

EXAM INFORMATION

Radial Distribution Function: $P(r) \equiv RDF(r) \equiv Br^2R(r)^2$, B is the normalization constant.

Order of Orbital Energies: Homonuclear Diatomic Molecules

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p < \sigma_g 2p < \pi_g^* 2p < \sigma_u^* 2p$$

Spherical Polar Coordinates

NOT NEEDED FOR THIS TEST

$$dV = r^2 \sin(\theta) dr d\theta d\varphi$$

$$0 \leq r < \infty$$

$$0 \leq \theta \leq \pi$$

$$0 \leq \varphi \leq 2\pi$$

Constants and Conversions:

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$m_e = 9.10 \times 10^{-31} \text{ kg}$$

$$m_p = 1.67 \times 10^{-27} \text{ kg}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

$$1 \text{ N} = 1 \text{ kg}\cdot\text{m}/\text{s}^2$$

$$1 \text{ au (hartree)} = 2625 \text{ kJ/mol}$$

$$1 \text{ au (hartree)} = 27.21 \text{ eV}$$

INTEGRALS

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

$$\int_0^4 x^4 e^{-x} dx = 8.91$$

$$\int_0^6 x^4 e^{-x} dx = 17.16$$

$$\int_0^9 x^4 e^{-x} dx = 22.68$$

$$\int_0^4 x^6 e^{-x} dx = 79.7$$

$$\int_0^6 x^6 e^{-x} dx = 283.5$$

$$\int_0^9 x^6 e^{-x} dx = 571.1$$

Name _____

(24) 1. Short Answer Questions

- (3) (a) One of the π molecular orbitals in the diatomic molecule, C_2 , is given approximately by: $\varphi = 0.82(2p_{ya}) - 0.82(2p_{yb})$

Is this a bonding or antibonding orbital? **WHY?**

- (2) (b) Consider the function, $u(1)v(2)[\alpha_1\beta_2 - \beta_1\alpha_2]$ (u and v are spatial functions). This function is (i) symmetric, (ii) antisymmetric, (iii) neither symmetric nor antisymmetric with respect to electron exchange. . **No explanation necessary**

- (6) (c) Consider an excited state wavefunction for He_2^+ ion . The simple product wavefunction is $\sigma_g 1s(1)\alpha_1 \cdot \sigma_u^* 1s(2)\beta_2 \cdot \pi_g 2p(3)\beta_3$

Write the **normalized** Slater determinant for the molecule in this configuration **AND** state how many terms one would have when the determinant is expanded.

1. Short Answer Questions (Cont'd)

- (6) (d) Write the complete electron configuration and give the bond order of the N_2^+ cation. Give the bond order and **explain why** the vibrational frequency is higher or lower than the frequency in the neutral molecule, N_2 .

- (4) (e) One variational wavefunction for the helium atom which was discussed in class was: $\varphi_1 = A \left[e^{-Z'(r_1+r_2)} (1 + br_{12}) \right]$, where Z' and b are positive ($Z' > 0$, $b > 0$)

Variational parameters.

Consider a second variational wavefunction: $\varphi_2 = A \left[e^{-Z'(r_1+r_2)} (1 - br_{12}) \right]$, where Z' and b are positive ($Z' > 0$, $b > 0$)

Explain, on the basis of electron correlation whether you would expect φ_2 to yield a higher or lower expectation value for the energy than φ_1 .

You MUST explain your answer to receive credit.

- (3) (f) HeH dissociates into He and H. It has been found that when the HeH dissociation energy is calculated using a linear combination of 8 atomic orbitals, the Dissociation Energy is **higher** than the value using only 3 atomic orbitals. **EXPLAIN WHY** this is or isn't a violation of the Variational Principle.

- (26) 2. The Radial part of one of the hydrogen atom wavefunctions is:

$$R(r) = r^2 e^{-r/3a_0}$$

The normalization constant of the radial distribution function is: $B = \frac{1}{720} \left(\frac{2}{3a_0} \right)^7$

Note: See RDF definition on information sheet.

- (8) (a) Calculate the **most probable value of r** (i.e. r_{mp}) for the electron (your answer can be left in terms of a_0).

You must show your work for credit.

2. Cont'd.

- (10) (b) What is the probability that the distance from the nucleus is greater than or equal to $6a_0$; i.e. What is $\text{Prob}(6a_0 \leq r < \infty)$?

2. Cont'd.

- (8) (c) The force between the electron and proton in a hydrogen atom is inversely proportional to r^2 ($f \propto 1/r^2$). Therefore the average of $(1/r^2)$ can be used to determine the average force between the electron and proton.

Calculate the average value of $1/r^2$; i.e. $\left\langle \frac{1}{r^2} \right\rangle$, for the electron (your answer can be left in terms of a_0).

