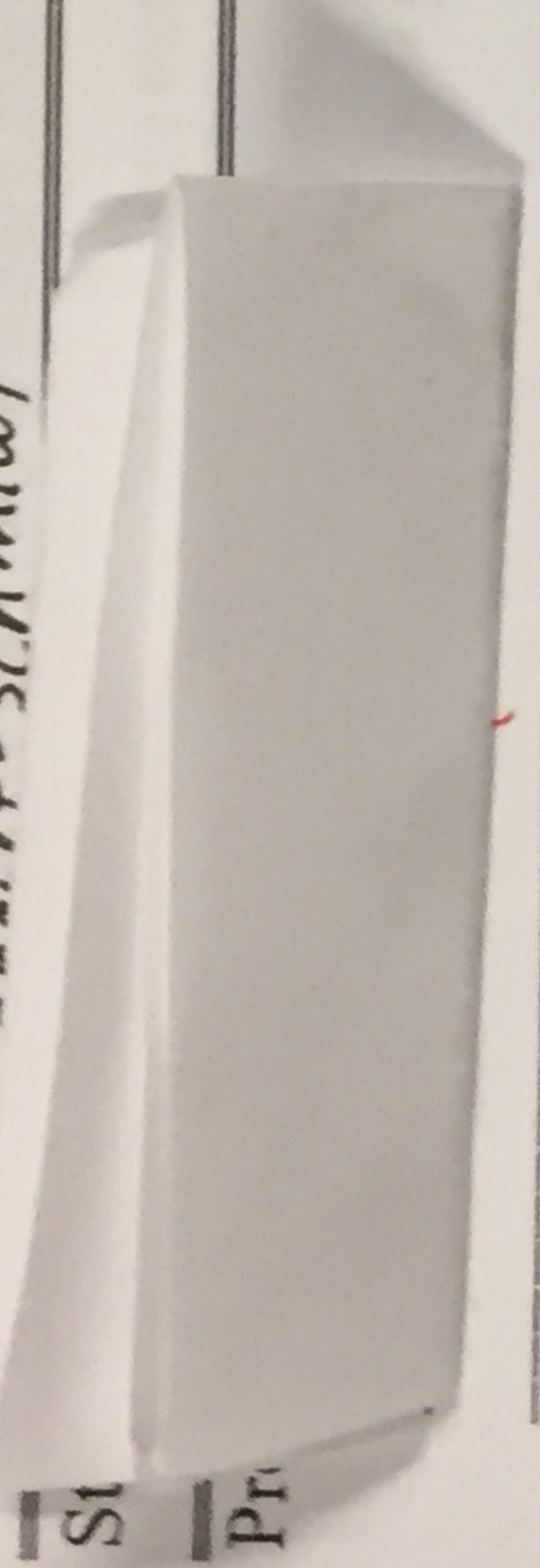


Chemistry 20A Midterm (II), Fall 2010  
November 19, 2010

Name: Alvin A. + Schmidt Section / T.A. Name: A 2D / Adam



2) 50 pts.: φ

3) 50 pts.: φ

4) 50 pts.: 39

Total pts.: 121

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

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$m_e = 9.1 \times 10^{-31} \text{ kg} = m_p / 1836$$

$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

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

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

The Periodic Table of the Elements

1	2																	10	11
H Hydrogen 1.00794	He Helium 4.003																	Ne Neon 20.1797	
3	4																	9	10
Li Lithium 6.941	Be Beryllium 9.012182																	F Fluorine 18.9984032	Ne Neon 20.1797
11	12																	17	18
Na Sodium 22.989769	Mg Magnesium 24.30409																	Cl Chlorine 35.4527	Ar Argon 39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
K Potassium 39.0983	Ca Calcium 40.078	Sc Scandium 44.955910	Ti Titanium 47.867	V Vanadium 50.9415	Cr Chromium 51.9961	Mn Manganese 54.938049	Fe Iron 55.845	Co Cobalt 58.933200	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.39	Ga Gallium 69.723	Ge Germanium 72.61	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.80		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90585	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.94	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 102.90550	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.90447	Xe Xenon 131.29		
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
Cs Cesium 132.90545	Ba Barium 137.327	La Lanthanum 138.9055	Hf Hafnium 178.49	Ta Tantalum 180.9479	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.222	Pt Platinum 195.078	Au Gold 196.96655	Hg Mercury 200.59	Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.98038	Po Polonium (209)	At Astatine (210)	Rn Radon (222)		
87	88	89	104	105	106	107	108	109	110	111	112	113	114						
Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (263)	Bh Bohrium (264)	Hs Hassium (265)	Mt Meitnerium (266)				Cn Copernicium (285)							
58	59	60	61	62	63	64	65	66	67	68	69	70	71						
Ce Cerium 140.116	Pr Praseodymium 140.90765	Nd Neodymium 144.24	Pm Promethium (145)	Sm Samarium 150.36	Eu Europium 151.964	Gd Gadolinium 157.25	Tb Terbium 158.92534	Dy Dysprosium 162.50	Ho Holmium 164.93032	Er Erbium 167.26	Tm Thulium 168.93421	Yb Ytterbium 173.04	Lu Lutetium 174.967						
90	91	92	93	94	95	96	97	98	99	100	101	102	103						
Th Thorium 232.0377	Pa Protactinium 231.03688	U Uranium 238.02891	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)						



1. (50 pts.)

- (10 pts.) What is Koopmans' approximation?
- (20 pts.) Explain the reasoning behind the Born-Oppenheimer Approximation.
- (20 pts.) Why can two arbitrary diatomic molecules with the same bond order have different bond energies? Give an example and explain how this could be possible.

10  
a) Koopman's approximation states that the ionization energy to eject an electron from a given ~~orbital~~ orbital is equal to the energy of that orbital

$$I E_a \approx \epsilon_a$$

20  
b) The Born-Oppenheimer Approximation assumes that since the nuclei are so much more massive as compared to the electrons, they will move much slower than the  $e^-$  (by about a factor of 100). The B-O Approx. finds the wave function of the electrons, assuming that the distance between the two nuclei ( $R_{AB}$ ) is fixed. Then the nuclei are adjusted, and ~~the~~ Schrödinger equation is solved again. After repeated ~~by~~ doing this, we get the wave function of the electron. Then we multiply this by the wave function of the oscillating nuclei to find the wave function of the molecule.

$$\Psi_{e^-} \times \Psi_{\text{nuclei}} = \Psi_{\text{molecule}}$$

10  
c) Bond order is simply an approximation. ~~Li<sub>2</sub>~~ ~~Li<sub>2</sub>~~ both have a bond order of 1, but He<sub>2</sub>'s bond energy is essentially 0 kJ/mol, while Li<sub>2</sub>'s bond energy is about 9 kJ/mol. This happens because the electrons being used for bonding ~~are~~ in Li<sub>2</sub> are further from the nuclei than those of He<sub>2</sub>. Also Li<sub>2</sub> has a valence electron out side of the inner most shell, which as a result makes it easier for Li<sub>2</sub> to form a bond, while He<sub>2</sub> has its outermost shell filled already.



