

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: $\Delta G^0 = -RT \ln(K_{eq}) = \Delta H^0 - T\Delta S^0$
This equation is not needed on this year's exam

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_{2h} Character Table

C _{2h}	E	C ₂	i	σ_h	
A _g	1	1	1	1	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	xz, yz
A _u	1	1	-1	-1	z
B _u	1	-1	-1	1	x, y

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 hartree (au) = 2625 kJ/mol

PERIODIC TABLE OF THE ELEMENTS

PERIODIC TABLE OF THE ELEMENTS

Key

1 H 1.008	Atomic Number Symbol Atomic Mass	
------------------------	--	--

18
VIIIA

2
He
4.003

17
VIIA

16
VIA

15
VA

14
IVA

13
IIIA

12
IIB

11
IB

10
VIII

9
VIII

8
VIII

7
VIIB

6
VIB

5
VB

4
IVB

3
IIIB

2
IIA

1
IA

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

73
Ta
180.9

74
W
183.8

75
Re
186.2

76
Os
190.2

77
Ir
192.2

78
Pt
195.1

79
Au
197.0

80
Hg
200.6

81
Tl
204.4

82
Pb
207.2

83
Bi
209.0

84
Po
(209)

85
At
(210)

86
Rn
(222)

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)

Lanthanide series

Actinide series

Approved by the I.U.P.A.C. Council in Geneva, August 30, 1997

Copyright © September • 1997 Educational Innovations, Inc.

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.

(09) 1. Short Answer (No explanation required)

(a) True/False: The derivative, $d\psi/dx$, must be continuous at boundaries in which the potential energy is finite (i.e. $V < \infty$).

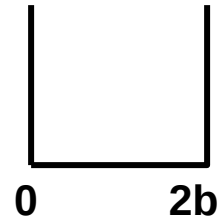
(b) Is the operator d^2/dx^2 Hermitian?

(c) Is the function, $Ae^{-\beta x}$, an Eigenfunction of the $\hat{p}^2$ operator?

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

- (12) 3. Consider a particle in a box, defined by the potential

$$\begin{aligned} V(x) &= 0 & 0 \leq x \leq 2b \\ V(x) &\rightarrow \infty & x < 0, x > 2b \end{aligned}$$



A suitable normalized wavefunction for this particle is: $\psi = A[x^2 - 2bx]$, $A = \sqrt{\frac{15}{16b^5}}$

Calculate the expectation value for the kinetic energy, $\left\langle \frac{p^2}{2m} \right\rangle$,

as a function of $\hbar$, b and m

(15) 4. The first two lines in the rotational Raman spectrum ($\Delta J = +2$) of the linear molecule SiO_2 [$^{16}\text{O}=\text{Si}=\text{O}$] are found at (1) 0.936 cm^{-1} , and (2) 1.560 cm^{-1} .

(5) a) Calculate the frequency (in cm^{-1}) of the **fourth (4th.)** line in the rotational Mookster Spectrum of SiO_2 . The selection rule for the Mookster Spectrum is $\Delta J = +3$

(10) b) Calculate the $\text{Si}=\text{O}$ bond length, in $\text{\AA}$.

(20) 5. The radial portion of one of the wavefunctions of the He^+ ion is:

$$R(r) = re^{\frac{-r}{a_0}}$$

(10) (a) Calculate the **normalized** radial distribution function [RDF(r) = P(r)] for an electron with this wavefunction (i.e. write the RDF and calculate the Normalization Constant, B).

Note: Your value for B should be a function of a_0

#5 Cont'd

(10) (b) The potential energy between the electron and the helium nucleus is given by:

$$V = -\frac{2e^2}{4\pi\epsilon_0 r}$$

Calculate the **average** value of the potential energy between the electron and nucleus.

You should leave your answer in terms of e , $4\pi\epsilon_0$, and a_0 .

- (8) 6. Consider a particle in a two dimensional box of length $a \times b$, where $b = \frac{a}{\sqrt{2}}$. Draw a table (or diagram) containing the lowest 5 energy levels of a particle in a two dimensional box of dimensions $a \times \frac{a}{\sqrt{2}}$.

Put the energies in units of $\frac{h^2}{ma^2}$ and show the set of quantum numbers corresponding to each level

- (6) 7. The three experimental ionization energies of the lithium atom are: $IE_1=5.39$ eV, $IE_2=75.66$ eV, $IE_3=122.40$ eV.

The correlation energy of the lithium atom is -0.046 au.

The Hartree-Fock energy of the Lithium +1 ions is: $E_{HF}(Li^+) = -7.236$ au

Use this data to determine the **Hartree-Fock estimate** of the first ionization energy of Li, **in eV**.

