

EXAM INFORMATION

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

p² Operator: $\hat{p}^2 = -\hbar^2 \frac{d^2}{dx^2}$

Heisenberg Uncertainty Principle: $\sigma_x \sigma_p \geq \frac{\hbar}{2}$

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

Particle in a Box

Energy Levels: $E_n = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3 \dots$

Harmonic Oscillator

Energy Levels and Frequency: $E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad n = 0, 1, 2, \dots \quad \omega = \sqrt{\frac{k}{\mu}} = 2\pi\nu = 2\pi c\tilde{\nu} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Rigid Rotor

Energy Levels: $E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) = hc\tilde{B}J(J+1) \quad \tilde{B} = \frac{h}{8\pi^2 I c} \quad J = 0, 1, 2, \dots \quad g_J = 2J + 1$

Moment of Inertia: Linear Polyatomic: $I = \sum m_i r_i^2$ **Diatomic:** $I = \mu r^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Quadratic Equation: $ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Thermodynamics: $\Delta G^0 = -RT \ln(K_{eq}) = \Delta H^0 - T\Delta S^0$

EXAM INFORMATION (CONT'D)

π Electron Charge: $q_{\mu} \equiv \sum_i^{orbs} n_i c_{i\mu}^2$

π Bond Order: $p_{\mu\nu} \equiv \sum_i^{orbs} n_i c_{i\mu} c_{i\nu}$

Transition Moment: $M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$

$$M_{0i}^x = e \langle \Psi_i | x | \Psi_0 \rangle$$

$$M_{0i}^y = e \langle \Psi_i | y | \Psi_0 \rangle$$

$$M_{0i}^z = e \langle \Psi_i | z | \Psi_0 \rangle$$

C_{2v} Character Table

C_{2v}	E	C₂	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A ₁	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	R _z	xy
B ₁	1	-1	1	-1	x, R _y	xz
B ₂	1	-1	-1	1	y, R _x	yz

Constants and Conversions:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PERIODIC TABLE OF THE ELEMENTS

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.008	2 He 4.003	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18	11 Na 23.00	12 Mg 24.30	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	72 Hf 178.5
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)	104 Rf (261)
101 Db (262)	102 Sg (263)	103 Bh (262)	104 Hs (265)	105 Ir 192.2	106 Os 190.2	107 Pt 195.1	108 Au 197.0	109 Hg 200.6	110 Tl 204.4	111 Pb 207.2	112 Bi 209.0	113 Po (209)	114 At (210)	115 Rn (222)	116 Fr (223)	117 Ac (224)	118 Th (226)

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Lanthanide series

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)

Actinide series

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Name _____

If you wish to have your final exam and course grade posted on the Web site, please provide me with a four (4) digit number which will be the ID number for your grade.

Four (4) digit number for posting.

- (05) 1. The calculated **Hartree-Fock (HF)** value of the ionization energy of a nitrogen atom is 1452 kJ/mol. **EXPLAIN** why you would expect the exact experimental value of the ionization energy to be **higher or lower** than the Hartree-Fock value?

- (06) 2. Calculate the value of the commutator, $\left[\frac{d}{dx}, \frac{d}{dx} + x^2 \right]$

- (15) 3. Consider a particle in a one dimensional box with the approximate ground state wavefunction:

$$\psi = Ax^2(a-x) \quad 0 \leq x \leq a$$

$$\psi = 0 \quad x < 0, x > a$$

Determine the normalization constant, A, **and** the probability that the particle's position will be between 0 and $a/2$.

Note: You should end up with a numerical answer for the probability.

- (15) 4. The C $\equiv$ C and C-H bond lengths in the linear molecule, acetylene [H- $^{12}\text{C}\equiv^{12}\text{C}$ -H], are 1.20 Å and 1.06 Å, respectively. Assume that the masses of the H and ^{12}C atoms are 1.00 and 12.00.

The selection rule for rotational Spookman spectra is $\Delta J = +4$

Calculate the frequencies (**in cm^{-1}**) of the first two lines in the rotational Spookman spectrum of acetylene.

(20) 5. The Radial part of a hypothetical hydrogen atom wavefunction is::

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

(10) (a) Calculate the normalization constant, B, of the Radial Distribution Function.
Your answer should be in terms of a_0 .

5. (Cont'd).

(10) (b) The average Potential Energy (V) of attraction between an electron and proton in a hydrogen atom is given by:

$$\langle V \rangle = \left\langle -\frac{e^2}{4\pi\epsilon_0 r} \right\rangle$$

Use your normalized Radial Distribution Function to determine $\langle V \rangle$

You should simplify your answer as much as possible, but can leave it in terms of e , ϵ_0 , π and a_0

- (20) 6. The bonding in Hydrogen Iodide (HI) can be described by a two orbital interaction between the 1s orbital on Hydrogen and the 5p orbital on Iodine. The Hamiltonian matrix elements (and overlap) are:

$$H_{HH} = -14. \text{ eV} \quad H_{II} = -10. \text{ eV} \quad H_{HI} = -3. \text{ eV} \quad S_{HH} = 0$$

Assume that the molecular wavefunction is: $\psi = c_H 1s_H + c_I 5p_I$

- (8) a) Set up the Secular Determinant and solve for the energy of the **Anti-Bonding** Orbital.

