

Name: KEY

Chemistry 56
Test 2
April 3, 2003

Instructions:

1. Write your name in the space above and on the backs of the other pages.
2. You may use both sides of an 8.5" x 11" sheet of paper filled with information as a reference. Please turn this sheet in when you turn in the test.
3. You are not allowed to use any other references.
4. You are allowed to use a calculator, but only for numerical calculations.
5. Your exam booklet should have **eight** pages total, with questions on pages 2-7, and a periodic table and other reference information on p. 8.
6. You have two hours and thirty minutes to work on this exam.

<u>Possible Points</u>	<u>Your Score</u>
Question 1 (10)	
Question 2 (30)	
Question 3, Page 4 (10)	
Question 3, Page 5 (20)	
Question 4 (8)	
Question 5 (22)	
Total (100)	

1. (10 points) Consider the following predictions of quantum mechanics: (a) In an one-electron atom or ion, for a given principal quantum n , increasing the electron's angular momentum does not increase the electron's energy. (b) However, when an atom or ion has more than one electron, increasing an electron's angular momentum does increase that electron's energy. Explain both (a) and (b) qualitatively.

(a) For a given n , $\uparrow l \Rightarrow$ more rotational KE, but also $\downarrow \#$ of radial nodes. I.e., the linear (radial KE) decreases \Rightarrow no overall change in E

(b). Now, $\uparrow l \Rightarrow e^-$ doesn't penetrate to the nucleus as well \Rightarrow ~~more~~ shielded from the nucleus \Rightarrow higher potential $E \Rightarrow$ higher E .

-4 (per part) something

\rightarrow or argument reversed

-3 no mention of rotational KE

-2 no mention of shielding

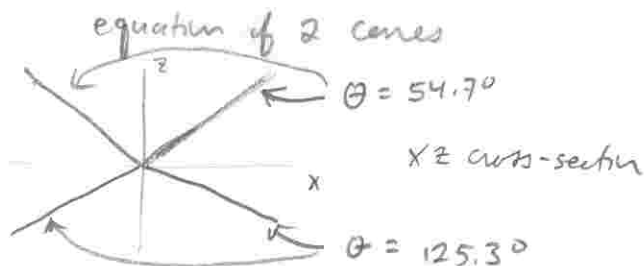
2. (30 points) So-called interhalogen species such as ClF_5 are well known. The central chlorine atom is permitted to violate the octet rule due to the presence of $3d$ orbitals that are close in energy to the $3s$ and $3p$ orbitals. The analytical form of the $3d_0$ orbital is given below:

$$|320\rangle = R_{32}Y_{20}, \text{ where } R_{32} = \frac{1}{81(30)^{1/2}a_0^{3/2}}\rho^2e^{-\rho/6}, \rho = \frac{2r}{a_0}, \text{ and } Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$$

While the above is exactly true only for one-electron species, it provides a reasonable model for the $3d_0$ orbital on Cl.

- (a) Find equations for all nodes of the $|320\rangle$ orbital.

6 pts $3\cos^2\theta - 1 = 0 \Rightarrow \cos^2\theta = \frac{1}{3} \Rightarrow \cos\theta = \pm\sqrt{\frac{1}{3}}$
 $\Rightarrow \theta = \cos^{-1}\left(\pm\sqrt{\frac{1}{3}}\right) = 54.7^\circ, 125.3^\circ$ (includes $r=0$)



-2 $\theta = 54.7^\circ$ only
 -5 something

[Problem 2 continues on the next page.]

(b) Find the locations (in Å) of all extrema of the radial wavefunction.

10 pts $\frac{dR_{32}}{dr} = \frac{dR_{nl}}{d\rho} \frac{d\rho}{dr} = 0$ and $\frac{d\rho}{dr} = \frac{2}{a_0}$

$$\frac{dR_{nl}}{d\rho} = \frac{1}{81\sqrt{30} a_0^{3/2}} \left[\rho^2 \left(-\frac{1}{6}\right) e^{-\rho/6} + 2\rho e^{-\rho/6} \right] = 0$$

$$\rho e^{-\rho/6} \left[-\frac{1}{6}\rho + 2 \right] = 0 \Rightarrow \rho = 12 = \frac{2r}{a_0} \Rightarrow r = 6a_0 = 6(0.5292 \text{ \AA})$$

$$\boxed{r = 3.175 \text{ \AA}}$$

-1 answer not in Å -3 algebra error

(c) Using only the radial wavefunction, find the average radius r (in Å) of a 3d orbital