$$KE = 75 - \frac{(1.7)^2}{1.2^2} (1.1) \times 10^{-18}$$

$$KE = 35$$

~~$$KE = h\nu - I.E$$

$$75 = h\nu - I.E$$~~

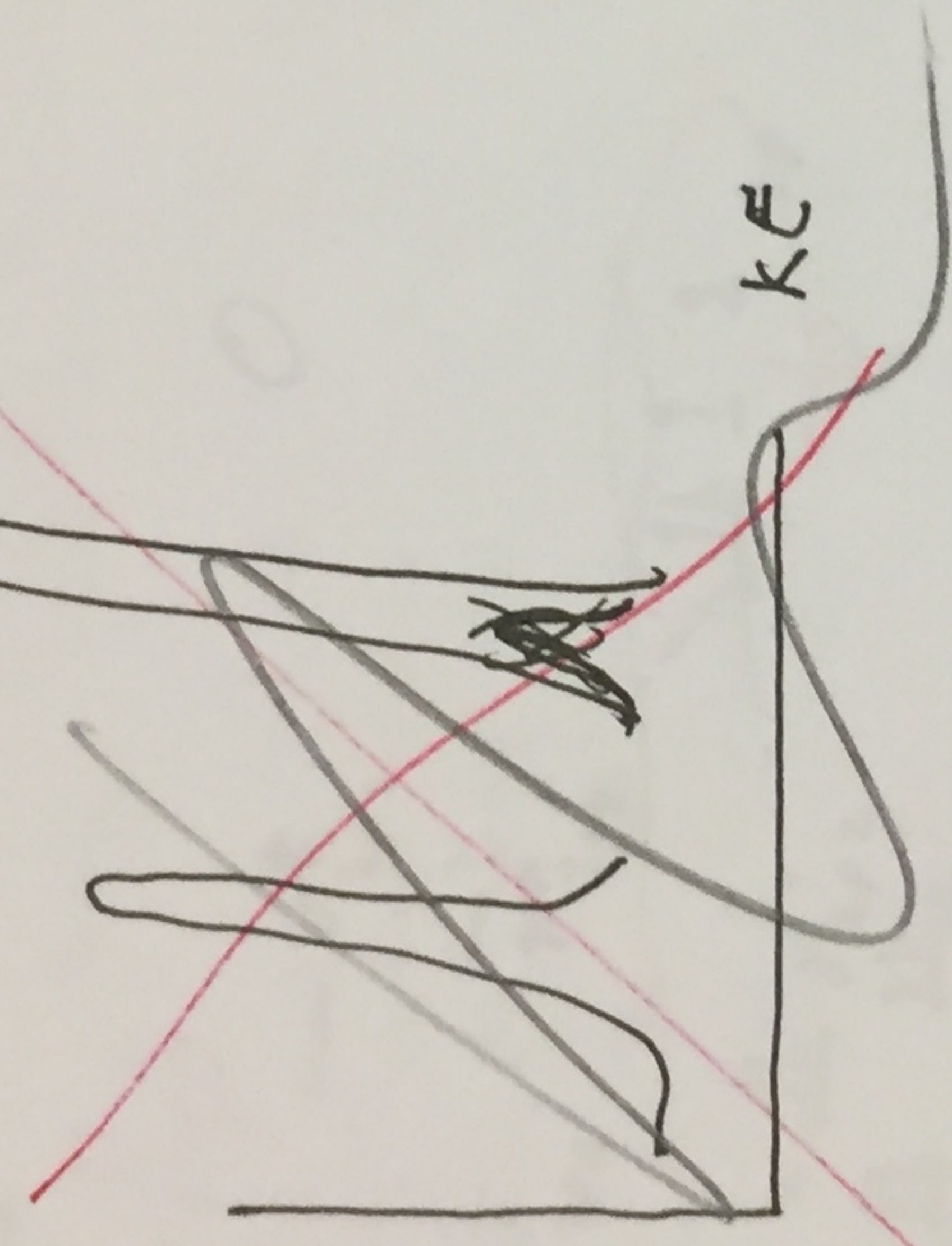
a) 2. (50 pts.)

a) (30 pts.) Calculate and plot the photoelectron spectrum (PES) of He for a 75 eV photon as a function of the electron kinetic energy and the orbital ionization energy.

Assume photoelectron peak intensities are the same heights in your plots.

b) (10 pts.) Why is there no vibration information in the He PES?

c) (10 pts.) What is the primary reason for the different ionization energies for the two He electrons?



0/30

~~$$E = h\nu$$

$$75 \text{ eV} \left( \frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = (1.626 \times 10^{-14} \text{ J})$$~~

b) 0/10

a) Different ionization energies because in the second  $e^-$  there is no  $e^- - e^-$  repulsion, and screens the full  $Z$  charge of  $+2$ .

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3. (50 pts.)

