$\psi_{210}(r) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

$$\psi_{200}(r) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$$\psi_{21\pm 1}(r) = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta e^{\pm i\phi}$$

Q4. a) Why are variational calculations important in quantum mechanics?

The Schrodinger equation can't be solved exactly for multi-electron molecules, so approximate numerical methods such as variational calculations are needed.

b) For chemical systems, why are variational calculations generally more useful than perturbation calculations?

need accurate unperturbed $\psi^{(0)}$ functions (not usually available)
 perturbation energies for electron-electron repulsions are large, required high-order calculations of $\Delta E^{(1)}, \Delta E^{(2)}, \Delta E^{(3)}, \dots$

c) For the hydrogen atom, the trial wave function $\psi(r) = e^{-cr}$ gives

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

Calculate the variational energy of the ground-state hydrogen atom.

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

$$2c \frac{\hbar^2}{8\pi^2 \mu} = \frac{e^2}{4\pi\epsilon_0}$$

$$c = \frac{e^2}{\epsilon_0} \frac{4\pi}{\hbar^2}$$

$$E'_{\min} = \left(\frac{e^2}{\epsilon_0} \frac{4\pi}{\hbar^2} \right)^2 \frac{\hbar^2}{8\pi^2 \mu} - \frac{e^2}{\epsilon_0} \frac{4\pi}{\hbar^2} \frac{e^2}{4\pi\epsilon_0}$$

$$= \frac{1}{8} \frac{e^4 \mu}{\epsilon_0^2 \hbar^2} - \frac{1}{4} \frac{e^4 \mu}{\epsilon_0^2 \hbar^2}$$

$$\left(\frac{1}{8} - \frac{1}{4} \right) = \frac{1}{8} - \frac{2}{8} = -\frac{1}{8}$$

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

d) Prove the energy calculated in c is consistent with the variational theorem.

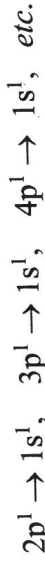
$$E_{\text{exact}} = E_1 \text{ for the Hydrogen}$$

$$= -\frac{e^4 \mu}{8 \epsilon_0^2 \hbar^2}$$

notice $E'_{\min} = E_{\text{exact}}$

variational theorem $E'_{\min} \geq E_{\text{exact}}$ is obeyed

Q5. The Lyman series in the emission spectrum of atomic hydrogen is produced by transitions from excited np^1 states to the $1s^1$ ground-state state:



a) Why is it necessary to consider transitions to the ground $1s^1$ state only from np^1 states?

selection rule $\Delta l = \pm 1$

$1s^1$ has $l=0$ np^1 has $l=1$ nd^1 has $l=2 \dots$
 $np^1 \rightarrow ns^1$ ($\Delta l = -1$) allowed $nd^1 \rightarrow ns^1 \dots$ not allowed
 $\Delta l = -2$ allowed

b) High-resolution spectroscopy shows that each line in the Lyman series is actually a doublet. For example, the $2p^1 \rightarrow 1s^1$ doublet is observed at $82,258.92 \text{ cm}^{-1}$ and $82,259.27 \text{ cm}^{-1}$.

Why are Lyman transitions doublets? To help answer this question, give

$l=0, m=0$

i) the spectroscopic term symbol for the final $1s^1$ state

$m=0$	M	M_S	M_J
1	0	$1/2$	$1/2$

$l=0$ \uparrow 0 \uparrow $-1/2$ \uparrow $1/2$
 $S=1/2$ $J=1/2$

$2s+1 = 2$ (doublet)

$2S_{1/2}$ (from $L=0$)

ii) the spectroscopic term symbols for the initial $2p^1$ states.

$l=1, m=-1, 0, 1$

$m=-1$	$m=0$	$m=+1$	M	M_S	M_J
1	1	1	-1	$1/2$	$-1/2$
			0	$1/2$	$1/2$
			1	$1/2$	$1/2$

$l=1$ \downarrow $l=1$ \downarrow $l=1$ \downarrow
 -1 $-1/2$ $-1/2$ $-1/2$
 0 $-1/2$ $-1/2$ $-1/2$
 1 $-1/2$ $-1/2$ $1/2$

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$(L=1)$ (twice) gives two P states

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

$J=1/2$ ($M_J = -1/2, 1/2$)
 $J=1/2$ ($M_J = -1/2, 1/2$)

c) Rank the term symbols for the $2p^1$ states in order of increasing energy.