14 pts $\langle r \rangle = \int_0^\infty R^* r R r^2 dr = \int_0^\infty R^2 r^3 dr = \frac{1}{81^2 (30) a_0^3} \int_0^\infty \rho^4 e^{-\rho/3} r^3 dr$

variable change: $r = \frac{a_0 \rho}{2} \Rightarrow dr = \frac{a_0}{2} d\rho$

$$\langle r \rangle = \frac{1}{81^2 (30) a_0^3} \int_0^\infty \rho^4 e^{-\rho/3} \left(\frac{a_0}{2}\right)^3 \rho^3 \left(\frac{a_0}{2}\right) d\rho$$

$$= \frac{1}{81^2 (30) a_0^3} \frac{a_0^4}{16} \int_0^\infty \rho^7 e^{-\rho/3} d\rho$$

$$= \frac{a_0}{3^8 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2} (7!) 3^8$$

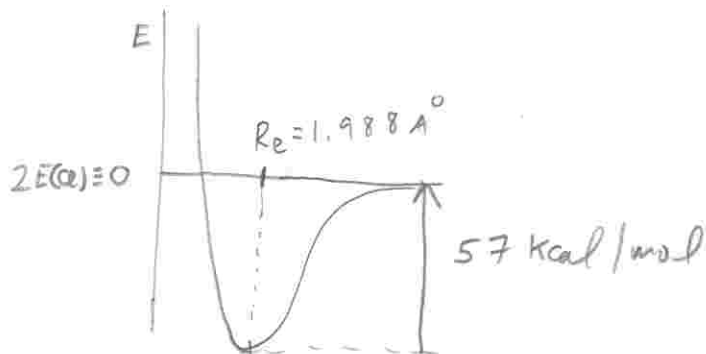
$$\langle r \rangle = \frac{21}{2} a_0 = \frac{21}{2} (0.5292 \text{ \AA}) = \boxed{5.557 \text{ \AA}}$$

-3 algebra error

-5 wrong differential

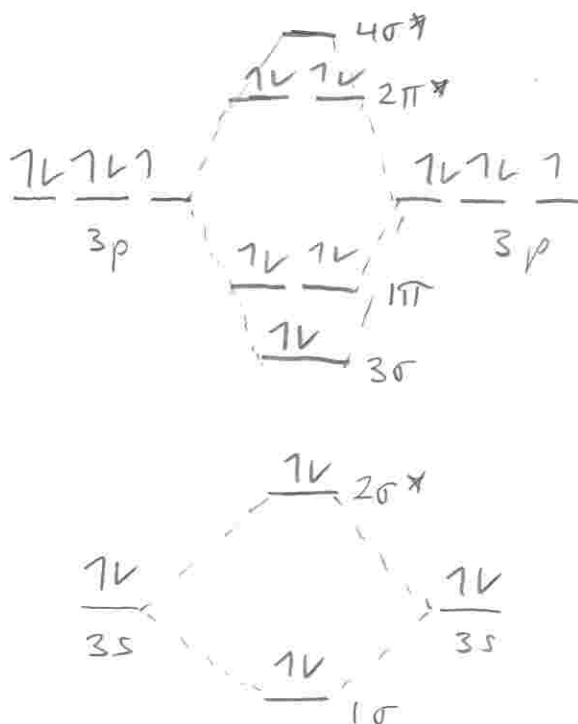
3. Chlorine-containing compounds play a critical role in stratospheric ozone depletion.

- (a) (5 points) Experiments reveal that the bond dissociation energy of Cl_2 is 57 kcal/mol, and that its equilibrium bond length is 1.988 Å. Sketch a potential energy diagram on which these experimental quantities are labeled.



everyone got perfectly right!