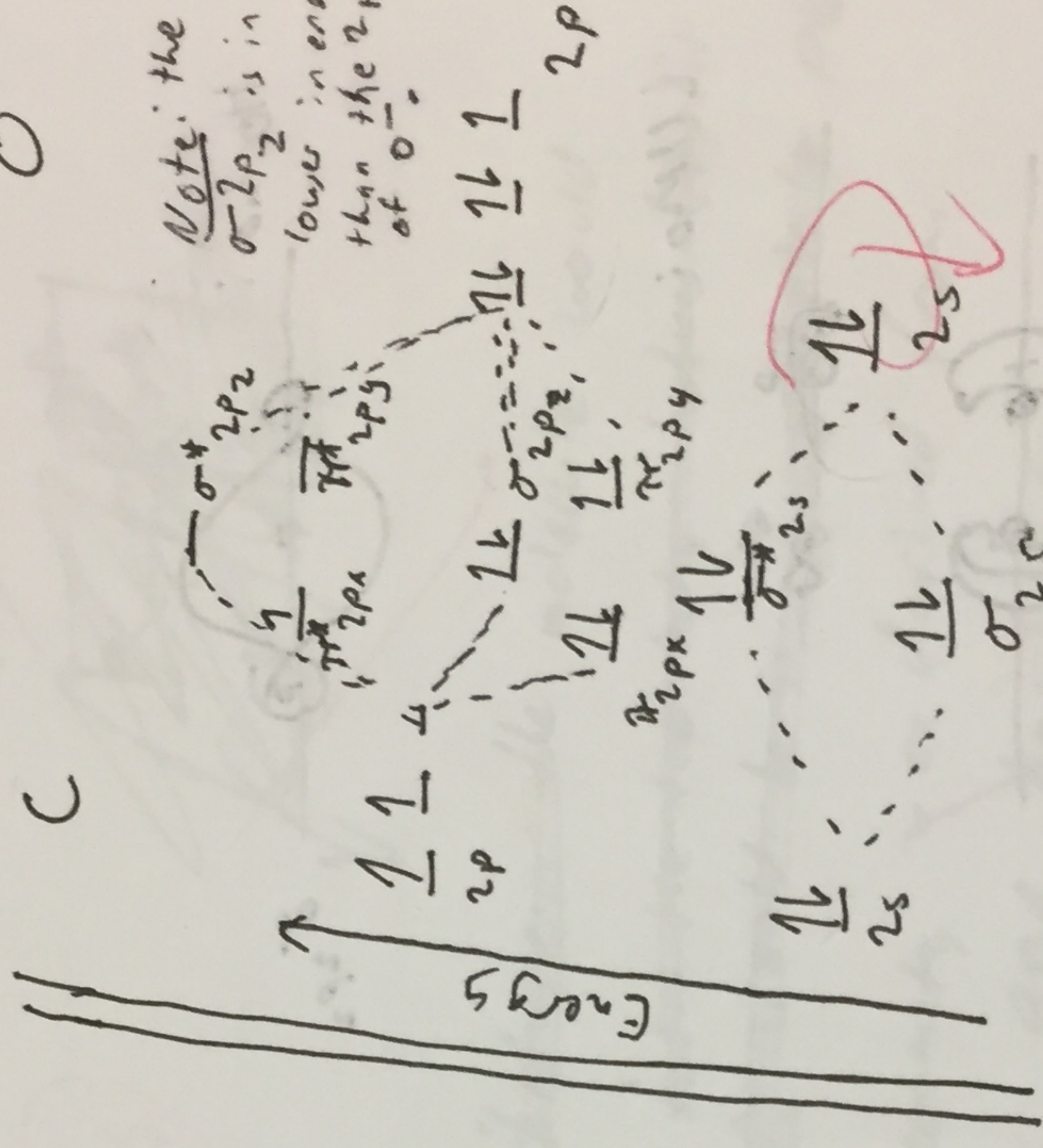
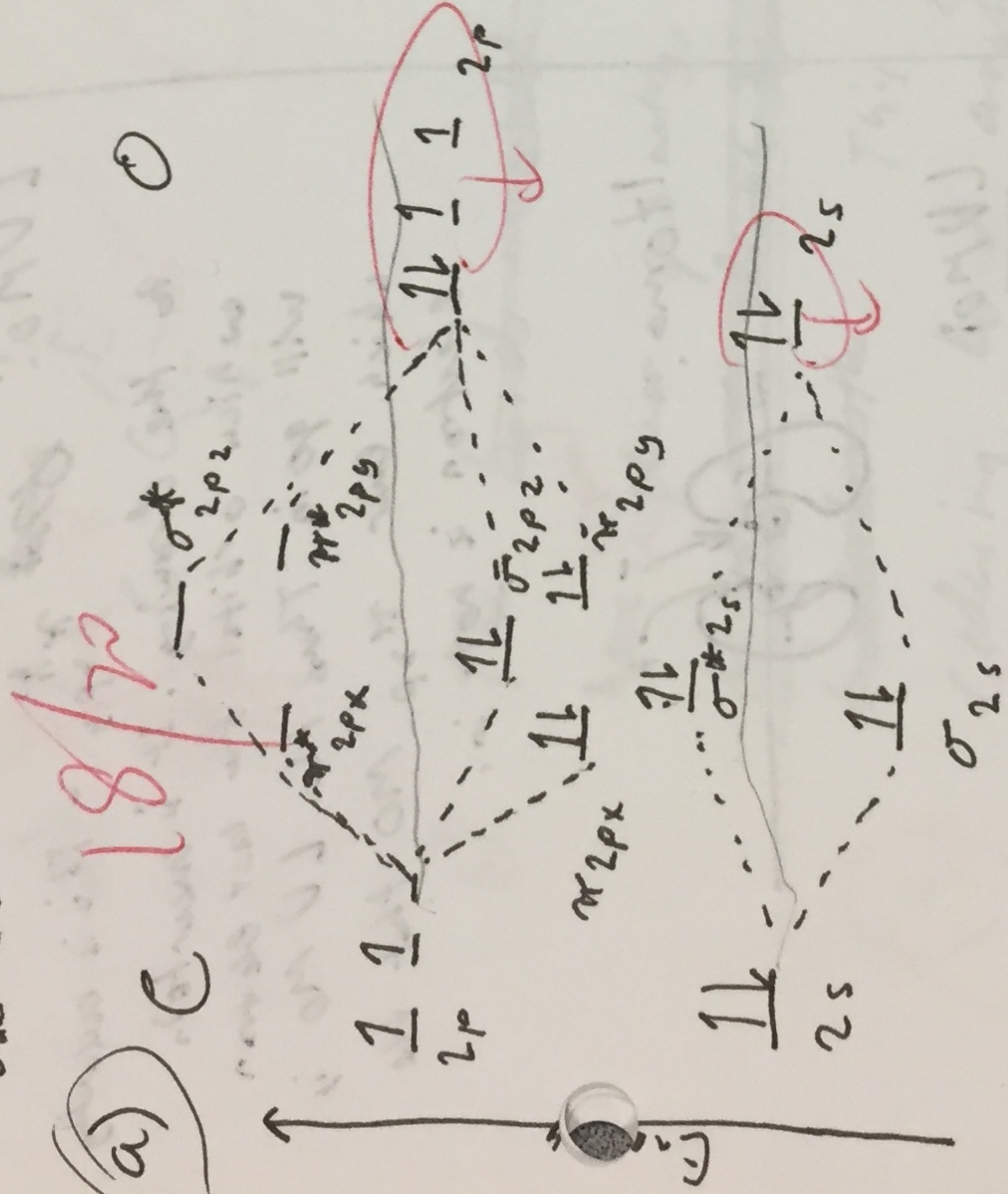
- a) (20 pts.) Construct the MO correlation diagram for CO and CO<sup>-1</sup> and give the molecular electron configuration for both molecules.
- b) (15 pts.) Sketch the electronic potential energy curves both for molecules on the same graph: show the relative bond energies, equilibrium lengths and first 3 vibrational energy levels.

c) (15 pts.) What are the HOMO and LUMO in these two molecules? Make a sketch of these two orbitals. Are the molecules diamagnetic or paramagnetic?