- (6) 3. As discussed in class, the antibonding orbital for H_2^+ is: $\psi = N(1s_a - 1s_b)$. $1s_a$ and $1s_b$ are normalized 1s atomic orbitals on each nucleus, and N is the normalization constant

Determine the normalization constant, N, as a function of S_{ab} (the overlap between the two 1s atomic orbitals). **You must show your work for credit.**

- (08) 4. A hypothetical wavefunction for a two electron system is:

$$\psi = N[2\psi_{1s}(1)\psi_{2p}(2) - 3\psi_{2p}(1)\psi_{1s}(2)]\alpha_1\beta_2$$

i.e. two times $\psi_{1s}(1)\psi_{2p}(2)$ - three times $\psi_{2p}(1)\psi_{1s}(2)$

Assuming that the individual spatial functions, ψ_{1s} and ψ_{2p} are individually normalized and that they are orthogonal to each other, determine the normalization constant, N , of the complete wavefunction above. **Show your work to receive credit.**

- (10) 5. Consider a hypothetical trial variational wavefunction for the ground state of the hydrogen atom, $\phi = \phi(\alpha)$, where α is a positive ($\alpha > 0$) Variational parameter. It was found that the expectation value for the energy, in a.u., using this trial wavefunction is:

$$\langle E \rangle = \langle \phi | H | \phi \rangle = A\alpha + \frac{B}{\alpha} - C, \quad \text{where } A = 1.8, B = 1.2 \text{ and } C = 3.4$$

Calculate the best value of the hydrogen atom energy(in a.u.) which can be obtained using this trial wavefunction. **Note:** your answer for $\langle E \rangle$ should be greater than -0.50 a.u. (i.e. less negative), which is the exact ground state energy of an electron in a hydrogen atom.

- (16) 6. Consider a beryllium atom, which has four electrons.
The experimental electronic energy of Be is: $E_{\text{exp}} = -14.670 \text{ au (hartrees)}$.
The Hartree-Fock energy of a neutral Be atom is: $E_{\text{HF}}(\text{Be}) = -14.567 \text{ au (hartrees)}$.
The Hartree-Fock orbital energies of the two occupied orbitals of Be are **-4.709 au**
and -0.301 au.
The electron affinity of Be is $EA(\text{Be}) = +1.98 \text{ eV}$

(5) a) Write the Hamiltonian of a Beryllium atom in MKS (SI) units.

(3) b) Describe what experimental data is necessary and how it is used to obtain the above experimental electronic energy of Be.

6. Cont'd.

- (3) c) Use the data at the beginning of the question to estimate the first ionization energy of Be, in electron volts (eV), **PLUS** give the two approximations that lower the accuracy of this estimate.

- (5) d) Use the data at the beginning of the question to estimate the Hartree-Fock energy of a Beryllium Anion, $E_{\text{HF}}(\text{Be}^{-1})$, in au (hartrees).

(10) 7. The Hamiltonian for the Li^{+1} ion is: $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{r_{12}}$

(8) a) An excited electronic configuration of Li^{+1} is: $(1s\alpha)^1(2p\beta)^1$. A simple product wavefunction for a Li^{+1} ion in this configuration is:

$$\psi = 1s(1)\alpha_1 2p(2)\beta_2$$

Use this product wavefunction to calculate the energy of a Li^{+1} ion in this configuration in terms of ϵ_{1s} , ϵ_{2p} and J_{1s2p} . You can ignore the spins for this part
You must show your work for credit.

Hint: You must separate the above Hamiltonian into 3 terms.

(2) b) Why doesn't your answer include an exchange integral, K_{1s2p} ?

Material - 2016

Chap. 6 - 26

26 - RDF: $P(\geq 6a_0) + \text{rmp} + \langle 1/r^2 \rangle$

Chap. 7 - 56

4 - SA - $\exp(-Zr_1+r_2)(1-b_{12})$ vs. $1+b_{12}$ - lower or higher E

6 - SA - He_2^+ Slater Det.

2 - SA - $uv(a_1b_2-b_1a_2)$ - Sym/Antisym/neither

10 - Var. Prin. calc.

16 - Be atom - 4 parts

8 - Normalize hypothetical wfn

10 - Li^+ - Calc E in terms of e_{1s} , e_{2p} , J - why no K

Chap. 8 - 18

3- SA - bonding or anti-bonding π MO

6 - SA - N_2^+ config. + BO + Vib. freq relative to N_2

3 - SA - HeH - De with more orbs higher - viol of Var Prin?

6 - Normalize H_2^+ AB Orb.

Material - 2015 (last year)

Chap. 6 - 25

- 20 - $\langle \cos^2\theta \rangle$ and RDF probability from 6 ao to 12 ao
- 5 - transition wavelength in Li^{2+}

Chap. 7 - 50

- 4 - SA - EA of Oxygen
- 4 - SA - Exchange Integral
- 6 - SA - Excited state Sec. Determin.
- 2 - SA - Function symmetry
- 8 - Normalize Spin Function
- 10 - Var. Prin.
- 16 - Lithium Energies

Chap. 8 - 25

- 5 - SA - Hamiltonian for HeH^+
- 3 - SA - Why Sec. Det. must = 0
- 6 - SA - Exc. State - N_2 config.
- 3 - SA - Sketch orb. and state what g stands for
- 8 - HF Dissociation Energy of HeH^+