

EXAM INFORMATION

Radial Distribution Function: $P(r) \equiv RDF(r) \equiv Br^2 R(r)^2$, 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

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

$$0 \leq r < \infty$$

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

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

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

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

$$\int_0^3 x^6 e^{-x} dx = 24$$

$$\int_0^6 x^6 e^{-x} dx = 283$$

$$\int_0^{12} x^6 e^{-x} dx = 687$$

$$\int_0^3 x^8 e^{-x} dx = 153$$

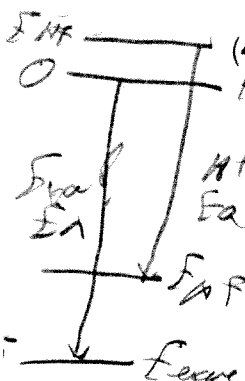
$$\int_0^6 x^8 e^{-x} dx = 6159$$

$$\int_0^{12} x^8 e^{-x} dx = 34070$$

Name

Solutions

(33) 1. Short Answer Questions



- (4) (a) The experimental electron affinity of an oxygen atom is -142 kJ/mol. **Explain** why you would expect the Hartree-Fock estimate of an oxygen atom to be **more or less** negative than the experimental value.

Less negative because the corr. energy of O^- is greater than " " " O .

- (4) (b) Write down the expression for the Exchange Integral $[K_{1s2s}]$ for the exchange interactions between electrons in 1s and 2s orbitals. Use atomic units, and write the integrals in standard double integral form.

$$\int \int \psi_{1s}(1) \psi_{2s}(1) \frac{1}{r_{12}} \psi_{1s}(2) \psi_{2s}(2) d\vec{r}_1 d\vec{r}_2$$

- (5) (c) Write the Hamiltonian for the two electrons in the HeH^+ molecular ion, in SI (MKS) units.

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_{1He}} - \frac{1e^2}{4\pi\epsilon_0 r_{2He}} - \frac{2e^2}{4\pi\epsilon_0 r_{1H}} - \frac{1e^2}{4\pi\epsilon_0 r_{2H}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

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

Symmetric

1. Short Answer Questions (Cont'd.)

- (6) (e) Consider an excited state of the B^+ ion with the configuration: $1s^2 2s^1 3s^1$. A simple product wavefunction for a lithium atom in this configuration is:

$$\psi = 1s(1)\alpha_1 1s(2)\beta_2 2s(3)\beta_3 3s(4)\beta_4$$

Write the **normalized** Slater determinant for the appropriately **antisymmetric** wavefunction with this configuration.

$4! = 24$
 24 terms

$4! = \frac{1}{\sqrt{24}}$

$$\begin{vmatrix} 1s(1)\alpha_1 & 1s(1)\beta_1 & 2s(1)\beta_1 & 3s(1)\beta_1 \\ 1s(2)\alpha_2 & 1s(2)\beta_2 & 2s(2)\beta_2 & 3s(2)\beta_2 \\ 1s(3)\alpha_3 & 1s(3)\beta_3 & 2s(3)\beta_3 & 3s(3)\beta_3 \\ 1s(4)\alpha_4 & 1s(4)\beta_4 & 2s(4)\beta_4 & 3s(4)\beta_4 \end{vmatrix}$$

- (6) (f) Write the complete electron configuration and give the bond order of the N_2 molecule in the **lowest excited electronic state**.

$14 = 6 + 8$

Is the bond length in the excited state higher or lower than the ground state vibrational frequency (explain your reasoning)?

Bond length

$$(\pi_g^*)^2 (\pi_u^*)^2 (\pi_g^*)^2 (\pi_u^*)^2 (\pi_u^*)^2 (\pi_g^*)^2 (\pi_g^*)^2 (\pi_g^*)^2$$

$BO = \frac{1}{2}(9 - 5) = 2$ vs $BO = 3$ in ground state

The excited state bond length is higher than the ground state because the BO is lower

- (3) (g) As discussed in class, the Secular Determinant is the determinant of the coefficients of the homogeneous linear equations which result from use of the Variational Theorem to minimize the energy.