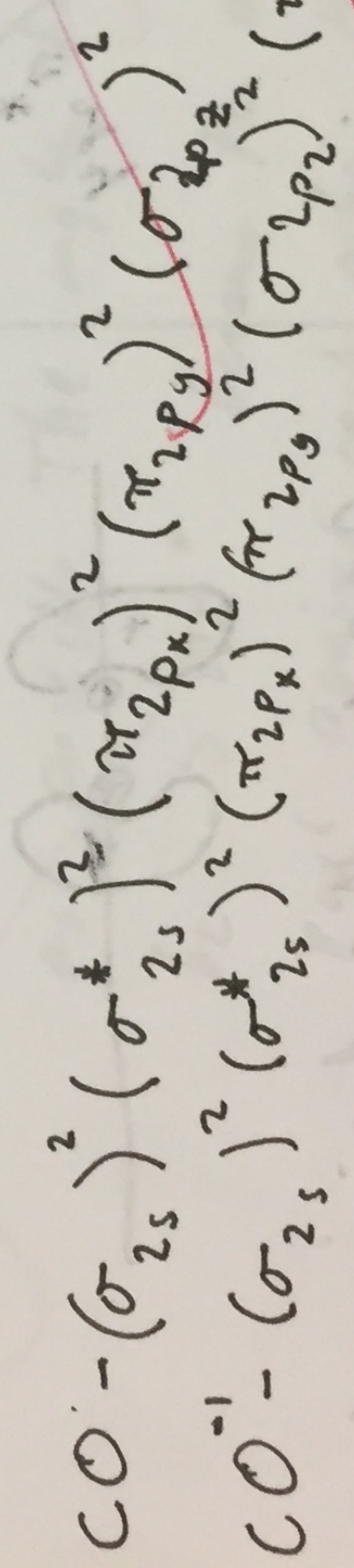
Bond order:  $\frac{1}{2}(8-2) = 3$

Bond order:  $\frac{1}{2}(8-3) = \frac{5}{2} = 2.5$

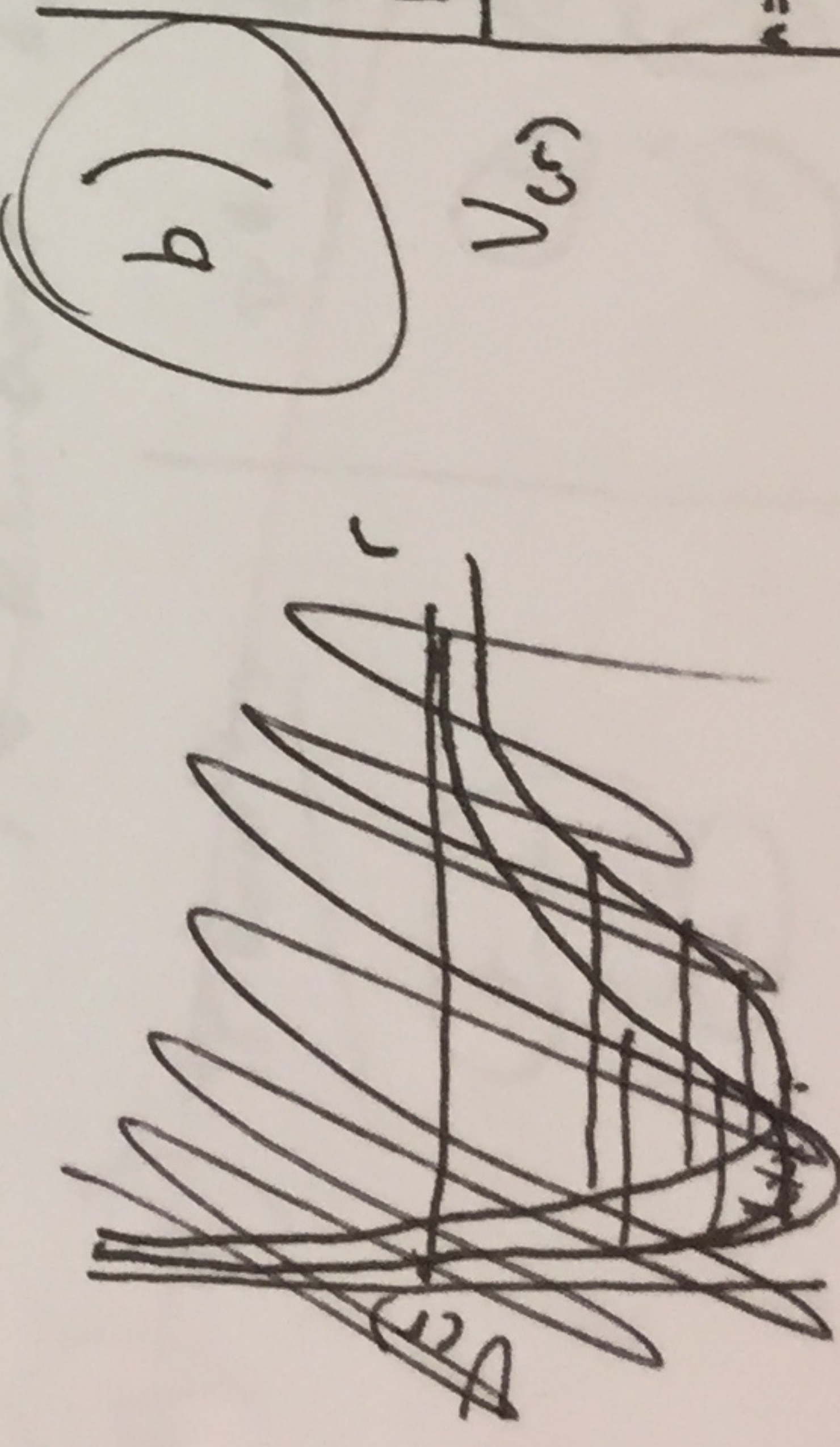
*C is on back*



Note: the  $\sigma_{2p_z}$  is in fact lower in energy than the  $2p$  orbitals of  $O^-$ .



