

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

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

$$0 \leq r < \infty$$

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

$$0 \leq \phi \leq 2\pi$$

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

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

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

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

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

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

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

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

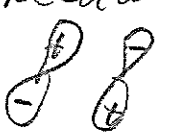
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Solutions

(24) 1. Short Answer Questions

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

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

Antibonding because π atomic orbitals have opposite sign.  - Node between atoms.

- (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**

iii) Neither Sym. nor Antisym.

- (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.

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} \sigma_g 1s(1)\alpha_1 & \sigma_u^* 1s(1)\beta_1 & \pi_g 2p(1)\beta_1 \\ \sigma_g 1s(2)\alpha_2 & \sigma_u^* 1s(2)\beta_2 & \pi_g 2p(2)\beta_2 \\ \sigma_g 1s(3)\alpha_3 & \sigma_u^* 1s(3)\beta_3 & \pi_g 2p(3)\beta_3 \end{vmatrix}$$

There are $3! (6)$ terms.

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 .

13 electrons: $\sigma_{g1s}^2 \sigma_{u1s}^2 \sigma_{g2s}^2 \sigma_{u2s}^2 \pi_{u2p}^4 \sigma_{g2p}^1$
 $BO = \frac{1}{2}(9 - 4) = 2.5$ (vs. $BO = 3$ in N_2)
 N_2^+ has lower frequency due to lower BO

- (4) (e) One variational wavefunction for the helium atom which was discussed in class was: $\phi_1 = A[e^{-Z'(r_1+r_2)}(1 + br_{12})]$, where Z' and b are positive ($Z' > 0$, $b > 0$)

Variational parameters.

Consider a second variational wavefunction: $\phi_2 = A[e^{-Z'(r_1+r_2)}(1 - br_{12})]$, 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.

ϕ_2 has higher energy.
 ϕ_1 has higher ϕ^2 for bigger r_{12} [1 + r_{12}] ← Correlates for e^- com because high value of r_{12}
 ϕ_2 has lower ϕ^2 for bigger r_{12} [1 - r_{12}]

- (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.

Not a violation. The var. prin. predicts lower energy for a given molecule with better basis set. However D_e is the difference of two energies
 $D_e = E(He + H) - E(HeH)$

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

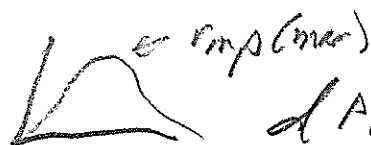
$$R(r) = r^2 e^{-r/3a_0}$$

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).

$$P(r) = B r^2 R^2 = B r^2 [r^2 e^{-r/3a_0}]^2 = B r^6 e^{-2r/3a_0}$$



$$\frac{dP(r)}{dr} = 0 = B \frac{d}{dr} (r^6 e^{-2r/3a_0})$$

$$= B \left[r^6 \frac{d}{dr} e^{-2r/3a_0} + e^{-2r/3a_0} \frac{d}{dr} r^6 \right]$$

$$= B \left[r^6 \left(-\frac{2}{3a_0} \right) e^{-2r/3a_0} + e^{-2r/3a_0} (6r^5) \right]$$

$$= B r^5 e^{-2r/3a_0} \left[-\frac{2}{3a_0} r + 6 \right]$$

//
0

$$-\frac{2}{3a_0} r_{mp} + 6 = 0$$

$$\therefore r_{mp} = 6 \cdot \frac{3a_0}{2} = \boxed{9a_0}$$

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 $\text{Prob}(6a_0 \leq r < \infty)$?

$$\text{Prob}(6a_0 \leq r < \infty) = 1 - \text{Prob}(0 \leq r \leq 6a_0)$$

$$P(r) = Br^6 e^{-2r/3a_0}$$

$$\text{Prob}(0 \leq r \leq 6a_0) = B \int_0^{6a_0} r^6 e^{-2r/3a_0} dr$$

$$= B \left[\int_0^4 \left(\frac{3a_0}{2} x \right)^6 e^{-x} \left(\frac{3a_0}{2} dx \right) \right]$$

$$= B \left(\frac{3a_0}{2} \right)^7 \int_0^4 x^6 e^{-x} dx$$

$$= \frac{1}{720} \left(\frac{2}{3a_0} \right)^7 \left(\frac{3a_0}{2} \right)^7 (79.7) \quad \leftarrow \text{from integral on info sheet}$$

$$= \frac{79.7}{720} = 0.11$$

$$\therefore \text{Prob}(6a_0 \leq r < \infty) = 1 - 0.11$$

$$= \boxed{0.89}$$

$$x = \frac{2r}{3a_0}$$

$$r = \frac{3a_0}{2} x$$

$$dr = \frac{3a_0}{2} dx$$

$$r_0 = 6a_0 \rightarrow$$

$$x_1 = \frac{2}{3a_0}(6a_0) = 4$$

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. $\langle \frac{1}{r^2} \rangle$, for the electron (your answer can be left in terms of a_0).

$$\begin{aligned}
 \langle \frac{1}{r^2} \rangle &= \int_0^\infty \frac{1}{r^2} P(r) dr = \int_0^\infty \frac{1}{r^2} (B r^6 e^{-2r/a_0}) dr \\
 &= B \int_0^\infty r^4 e^{-2r/3a_0} dr \quad \left[\int_0^\infty x^n e^{-kx} = \frac{n!}{k^{n+1}} \right] \\
 &= B \frac{4!}{\left(\frac{2}{3a_0}\right)^5} = \frac{1}{720} \left(\frac{2}{3a_0}\right)^7 \cdot \frac{24}{\left(\frac{2}{3a_0}\right)^5} \\
 &= \frac{1}{30} \left(\frac{2}{3a_0}\right)^2 = \frac{1}{30} \times \frac{4}{9a_0^2} \\
 &= \frac{0.0148}{a_0^2} \approx \boxed{\frac{0.015}{a_0^2}}
 \end{aligned}$$

