EXAM INFORMATION

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

Order of Orbital Energies: Homonuclear Diatomic Molecules
\( \sigma_g \, 1s < \sigma_u \, 1s < \sigma_g \, 2s < \pi_u \, 2s < \sigma_g \, 2p < \pi_g \, 2p < \sigma_u \, 2p \)

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:
\[
\begin{align*}
 h &= 6.63 \times 10^{-34} \ \text{J} \cdot \text{s} \\
 \hbar &= h/2\pi = 1.05 \times 10^{-34} \ \text{J} \cdot \text{s} \\
 k &= 1.38 \times 10^{-23} \ \text{J/K} \\
 c &= 3.00 \times 10^8 \ \text{m/s} = 3.00 \times 10^{10} \ \text{m/s} \\
 N_A &= 6.02 \times 10^{23} \ \text{mol}^{-1} \\
 m_e &= 9.10 \times 10^{-31} \ \text{kg} \\
 m_p &= 1.67 \times 10^{-27} \ \text{kg} \\
 1 \ \text{Å} &= 10^{-10} \ \text{m} \\
 1 \ \text{eV} &= 1.60 \times 10^{-19} \ \text{J} \\
 1 \ \text{amu} &= 1.66 \times 10^{-27} \ \text{kg} \\
 1 \ \text{J} &= 1 \ \text{kg} \cdot \text{m}^2/\text{s}^2 \\
 1 \ \text{N} &= 1 \ \text{kg} \cdot \text{m/s}^2 \\
 1 \ \text{au} \ (\text{hartree}) &= 2625 \ \text{kJ/mol} \\
 1 \ \text{au} \ (\text{hartree}) &= 27.21 \ \text{eV}
\end{align*}
\]

INTEGRALS
\[
\begin{align*}
 \int_0^\infty x^n e^{-ax} \, dx &= \frac{n!}{a^{n+1}} \\
 \int_0^4 x^4 e^{-x} \, dx &= 8.91 \\
 \int_0^6 x^4 e^{-x} \, dx &= 17.16 \\
 \int_0^9 x^4 e^{-x} \, dx &= 22.68 \\
 \int_0^4 x^6 e^{-x} \, dx &= 79.7 \\
 \int_0^6 x^6 e^{-x} \, dx &= 283.5 \\
 \int_0^9 x^6 e^{-x} \, dx &= 571.1
\end{align*}
\]
1. **Short Answer Questions**

(a) One of the \( \pi \) molecular orbitals in the diatomic molecule, \( C_2 \), is given approximately by:
\[
\varphi = 0.82(2p_x) - 0.82(2p_y)
\]
Is this a bonding or antibonding orbital? **WHY?**

(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**

(c) Consider an excited state wavefunction for \( He_2^+ \) ion. The simple product wavefunction is
\[
\begin{align*}
\sigma_g^+ & 1s(1)\alpha_i \cdot \sigma_u^+ 1s(2)\beta_i \cdot \pi_g^+ 2p(3)\beta_i
\end{align*}
\]
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:  
\[ \phi_1 = A \left[ e^{-Z(r_1+r_2)} \left( 1 + br_{12} \right) \right], \]  where $Z'$ and $b$ are positive ($Z'>0$, $b>0$) Variational parameters.
Consider a second variational wavefunction:  
\[ \phi_2 = A \left[ e^{-Z'(r_1+r_2)} \left( 1 - br_{12} \right) \right], \]  where $Z'$ and $b$ are positive ($Z'>0$, $b>0$).

Explain, on the basis of electron correlation whether you would expect $\phi_2$ to yield a higher or lower expectation value for the energy than $\phi_1$.  
**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.**
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 \( r^2 \) \( (f \propto \frac{1}{r^2}) \). Therefore the average of \( \frac{1}{r^2} \) can be used to determine the average force between the electron and proton.

Calculate the average value of \( \frac{1}{r^2} \); i.e. \( \left\langle \frac{1}{r^2} \right\rangle \), for the electron (your answer can be left in terms of \( a_0 \)).
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). \textbf{You must show your work for credit.}
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.**
5. Consider a hypothetical trial variational wavefunction for the ground state of the hydrogen atom, \( \varphi = \varphi(\alpha) \), where \( \alpha \) 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:

\[
\langle E \rangle = \langle \varphi | H | \varphi \rangle = A \alpha + \frac{B}{\alpha} - C ,
\]

where \( A = 1.8 \), \( B = 1.2 \) 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.
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 \(-4.709 \text{ au}\) and \(-0.301 \text{ au}\).

The electron affinity of Be is \( E_{\text{A}}(\text{Be}) = 1.98 \text{ eV} \). 

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

(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, $E_{HF}(\text{Be}^-)$, in au (hartrees).
The Hamiltonian for the Li\(^{+1}\) ion is:

\[ H = -\frac{1}{2} \nabla_i^2 - \frac{1}{2} \nabla_j^2 - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{r_{12}} \]

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:

\[ \psi = 1s(1\alpha) \cdot 2p(2\beta) \]

Use this product wavefunction to calculate the energy of a Li\(^{+1}\) ion in this configuration in terms of \(\varepsilon_{1s}, \varepsilon_{2p}\) 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.

b) Why doesn't your answer include an exchange integral, \(K_{1s2p}\)?
Material - 2016

Chap. 6 - 26
26 - RDF: $P(>=6\text{ao}) + \text{rmp} + \langle 1/r^2 \rangle$

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 - $uv(a_{1b2}-b_{1a2})$ - 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 pi 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 - $<\cos^2\theta>$ and RDF probability from 6 ao to 12 ao
5 - transition wavelength in Li2+

Chap. 7 - 50
4 - SA - EA of Oxygen
4 - SA - Exchange Integral
6 - SA - Excited slate 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 - N2 config.
3 - SA - Sketch orb. and state what g stands for
8 - HF Dissociation Energy of HeH+