Explain why the Secular Determinant must be equal to zero.

Only if the Sec. Det. = 0 do the homogeneous equations have a non-trivial solution ($c_i \neq 0$)

- (3) (h) Sketch the $\pi_g^* 2p$ orbital in a homonuclear diatomic molecule **AND** state what the letter, "g", stands for.



$g = \text{symm. w.r.t inversion}$

For #2 -#3: The energy levels of hydrogenlike atoms are given by:

$$E_n = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{n^2} = -\frac{1}{2} (2625 \text{ kJ}) \frac{Z^2}{n^2}$$

Note: Both questions use the above formula, but are not related to each other.

- (5) 2. Calculate the wavelength of the emitted light (in nm) when an electron in the $n = 5$ level of the Li^{2+} ion drops to the $n = 3$ level.

$Z=3$

$$\Delta E = E_{\text{photon}} = E_5 - E_3 = -\frac{1}{2} (2625 \text{ kJ}) \frac{3^2}{5^2} - \left(-\frac{1}{2} (2625 \text{ kJ}) \cdot \frac{3^2}{3^2} \right)$$

$$= 840 \text{ kJ} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23}} = 1.40 \times 10^{-18} \text{ J}$$

$$E_{\text{photon}} = h\nu = hc/\lambda \rightarrow \lambda = \frac{hc}{E_{\text{photon}}} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s}) (3 \times 10^8 \text{ m/s})}{1.40 \times 10^{-18} \text{ J}}$$

$$= 1.43 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = \boxed{143 \text{ nm}}$$

Homolytic

- (8) 3. The Hartree-Fock energy of HeH^+ is -2.931 a.u.

Calculate the Dissociation Energy, D_e , of HeH^+ , in electron volts (eV).

$$\text{HeH}^+ \rightarrow \text{He}^+ + \text{H} \quad E_{\text{H}} = -\frac{1}{2} (2625 \text{ kJ}) \frac{1^2}{1^2} = -1312.5 \text{ kJ}$$

$$E_{\text{He}} = -\frac{1}{2} (2625) \frac{2^2}{1^2} = -5250 \text{ kJ}$$

$$E(\text{He}^+ + \text{H}) = -6563 \text{ kJ} \times \frac{1 \text{ a.u.}}{2625 \text{ kJ}} \times \frac{27.21 \text{ eV}}{1 \text{ a.u.}}$$

$$= -68.03 \text{ eV}$$

$$E(\text{HeH}^+) = -2.931 \text{ a.u.} \times \frac{27.21 \text{ eV}}{1 \text{ a.u.}} = -79.75 \text{ eV}$$

$$D_e = E(\text{He}^+ + \text{H}) - E(\text{HeH}^+) = -68.03 - (-79.75)$$

$$\approx \boxed{11.7 \text{ eV}}$$

(20) 4. One of the hydrogen atom wavefunctions is:

$$\psi = Ar^3 e^{-r/4a_0} \sin(\theta) e^{i\phi}$$

(10) (a) Set up the expression to calculate the average value of $\cos^2(\theta)$, $\langle \cos^2(\theta) \rangle$. Your answer should be of the form: $\langle \cos^2(\theta) \rangle = A^2 I_R I_\theta I_\phi$, where I_R , I_θ , and I_ϕ are integrals over dr , $d\theta$ and $d\phi$.