- (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.**

$$1 = \langle \psi | \psi \rangle = \langle N(1s_a - 1s_b) | N(1s_a - 1s_b) \rangle$$

$$= N^2 [\langle 1s_a | 1s_a \rangle - \langle 1s_a | 1s_b \rangle - \langle 1s_b | 1s_a \rangle + \langle 1s_b | 1s_b \rangle]$$

$$= N^2 [1 - S_{ab} - S_{ab} + 1] = N^2 [2 - 2S_{ab}]$$

$$N = \frac{1}{\sqrt{2 - 2S_{ab}}}$$

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

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

i.e. two times $1s(1)2p(2)$ - three times $2p(1)1s(2)$

Assuming that the individual spatial functions, $1s$ and $2p$ 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.**

$$\begin{aligned}
 1 &= \langle \psi | \psi \rangle = N^2 \langle [2 \cdot 1s(1)2p(2) - 3 \cdot 2p(1)1s(2)] | [2 \cdot 1s(1)2p(2) - 3 \cdot 2p(1)1s(2)] \rangle \\
 &= N^2 [4 \langle 1s(1) | 1s(1) \rangle \langle 2p(2) | 2p(2) \rangle - 6 \langle 1s(1) | 2p(1) \rangle \langle 2p(2) | 1s(2) \rangle \\
 &\quad - 6 \langle 2p(1) | 1s(1) \rangle \langle 1s(2) | 2p(2) \rangle + 9 \langle 2p(1) | 2p(1) \rangle \langle 1s(2) | 1s(2) \rangle] \\
 &= N^2 [4 \times 1 \times 1 - 6(0) - 6(0) + 9 \times 1 \times 1] \\
 1 &= N^2 (4 + 9) = 13 N^2
 \end{aligned}$$

$$N = \frac{1}{\sqrt{13}}$$

- (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.

Find α_{best}

$$\frac{d\langle E \rangle}{d\alpha} = 0 = A - \frac{B}{\alpha^2}$$

$$A = \frac{B}{\alpha^2} \rightarrow \alpha^2 = \frac{B}{A} \rightarrow \alpha_{best} = \sqrt{\frac{B}{A}}$$

$$= \sqrt{\frac{1.2}{1.8}}$$

$$= \sqrt{0.667}$$

$$= 0.816$$

$$\langle E \rangle_{best} = A\alpha_{best} + \frac{B}{\alpha_{best}} - C$$

$$= 1.8(0.816) + \frac{1.2}{0.816} - 3.4$$

$$= \boxed{-0.46 \text{ a.u.}}$$

- (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 $\text{EA}(\text{Be}) = +1.98 \text{ eV}$

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

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{\hbar^2}{2m} \nabla_3^2 - \frac{\hbar^2}{2m} \nabla_4^2 - \frac{4e^2}{4\pi\epsilon_0 r_1} - \frac{4e^2}{4\pi\epsilon_0 r_2} - \frac{4e^2}{4\pi\epsilon_0 r_3} - \frac{4e^2}{4\pi\epsilon_0 r_4} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{14}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} + \frac{e^2}{4\pi\epsilon_0 r_{24}} + \frac{e^2}{4\pi\epsilon_0 r_{34}}$$

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

Need all 4 experimental Ionization Energies

Then $E_{\text{exact}} = E_{\text{exp}} = -\sum_{i=1}^4 I_i$

$= -[I_1 + I_2 + I_3 + I_4]$

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.

Use Koopman's Theorem: $IE \approx -\epsilon_{HOMO}$

Neglect

$$= -(-0.301) \text{ au} \times \frac{27.21 \text{ eV}}{1 \text{ au}}$$

1) relaxation of remaining electron $\approx 8.2 \text{ eV}$

2) difference in correlation energy in Be & Be⁺

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

$$EA = +1.98 \text{ eV} \times \frac{1 \text{ au}}{27.21 \text{ eV}} = 0.0728 \text{ au} \approx 0.073 \text{ au}$$

$$EA \approx E_{HF}(\text{Be}^-) - E_{HF}(\text{Be})$$

$$\therefore E_{HF}(\text{Be}^-) = E_{HF}(\text{Be}) + EA$$

$$= -14.567 + 0.073$$

$$= -14.494 \text{ au}$$

(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.

$$H = \left(-\frac{1}{2}\nabla_1^2 - \frac{3}{r_1} \right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{3}{r_2} \right) + \frac{1}{r_{12}}$$

$$= H_1 + H_2 + \frac{1}{r_{12}}$$

$$\begin{aligned} \langle E \rangle &= \langle \alpha_1 | \alpha_1 \rangle \langle \beta_2 | \beta_2 \rangle \left\langle 1s(1) 2p(2) \left| H_1 + H_2 + \frac{1}{r_{12}} \right| 1s(1) 2p(2) \right\rangle \\ &= \underbrace{\langle 2p(2) | 2p(2) \rangle}_{1} \underbrace{\langle 1s(1) | H_1 | 1s(1) \rangle}_{\epsilon_{1s}} + \underbrace{\langle 1s(1) | 1s(1) \rangle}_{1} \underbrace{\langle 2p(2) | H_2 | 2p(2) \rangle}_{\epsilon_{2p}} \\ &\quad + \underbrace{\left\langle 1s(1) 2p(2) \left| \frac{1}{r_{12}} \right| 1s(1) 2p(2) \right\rangle}_{J_{1s2p}} \\ &= \boxed{\epsilon_{1s} + \epsilon_{2p} + J_{1s2p}} \end{aligned}$$

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

Because we used simple product instead of antisymmetric wave function.