Note: In case you need a reminder, the quadratic equation and its solutions is given on the information sheet.

6. (Cont'd)

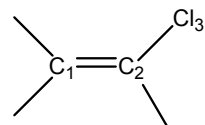
- (8) b) Use your answer in part (a) to calculate the coefficients, c_H and c_I , in the **Normalized anti-bonding** orbital.

Note: If you don't like your answer for part (a), assume that $E_{\text{antibond}} = -8.0 \text{ eV}$ (not the right answer) to work this part.

- (4) c) Assume for this part that the bonding orbital is: $\psi = N[(0.5) \cdot 1s_H + (0.9) \cdot 5p_I]$
What fraction of the charge of an electron in the bonding orbital is on the Iodine atom?

- (16) 7. Consider the chloroethene molecule (on right).
The Secular Determinant is:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 0.4 \\ 0 & 0.4 & x + 2.0 \end{vmatrix} = 0 \quad \text{where } x = \frac{\alpha - E}{\beta}$$



The two lowest energy solutions to the Secular Determinant are $x_1 = -2.10$ and $x_2 = -0.93$. Note: The Cl atom contributes two (2) electrons to the π system.

- (10) a) The normalized wavefunction corresponding to x_1 is:
 $\phi_1 = 0.115\chi_1 + 0.241\chi_2 + 0.964\chi_3$. [I'm giving this for use in parts (b) and (c)]

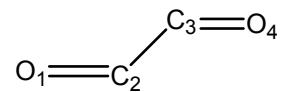
Determine the **normalized** molecular orbital, ϕ_2 , corresponding to x_2 , as a linear combination of the basis functions, χ_1 , χ_2 and χ_3 (χ_3 is on Cl).

7. (Cont'd)

(3) b) Determine the π electron charge on C_2 .

(3) c) Determine the π bond order, between C_2 and C_3 [P₂₃].

(08) 8. Consider the molecule, ethanedial (right)



The oxygen Hückel parameters are: $\alpha_o = \alpha + \beta$
 $\beta_o = 0.8\beta$

Write the Secular Determinant in terms of (i) α , β and E , (ii) $x [=(\alpha-E)/\beta]$

- (8) 9. Consider a particle in a two dimensional box of length $a \times b$, where $b = \sqrt{2} a$

Draw a diagram containing the lowest 6 energy **levels** of a particle in this two dimensional box. Put your answer in units of h^2/ma^2 .

Note: Give the set(s) of quantum numbers corresponding to each level

- (15) 10. The data in the table to the right was obtained from QM studies at 100°C.

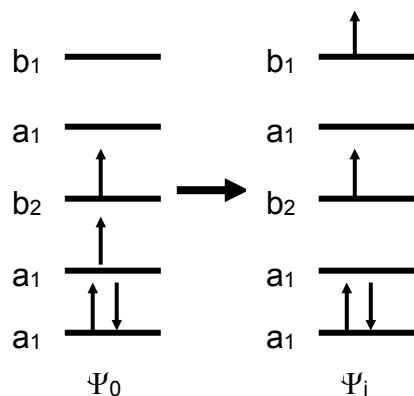
Molec.	E(el) au (hart)	H ⁰ au (hart)	S ⁰ J/mol-K
N ₂ O ₄	-409.331	-409.298	325.5
NO ₂	-204.652	-204.638	253.3

- (6) a) What 3 “corrections” are made to the QM electronic energy to determine the enthalpy in the table?

- (9) b) Calculate the equilibrium constant for the reaction, N₂O₄(g) ↔ 2 NO₂(g) at 100 °C.

- (8) 11. Consider a hypothetical AH₂ molecule with C_{2v} symmetry and a triplet ground state electronic configuration: (a₁)²(a₁)¹(b₂)¹

For the electronic transition below, show whether or not the transition is allowed, and if it is allowed, is it polarized **parallel** or **perpendicular** to the principal axis. **You MUST show your work to receive credit!!**



(18) 12. **Quantum Mechanics Basis Sets and Methods**

(3) (a) In the basis set, 4-21G (aka STO-4-21G), what does each number stand for?

(3) (b) In the CCSD(T) method, what does each letter stand for?

12. (Cont'd)

- (3) (c) Describe what it means to perform a Quantum Mechanical Calculation at the CISD/6-311+G(d,p)//HF/6-31G(d) level. Why is this an acceptable approach?
- (9) (d) Consider using a 6-31++G(2df,p) basis for a Quantum Mechanical calculation on HCP. Describe the types and numbers of STOs that are used on each of the three atoms (H, C, and P).