Notes: (1) It is **NOT** necessary for you to evaluate the integrals.
 (2) The volume element and integration limits in spherical polar coordinates are given in the information page

$$\begin{aligned} \langle \cos^2 \theta \rangle &= \iiint \psi^* \psi \cos^2 \theta dV \\ &= \iiint (Ar^3 e^{-r/4a_0} \sin \theta e^{-i\phi}) (Ar^3 e^{-r/4a_0} \sin \theta e^{i\phi}) \cos^2 \theta (r^2 \sin \theta dr d\theta d\phi) \\ &= A^2 \iiint (r^6 e^{-r/2a_0} \sin^2 \theta) (\cos^2 \theta) (r^2 \sin \theta dr d\theta d\phi) \\ &= \boxed{A^2 \int_0^\infty r^8 e^{-r/2a_0} dr \int_0^\pi \sin^3 \theta \cos^2 \theta d\theta \int_0^{2\pi} d\phi} \end{aligned}$$

4. (Cont'd)

For part (b), use the Radial Distribution Function for this wavefunction, which is given on the information page.

For this problem, the normalization constant of the RDF is: $B = \frac{1}{40320} \left(\frac{1}{2a_0} \right)^9$

(10) (b) Calculate the probability that the distance of the electron from the nucleus is between $6a_0$ and $12a_0$. You should get a numerical value for this probability.

$$P(r) = B r^2 / |R|^2 = B r^2 (r^6 e^{-r/2a_0}) = B r^8 e^{-r/2a_0}$$

$$x = \frac{r}{2a_0} \rightarrow r = 2a_0 x \quad dr = 2a_0 dx$$

$$\begin{aligned} r_1 &= 6a_0 \\ x &= \frac{6a_0}{2a_0} = 3 \\ r_2 &= 12a_0 \\ x &= \frac{12a_0}{2a_0} = 6 \end{aligned}$$

$$P_{\text{prob}}(6a_0 \leq r \leq 12a_0) = B \int_{6a_0}^{12a_0} r^8 e^{-r/2a_0} dr = B \int_3^6 (2a_0 x)^8 e^{-x/2a_0} (2a_0) dx$$

$$= B (2a_0)^9 \int_3^6 x^8 e^{-x} dx$$

$$= B (2a_0)^9 \left[\int_0^6 x^8 e^{-x} dx - \int_0^3 x^8 e^{-x} dx \right]$$

$$= \frac{1}{40320} \left(\frac{1}{2a_0} \right)^2 (2a_0)^9 [6159 - 153]$$

$$= \frac{6159 - 153}{40320}$$

$$= \frac{6006}{40320} = 0.149 \approx \boxed{0.15}$$

From numerical integral
or into B.

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

$$\psi = N [1s(1)2s(2)] \cdot [3 \cdot \alpha_1 \beta_2 + 2 \cdot \beta_1 \alpha_2]$$

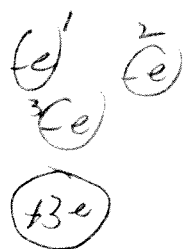
Assuming that the individual spatial functions, 1s and 2s are individually normalized, determine the normalization constant, N, of the complete wavefunction above.

Show your work to receive credit.

$$\begin{aligned} 1 &= \langle \psi | \psi \rangle = N^2 \langle 1s(1) | 1s(1) \rangle \langle 2s(2) | 2s(2) \rangle \langle 3\alpha_1\beta_2 + 2\beta_1\alpha_2 | 3\alpha_1\beta_2 + 2\beta_1\alpha_2 \rangle \\ 1 &= N^2 [9 \langle \alpha_1 | \alpha_1 \rangle \langle \beta_2 | \beta_2 \rangle + 6 \langle \alpha_1 | \beta_2 \rangle \langle \beta_2 | \alpha_1 \rangle + 2 \langle \beta_1 | \alpha_1 \rangle \langle \alpha_2 | \beta_2 \rangle + 4 \langle \beta_1 | \beta_1 \rangle \langle \alpha_2 | \alpha_2 \rangle] \\ &= N^2 [9(1) + 6(0) + 2(0) + 4(1)] \\ 1 &= 13 N^2 \rightarrow N = \frac{1}{\sqrt{13}} \end{aligned}$$

- (16) 6. The three experimental ionization energies of the lithium atom are: $IE_1=520.$ kJ/mol, $IE_2=7300.$ kJ/mol, $IE_3=11,810$ kJ/mol. The correlation energy of the lithium atom is -120.8 kJ/mol. The Hartree-Fock energies of the Lithium +1 and -1 ions are: $E_{HF}(Li^+) = -7.236$ au and $E_{HF}(Li^-) = -7.477$ au.