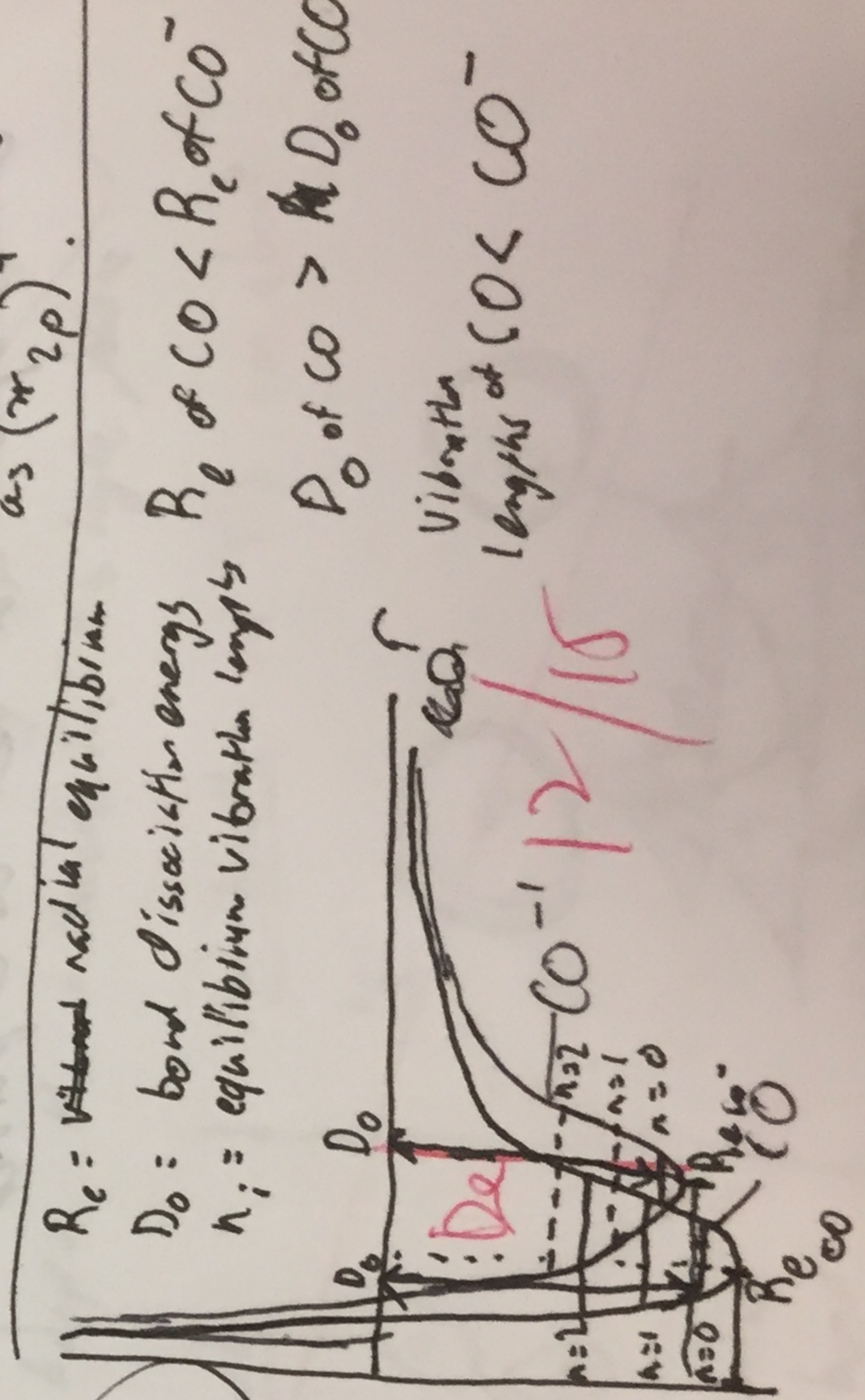
Note: the  $(\pi_{2px})^2$  and  $(\pi_{2py})^2$  MO<sup>-1</sup> orbitals can be written together as  $(\pi_{2p})^4$ .



$R_e$  = ~~the~~ radial equilibrium

$D_0$  = bond dissociation energy

$n_i$  = equilibrium vibrational lengths



$R_e$  of CO <  $R_e$  of CO<sup>-1</sup>

$D_0$  of CO >  $D_0$  of CO<sup>-1</sup>

Vibrational lengths of CO < CO<sup>-1</sup>

$CO^{-1}$  12/15



9)

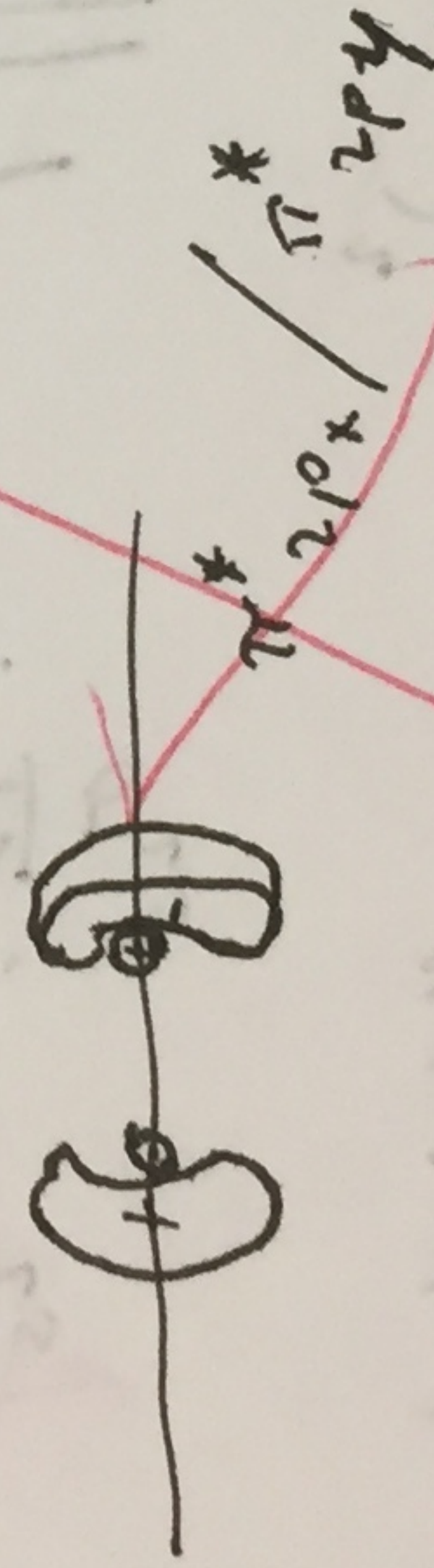
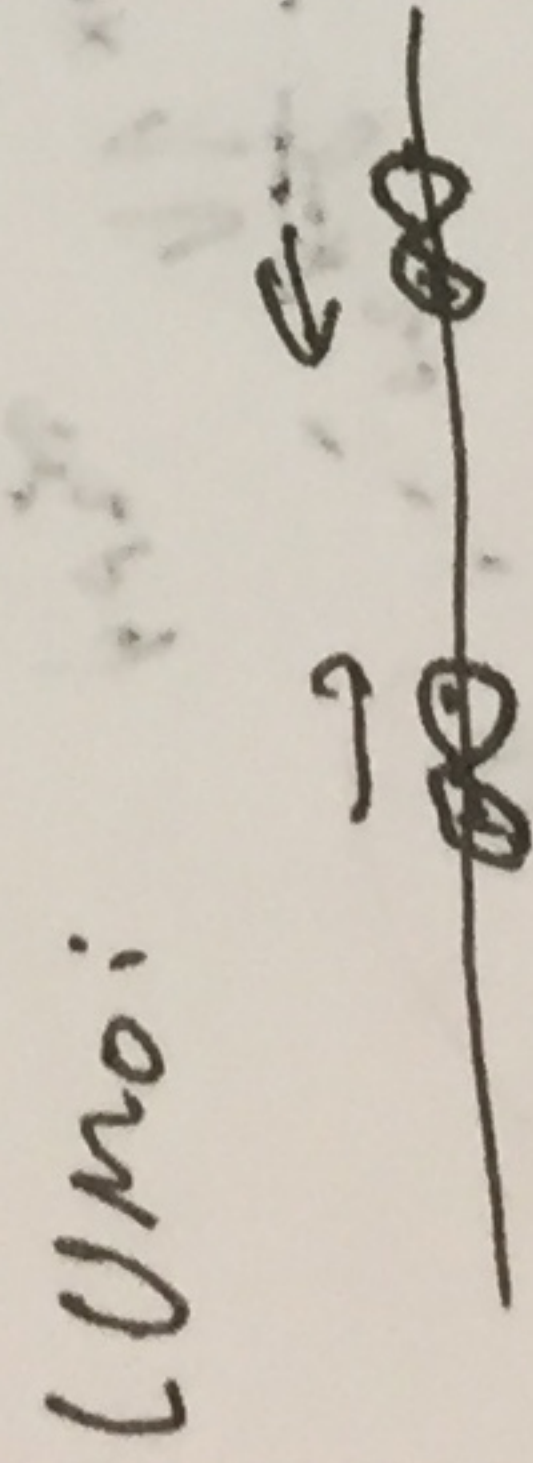
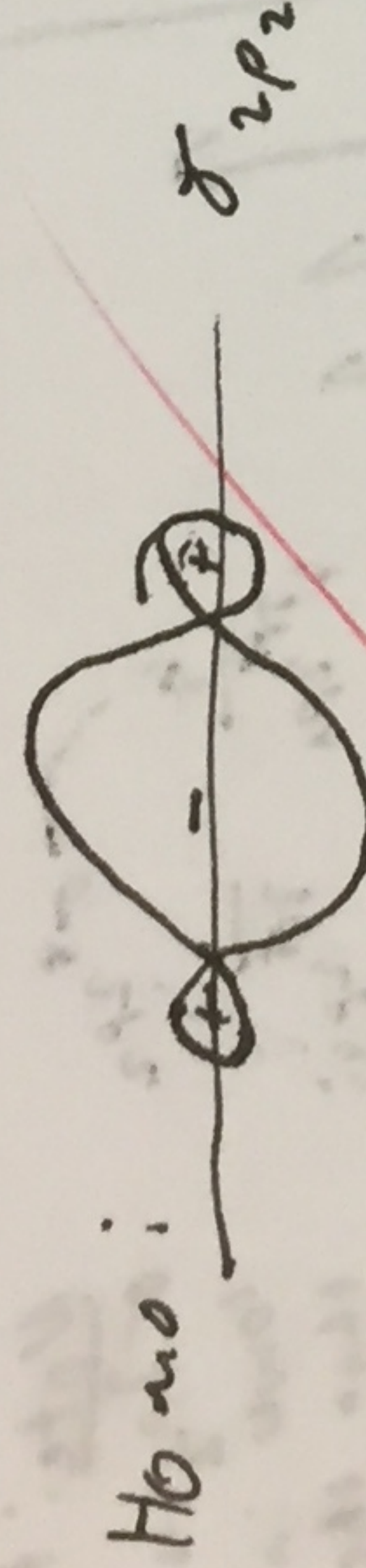
12/15