Note: It should be similar in magnitude, but not the same, as the experimental ionization energy (5.39 eV).

- (20) 8. The bonding in Lithium Hydride (LiH) can be described by a two orbital interaction between the 2s orbital on Lithium and the 1s orbital on Hydrogen. The Hamiltonian matrix elements (and overlap) are:

$$H_{LiLi} = -8 \text{ eV} \quad H_{HH} = -14 \text{ eV} \quad H_{LiH} = -4.0 \text{ eV} \quad S_{LiH} = 0$$

Assume that the molecular wavefunction is: $\psi = c_{Li} 2s_{Li} + c_H 1s_H$

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

8. Cont'd.

- (8) b) Use your answer in part (a) to calculate the **normalized** coefficients, c_H and c_{Li} , in the bonding orbital. Be sure to normalize the orbital.

Note: If you don't like your answer for part (a), assume that $E_{\text{bond}} = -20 \text{ eV}$ (not the right answer) to work this part.

- (4) c) Assume for this part that the antibonding orbital is: $\psi = N[0.65 \cdot 2s_{Li} + 0.35 \cdot 1s_H]$

What fraction of the charge of an electron in the antibonding orbital is on the Lithium atom?

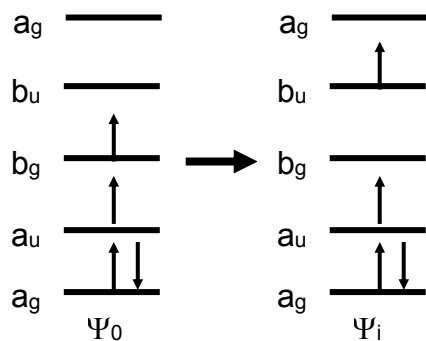
(18) 9. **QM Methods and Basis Sets**

- (3) (a) In the CISD(T) method, what does each letter stand for?
- (3) (b) Consider the 4-31G (aka STO-4-31G) basis set. What does each number stand for?
- (9) (c) Consider using the 6-311+G(d,2p) to perform a Quantum Mechanical calculation on the HSF molecule. Describe the types and numbers of STOs that are used on each of the 3 atoms (H, F and S)
- (3) (d) Why is the Hartree-Fock method called a "Self-Consistent" (SCF) method.

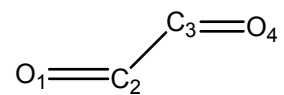
- (08) 10. Consider the electronic transition below, arising from the lowest triplet state of (E)-1,2-dichloroethene [C_{2h} symmetry], ... $(a_g)^2(a_u)^1(b_g)^1$ [diagram below and character table in information section at top of exam].

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) 11. Consider the molecule, ethanedial (right)



The oxygen Hückel parameters are: $\alpha_{\text{O}} = \alpha + \beta$

$$\beta_{\text{O}} = 0.8\beta$$

Notes: (1) H atoms on C_2 and C_3 are not shown
(2) Each O atom contributes one (1) electron to the π -system

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

11. Cont'd.

For Parts b-d: The two occupied MOs and their energies are:

$$\begin{aligned}\varphi_1 &= 0.50 \chi_1 + 0.50 \chi_2 + 0.50 \chi_3 + 0.50 \chi_4 & E_1 &= \alpha + 1.80 \beta \\ \varphi_2 &= 0.67 \chi_1 + 0.23 \chi_2 - 0.23 \chi_3 - 0.67 \chi_4 & E_2 &= \alpha + 1.28 \beta\end{aligned}$$

(3) b) Determine the π electron charge on O₁.

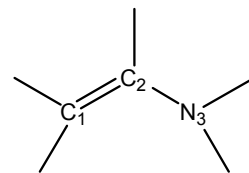
(3) c) Determine the O₁-C₂ bond order (P_{12}).

(4) d) The energy of the occupied π orbital in formaldehyde (H₂C=O) is $E_1 = \alpha + 1.44\beta$. Calculate the π Delocalization Energy in Ethanedial.

(10) 12. Consider the ethenamine molecule (on right).

The Secular Determinant is:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 0.8 \\ 0 & 0.8 & x+1.5 \end{vmatrix} = 0 \quad \text{where } x = \frac{\alpha - E}{\beta}$$



The two solutions to the Secular Determinant corresponding to occupied orbitals are $x_1 = -1.95$ and $x_2 = -0.68$.

Determine the **normalized** Anti-bonding Molecular Orbital, ϕ_2 , corresponding to $x_2 = -0.63$ as a linear combination of the basis functions, χ_1 , χ_2 and χ_3 (χ_3 is on the nitrogen).