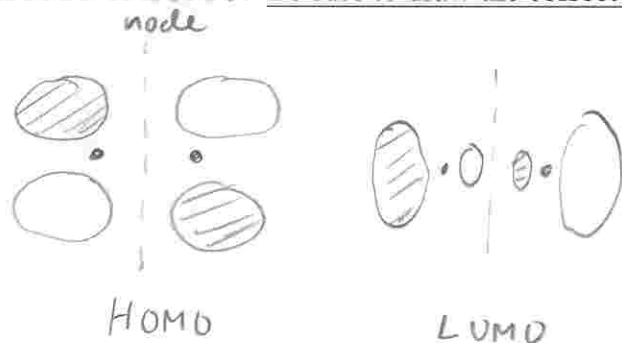
- (b) (5 points) Draw the energy-level diagram for Cl_2 . Label all valence atomic and molecular orbitals, and show what orbitals are occupied in Cl_2 's ground electronic state.



-1 mislabeled AO's
-1 misordered AO's

[Problem 3 continues on the next page.]

- (c) (6 points) Sketch the boundary surfaces of Cl_2 's highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO). Label your sketches as **HOMO** or **LUMO**. Be sure to draw the correct relative sizes of each of the lobes.



-3 one wrong
 -6 neither right
 -5 one correct & sketch mislabeled

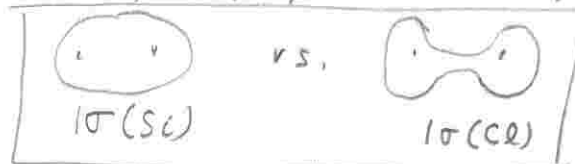
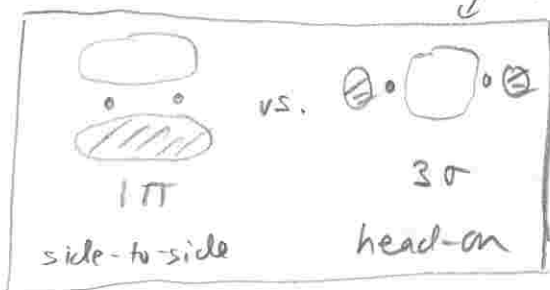
- (d) (6 points) Short UV radiation in the upper atmosphere produces a measurable amount of the Cl_2^+ molecular cation. Experiments reveal that the bond dissociation energy of Cl_2^+ is 99 kcal/mol, and that its equilibrium bond length is 1.89 Å. Use the concept of bond order to rationalize the data for Cl_2 (given in part (a)) and Cl_2^+ .

$$\text{Cl}_2: b = \frac{1}{2}(8-6) = 1 \quad \text{Cl}_2^+: b = \frac{1}{2}(8-5) = 1.5$$

Higher b , for the same pair of nuclei, means shorter and stronger bonds. This is consistent with the data.

- (e) (8 points) Note and explain any differences in the energy level diagrams of Cl_2 and Si_2 .

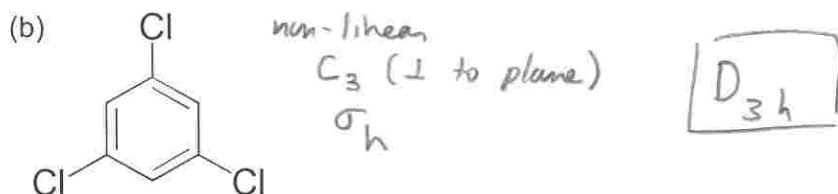
In Si_2 , $E(1\pi) < E(3\sigma)$. In spite of the better overlap in the 3σ MO, the e^- 's in 3σ are more repelled by the e^- 's in the 1σ MO, since 1σ and 3σ occupy largely the same space.



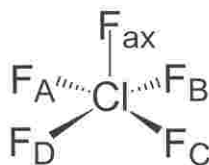
For Cl_2 , $E(3\sigma) < E(1\pi)$, because the larger Z_{eff} on Cl (compared to Si) pulls e^- density in the 1σ MO away from the internuclear region.

-1 minor error -3 incomplete -5 incorrect explanation

4. (8 points) Determine the point group to which each of the following molecules belong. You do not need to justify your answers. However, no partial credit will be awarded for wrong answers unless you write down your reasoning.