CO

HOMO:  $\sigma_{2p_z}$

LUMO:  $\pi^*_{2p_x}$  and  $\pi^*_{2p_y}$

These have degenerate energies, so the are both the lowest unoccupied molecular orbitals



~~Dia magnetic - all  $e^-$  are paired~~

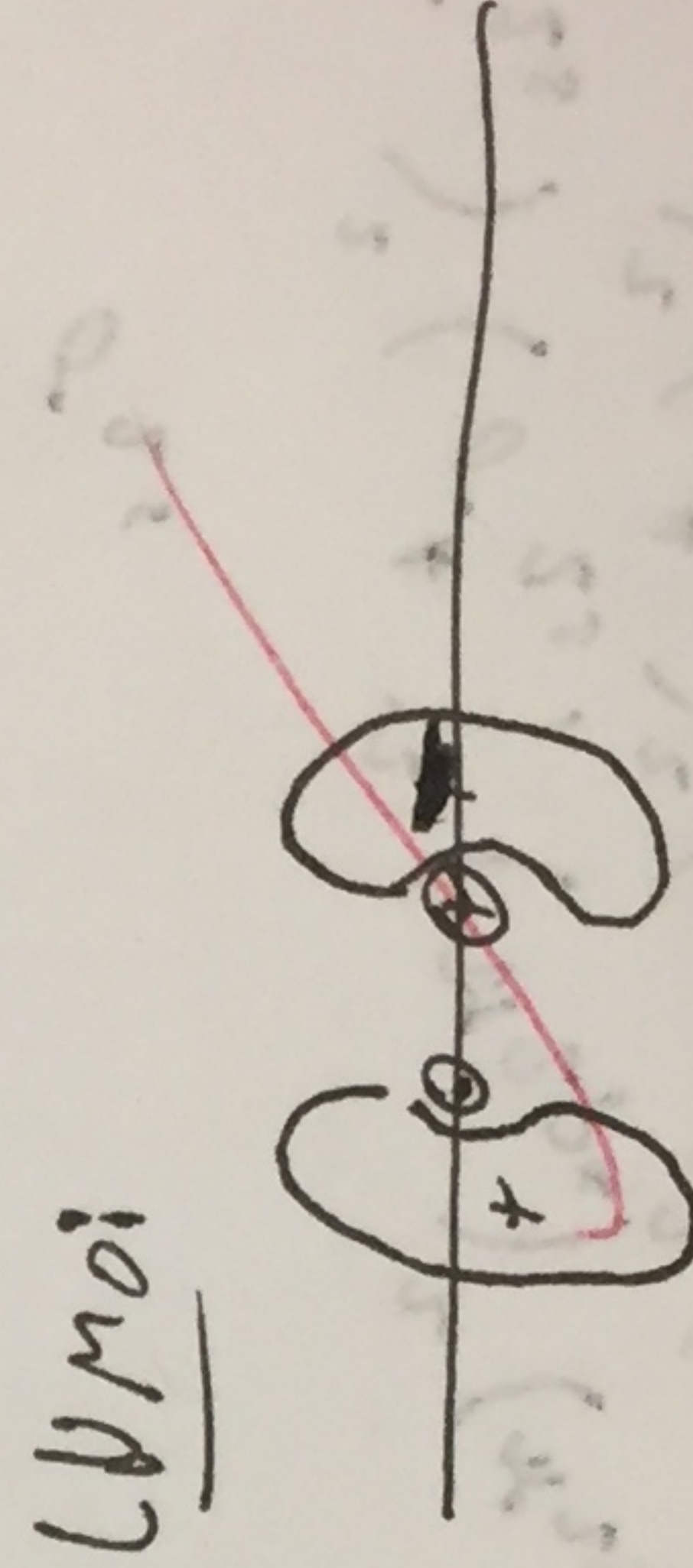
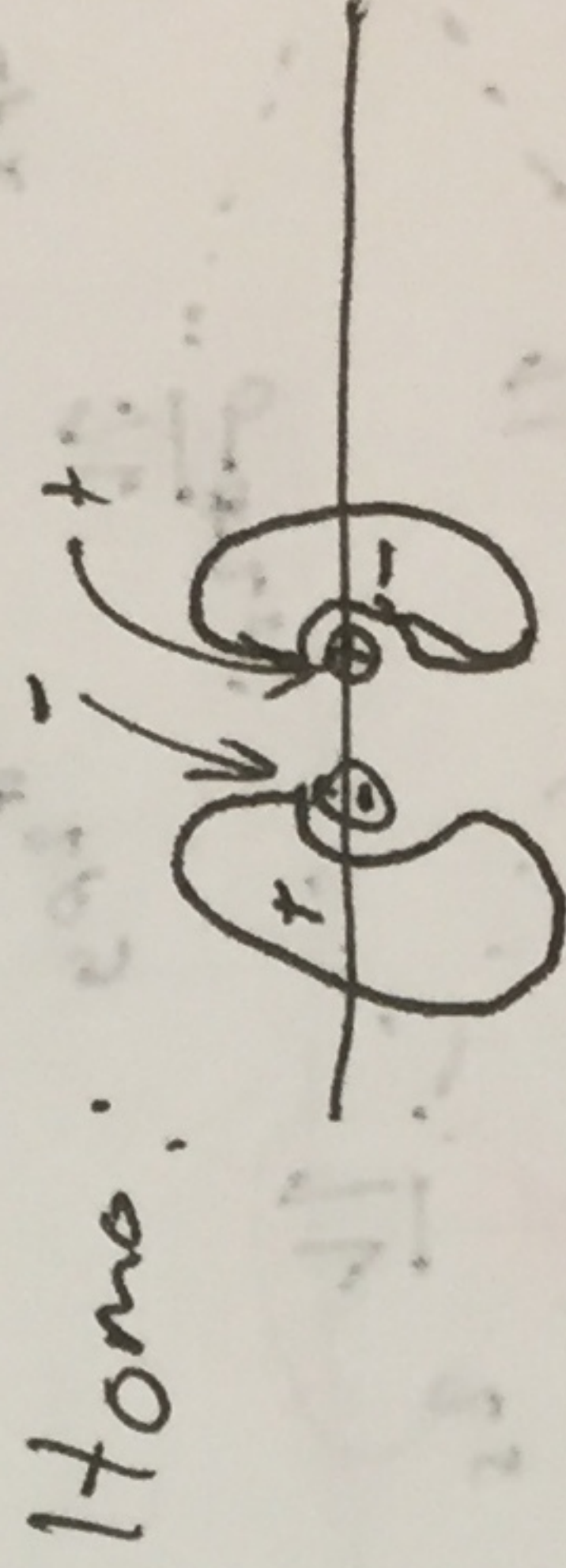
CO