- (4) a) Write the Hamiltonian for the lithium atom in SI Units.



$$\begin{aligned} H &= -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{\hbar^2}{2m} \nabla_3^2 \\ &\quad - \frac{3e^2}{4\pi\epsilon_0 r_1} - \frac{3e^2}{4\pi\epsilon_0 r_2} - \frac{3e^2}{4\pi\epsilon_0 r_3} \\ &\quad + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{13}} + \frac{e^2}{4\pi\epsilon_0 r_{23}} \end{aligned}$$

6. (Cont'd)

- (6) b) Use the data at the beginning of the problem to calculate the Hartree-Fock estimate of the first ionization energy, in kJ/mol.

$$E_{\text{exact}} = -I_1 - I_2 - I_3 = -520 - 7300 - 11,810 = -19630 \text{ kJ/mol}$$

$$E_{\text{corr}} = -120.8 \text{ kJ/mol}$$

$$E_{\text{exact}}(\text{Li}) = E_{\text{HF}}(\text{Li}) + E_{\text{corr}}(\text{Li})$$

$$\text{or } E_{\text{HF}}(\text{Li}) = E_{\text{exact}}(\text{Li}) - E_{\text{corr}}(\text{Li}) = -19630 - (-120.8) = -19509.2 \text{ kJ/mol}$$

$$E_{\text{HF}}(\text{Li}^+) = -2.236 \text{ au} \times \frac{2625 \text{ kJ/mol}}{1 \text{ au}} = -18994.5 \text{ kJ/mol}$$

$$I_{\text{HF}} = E_{\text{HF}}(\text{Li}^+) - E_{\text{HF}}(\text{Li})$$

$$= -18994.5 - (-19509.2) = 514.7$$

$$\approx \boxed{515 \text{ kJ/mol}}$$

- (6) c) Use the data at the beginning of the problem to calculate the Hartree-Fock estimate of the electron affinity, in kJ/mol.

$$E_{\text{HF}}(\text{Li}) = -19509.2 \text{ kJ/mol (from (b))}$$

$$E_{\text{HF}}(\text{Li}^-) = -2.477 \text{ au} \times \frac{2625 \text{ kJ/mol}}{1 \text{ au}} = -19,627.1 \text{ kJ/mol}$$

$$EA_{\text{HF}} = E_{\text{HF}}(\text{Li}^-) - E_{\text{HF}}(\text{Li})$$

$$= -19,627.1 - (-19,509.2)$$

$$= -117.9 \text{ kJ/mol}$$

$$\approx \boxed{-118 \text{ kJ/mol}}$$

- (10) 7. Consider a trial variational wavefunction for a hypothetical multielectron atom, which is of the form: $\varphi = \varphi(\alpha)$, where α is a positive Variational parameter (i.e. $\alpha > 0$). It was found that the expectation value for the energy, in a.u., using this trial wavefunction is:

$$\langle E \rangle = \langle \varphi | H | \varphi \rangle = 5\alpha^3 - 6\alpha - 2$$

Calculate the best value of the helium atom energy which can be obtained using this trial wavefunction.

$$\frac{d\langle E \rangle}{d\alpha} = 0 = 15\alpha^2 - 6 + 0$$

$$\alpha^2 = \frac{6}{15} = 0.40$$

$$\alpha = \sqrt{0.40} = 0.632$$

$$\begin{aligned}\langle E \rangle &= 5\alpha^3 - 6\alpha - 2 \\ &= 5(0.632)^3 - 6(0.632) - 2 \\ &= \boxed{-4.53 \text{ a.u.}}\end{aligned}$$