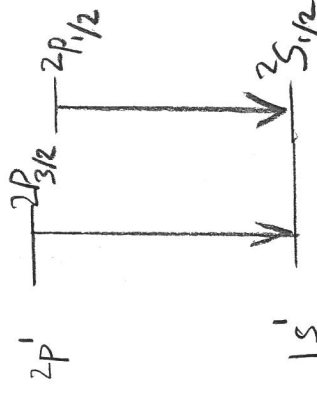
$2P_{1/2}$ (lower J value, Hund's rule #3)

d) Assign spectroscopic term symbols to the initial and final states for

i) the $82,258.92 \text{ cm}^{-1}$ transition



ii) the $82,259.27 \text{ cm}^{-1}$ transition



Q6. Give short qualitative answers to the following questions.

a) The energies of hydrogen atoms increase with principal quantum number n . Electronic configuration data (e.g., $[\text{Ar}]4s^23d^3$ for vanadium) show, however, the 4s subshell fills before the 3d subshell in multi-electron atoms. Why?

less shielding from the nucleus of the more compact 4s electron lowers than energy (relative to the 3d energy) \Rightarrow higher effective Z for 4s electrons relative to Z for 3d electrons

b) The electronic configuration $[\text{Ar}]4s^23d^3$ of vanadium ($Z = 23$) suggests the configuration of chromium ($Z = 24$) should be $[\text{Ar}]4s^23d^4$. But the electronic configuration of chromium is actually $[\text{Ar}]4s^13d^5$. Why?

$[\text{Ar}]4s^13d^5$ has 6 unpaired electrons compared to a maximum of 4 unpaired electrons for $[\text{Ar}]4s^23d^4$

$[\text{Ar}]4s^13d^5$ has higher spin multiplicity (Hund's Rule #1) and \therefore lower energy

c) Explain the following trend in atomic radii:

B \rightarrow Ne 2p electrons have about the same shieldy (by 1s, 2s electrons), but the nuclear charge Z increases from 5 for B to 10 for Ne, pulling in the 2p electrons as Z increases \Rightarrow decrease in atomic radii

$[\text{Be}]2p^1$	77.6 pm
$[\text{Be}]2p^2$	62.0 pm
$[\text{Be}]2p^3$	52.1 pm
$[\text{Be}]2p^4$	45.0 pm
$[\text{Be}]2p^5$	39.6 pm
$[\text{Be}]2p^6$	35.4 pm

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d) Explain the following trend in atomic radii:

helium	29.1 pm
neon	35.4 pm
argon	65.9 pm
krypton	79.5 pm

increasing principal quantum number n (also, increasing shielding)

(recall the size of the hydrogen atom increases drastically with n)

e) The ionization energy of neon ($Z = 10$) is 21.6 eV. The ionization energy of sodium ($Z = 11$), the next element, is sharply lower, only 5.1 eV. Why?

The 3s¹ electron in Na is significantly farther than the 2p electrons in Ne (see part d).

Also, the 3s¹ electron is more strongly shielded from the nucleus (by 1s, 2s, 2p electrons) than the 2p electrons in Ne (by 1s, 2s electrons)

f) Helium has the highest ionization energy (24.58 eV) of all the elements. Why?

The 1s² electrons in He are closest to the nucleus and experience very little shielding

g) Ground-state He, Be, Ne, Mg, Ar, Ca and Kr atoms all have ¹S₀ term symbols. Why?

filled shells (e.g., 1s² for He) or filled

subshells (e.g., 2s² for Be)

$$\Rightarrow \sum m_l = 0 = M \Rightarrow L = 0 \quad 1S_0 \text{ states}$$

$$\sum m_s = 0 = M_s \Rightarrow S = 0$$

Q7. a) Give two reasons why the wave function $\psi_A = 1s(1)\alpha(1)1s(2)\beta(2)$ is unacceptable for the helium atom

i) electrons are distinguishable e.g., electron 1 is 1,

ii) ψ_A is not antisymmetric when electrons 1 and 2 are interchanged

b) The determinantal wave function for helium is

$$\psi_B = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

Show ψ_B is the product of a spatial function (of 1s orbitals) and a spin function.

$$\psi_B = \frac{1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2)}{\sqrt{2}}$$

$$= \frac{[1s(1)1s(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]}{\sqrt{2}}$$

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spatial factor $1s(1)1s(2)$

spin factor $\alpha(1)\beta(2) - \beta(1)\alpha(2)$

normalization factor $\frac{1}{\sqrt{2}}$

c) Why is it important for atomic wave functions to be antisymmetric with respect to the interchange of any two electrons?

Pauli Exclusion Principle (from the Dirac equation)

d) Prove ψ_B is antisymmetric.

$$\psi_B(1,2) = \frac{1s(1)1s(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]}{\sqrt{2}}$$

$$\psi_B(2,1) = \frac{1s(2)1s(1) [\alpha(2)\beta(1) - \beta(2)\alpha(1)]}{\sqrt{2}}$$

$$= - \frac{1s(1)1s(2) [\beta(2)\alpha(1) - \alpha(2)\beta(1)]}{\sqrt{2}}$$

$$= - \frac{1s(1)1s(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)]}{\sqrt{2}}$$

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