HOMO:  $\pi^*_{2p_x}$

This according to my drawing. the last electron could also be in  $\pi_{2p_y}$  since the energies are degenerate

LUMO:  ~~$\pi^*_{2p_y}$~~   $\pi^*_{2p_y}$  - This is according

to the drawing. It is uncertain which orbital the last electron will go in. Thus the LUMO is which ever  $\pi_{2p}$  MO that the electron is not in.

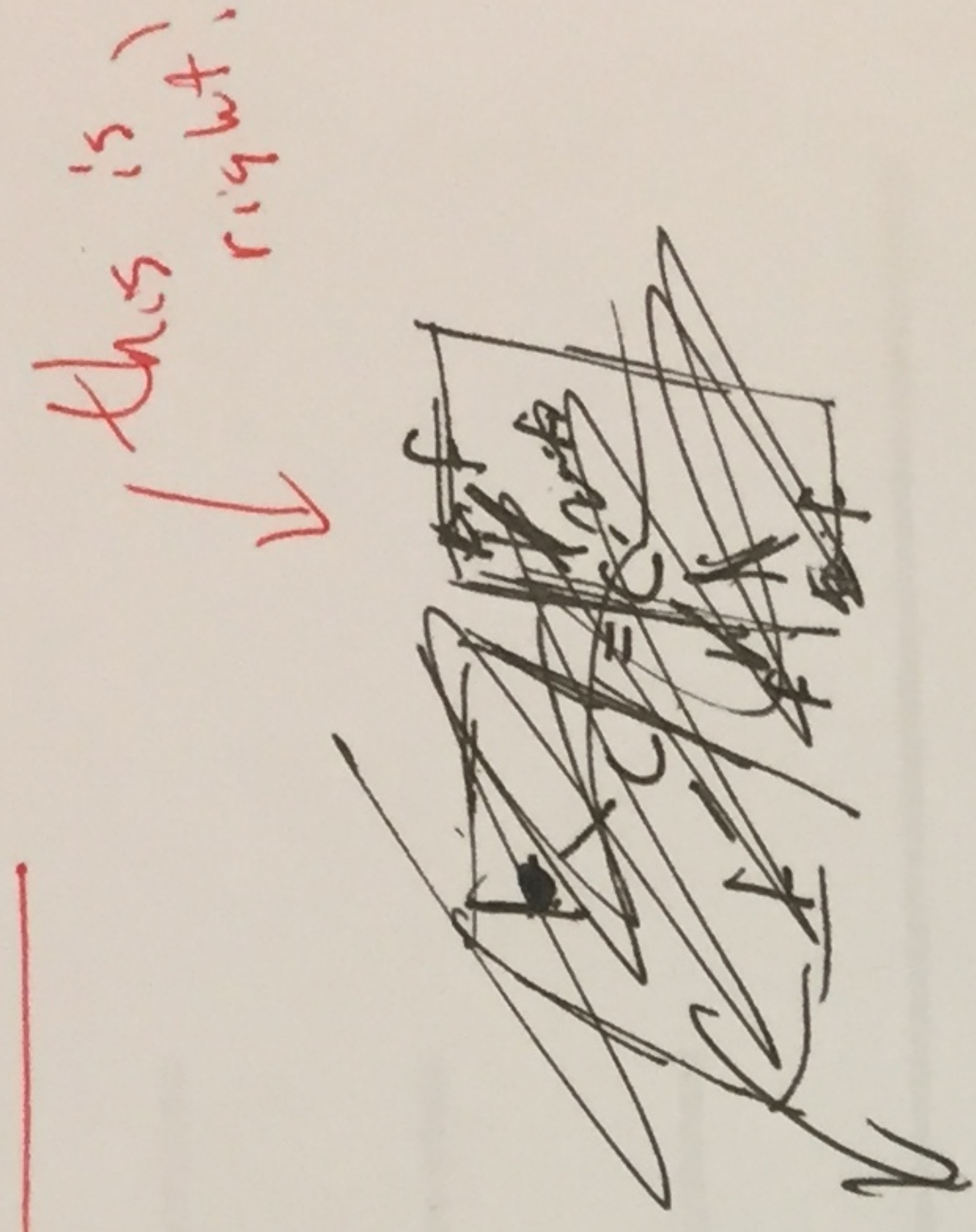
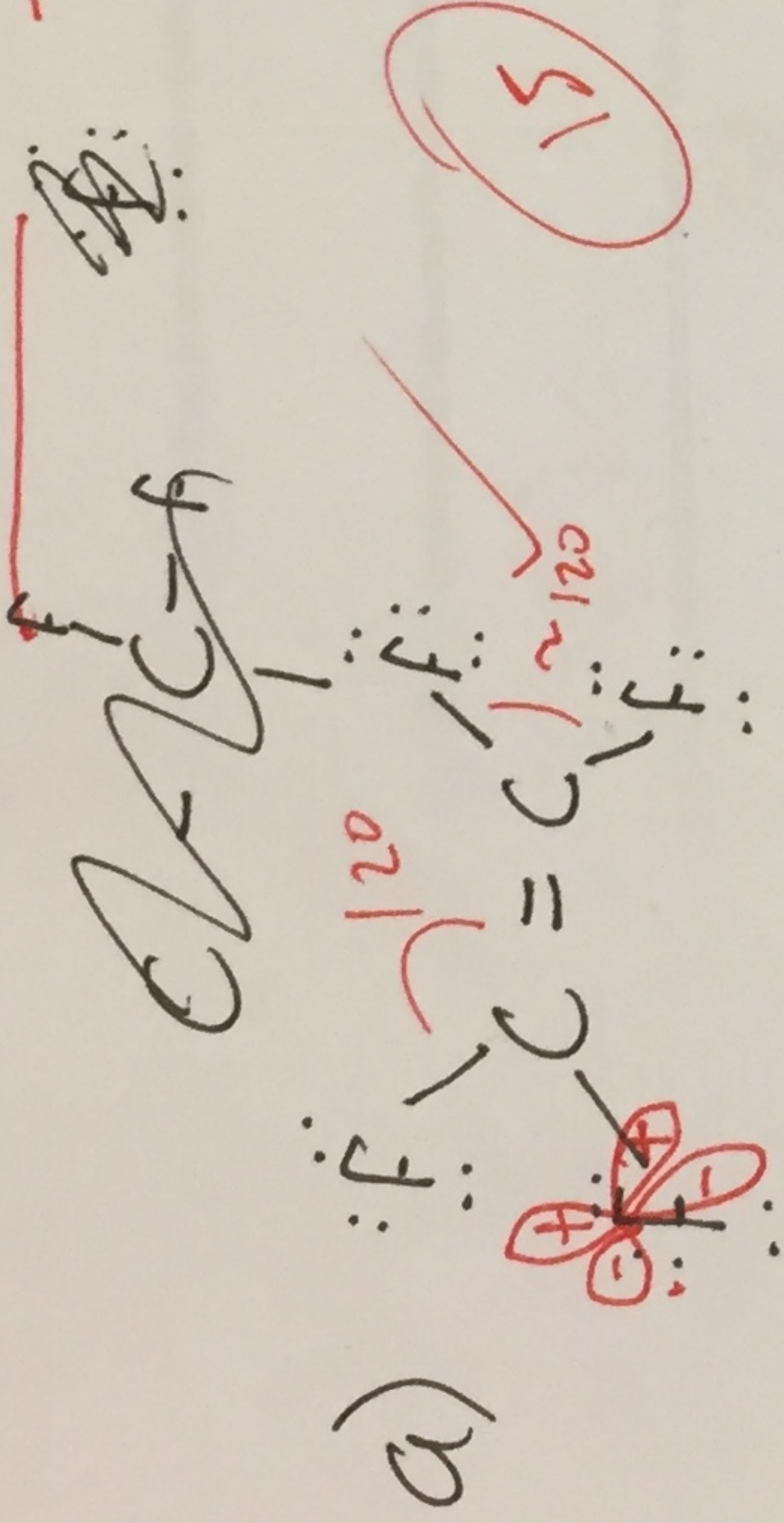