5. (22 points) The chlorine pentafluoride (ClF_5) mentioned in Problem #2 has a square pyramidal shape, and therefore belongs to the C_{4v} point group:



The C_4 axis (which, by definition, is the z -axis) coincides with the Cl-F_{ax} bond. Assume that the other four Cl-F bonds are all of the same length, and lie in a plane perpendicular to the C_4 axis. The character table for C_{4v} is given below:

$C_{4v}, 4mm$	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$	$h = 8$
A_1	1	1	1	1	-1	$z, z^2, x^2 + y^2$
A_2	1	1	1	-1	1	R_z
B_1	1	1	-1	1	-1	$x^2 - y^2$
B_2	1	1	-1	-1	1	xy
E	2	-2	0	0	0	$(x, y), (xz, yz)$ (R_x, R_y)

NO! should be -1
(typo in Atkins and de Paula, 7th ed)

[Problem 5 continues on the next page.]

(a) Is an $A_2 \leftarrow B_1$ electric dipole transition allowed for ClF_5 ? Justify your answer.

6 pts

	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
A_2	1	1	1	-1	1
B_1	1	1	-1	1	-1
$(x,y): E$	2	-2	0	0	0
product	2	-2	0	0	0

$\hat{C} E \Rightarrow x,y$ not allowed

Error in $\chi(2\sigma_d)$ for A_2 precludes a definite answer for z-polarization

(b) Consider the following combination of the $2p_z$ orbitals on the four co-planar F atoms:

6 pts $\psi = p_z(A) - p_z(B) + p_z(C) - p_z(D)$. Determine the symmetry species spanned by ψ , and predict which (if any) of the d orbitals on Cl are allowed to have non-zero overlap with ψ .

$$\hat{E} \begin{pmatrix} A \\ -B \\ C \\ -D \end{pmatrix} = \begin{pmatrix} A \\ -B \\ C \\ -D \end{pmatrix} \Rightarrow \chi = 4$$

$$\hat{C}_2 \begin{pmatrix} A \\ -B \\ C \\ -D \end{pmatrix} = \begin{pmatrix} C \\ -D \\ A \\ -B \end{pmatrix} \Rightarrow \chi = 0$$

$$\hat{C}_4 \begin{pmatrix} A \\ -B \\ C \\ -D \end{pmatrix} = \begin{pmatrix} -D \\ A \\ -B \\ C \end{pmatrix} \Rightarrow \chi = 0$$

$$\hat{\sigma}_v \begin{pmatrix} A \\ -B \\ C \\ -D \end{pmatrix} = \begin{pmatrix} A \\ -D \\ C \\ -B \end{pmatrix} \Rightarrow \chi = 2$$

$$\hat{\sigma}_d \begin{pmatrix} A \\ -B \\ C \\ -D \end{pmatrix} = \begin{pmatrix} -B \\ A \\ -D \\ C \end{pmatrix} \Rightarrow \chi = 0$$

$$d_{z^2} : A_1 \quad a_{A_1} = \frac{1}{8} [1 \cdot 1 \cdot 4 + 2 \cdot 1 \cdot 2] = 1$$

$$d_{x^2-y^2} : B_1 \quad a_{B_1} = \frac{1}{8} [1 \cdot 1 \cdot 4 + 2 \cdot 1 \cdot 2] = 1$$

$$d_{xy} : B_2 \quad a_{B_2} = \frac{1}{8} [1 \cdot 1 \cdot 4 + 2(-1)(2)] = 0$$

$$\{d_{xz}, d_{yz}\} : E \quad a_E = \frac{1}{8} [1 \cdot 2 \cdot 4] = 1$$

$\therefore d_{z^2}, d_{x^2-y^2}$, or a combination of d_{xz} and d_{yz} on Cl have non-zero overlap with ψ on the F atoms.

- 13 something
- 8 fundamentally flawed proof
- 4 error in 1 symmetry element
- 2 correct decomposition, but missed a d-orbital

Possibly Useful Information

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$a_0 = 0.5292 \text{ \AA}$$

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

$$\int \sin ax \sin bx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)}, a^2 \neq b^2$$

$$\hbar = 1.055 \times 10^{-34} \text{ J s}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

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

$$\int \sin^2 ax dx = \frac{1}{2}x - \frac{1}{4a} \sin 2ax$$

1 H 1.0079																2 He 4.0026	
3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	*La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 †Ac 227.03															

* 58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
† 90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	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)