~~para magnetic - 1  $e^-$  is not paired~~



4. (50 pts.)

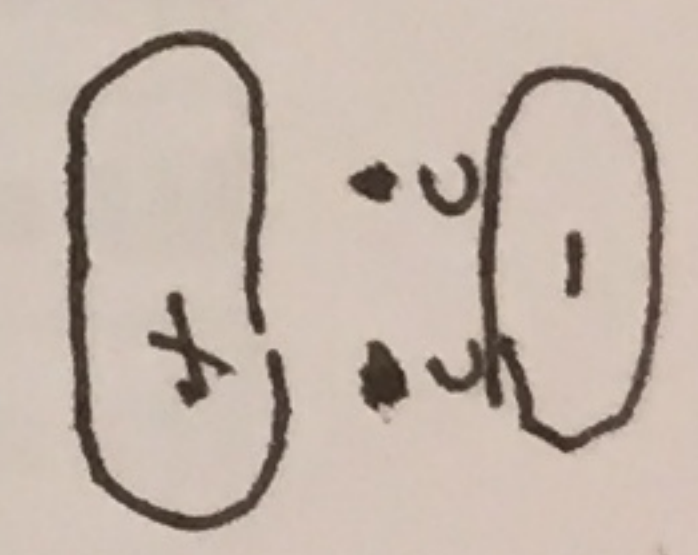
- a) (15 pts.) What is a possible Lewis dot structure for  $C_2F_4$ ?  
 b) (20 pts.) What is the geometry of the molecule, include estimated bond angles in your structure and please explain how your molecular structure was derived.  
 c) (15 pts.) Sketch the  $\pi$  bonding,  $\pi$  anti-bonding, and non-bonding orbitals for this molecule in order of increasing energy and explain your reasoning!



b) The ~~bonds would be in the molecule would~~ have <sup>trigonal</sup> planar geometry, ~~but the two lone pairs (split on the C double bond) would be in perpendicular planes to each other.~~ This geometry was derived from reducing bond angles and bond stresses as much as possible. The angles between the 2 F atoms would be  $> 120^\circ$  because they are rather large atoms and push against each other. The  $\pi$  bond keeps the molecule in a single plane.

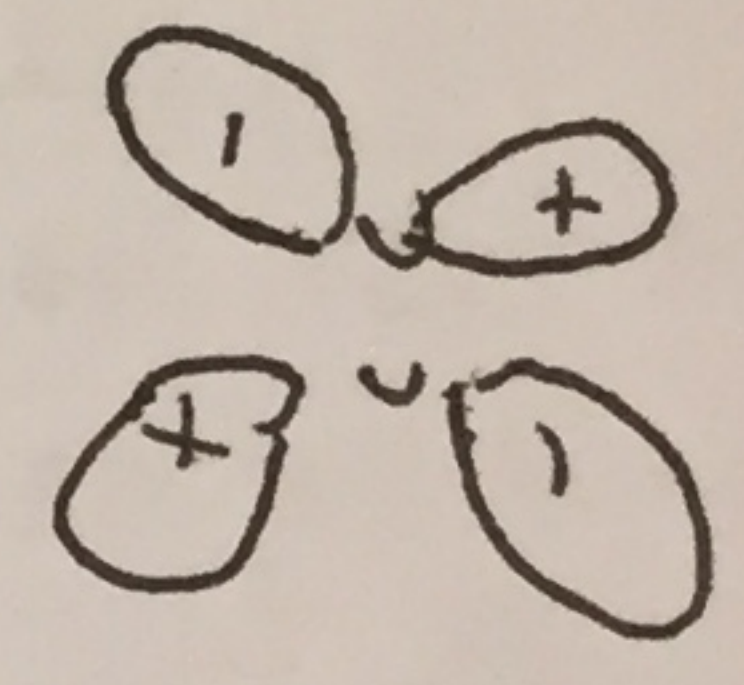
(15)

c)  $\pi$  bond's



found between the Carbons in the  $C=C$  bond

$\pi^*$  bond's



found in the  $C=C$  bond

non-bonding on F's, see above

