1. (25 points) **A square and not so square box**
An electron in a particular nanodevice may be treated as a quantum particle
in a two-dimensional box.

$2-D$ box

$\downarrow$ lowest

$n=1$

(a) (5 points) The energy of the electron in its ground state is $E_0 = 1\text{eV}$.
What is the length of the edges L of the square box?

(b) (5 points) Find the lowest six energy levels of the particle (in electron
volts). Make an energy level diagram and be sure to label the degeneracies of
each level.

(c) (10 points) The manufacturing process of these nanodevices is not perfect.
Some boxes end up being asymmetric with box edges of length $L_x > L_y$. Assume
that L_x is unchanged, e.g., $L_x = L$, your answer from part a. The manufacturing
company wants to know if L_y is ten percent or more larger than L_x. They plan
to determine this by looking for a split in the longest wavelength absorption line
when nanodevices in their ground state are irradiated. They need you to tell
them how precisely they need to measure the wavelength of these absorption
lines to observe this manufacturing defect.

(d) (5 points) If the difference in box lengths is $\Delta L = L_y - L_x \ll L_x$, there
is now a new, very long wavelength emission line associated with the transition
between formerly degenerate first excited states, which are now split by the fact
that $\Delta L > 0$. Find the wavelength of this emission line in terms of ΔL and
the quantities given above. If $\Delta L = 0.01L$ what is this wavelength and in what
part of the electromagnetic spectrum is this radiation? In other words is this
an x-ray photon, a radio photon, or something else?

(a) $E_n = \dfrac{h^2}{8mL^2}(n_1^2 + n_2^2)$ $m = 9.109 \times 10^{-31}$ kg

$L = ?$

$h = 6.626 \times 10^{-34}$ J·s

$n = 1,1$

ground state

$1\text{eV} = 1.602 \times 10^{-19}$ J

$1.602 \times 10^{-12} = \dfrac{h^2 n^2}{8mL^2}$

$8mL^2 = \dfrac{h^2 n^2}{1\text{eV}}$

$L = \sqrt{\dfrac{h^2(2 \cdot 1^2)}{(1\text{eV})(8m)}}$

$8.67 Å$

$L = 8.67 \times 10^{-10}$ m

$L = 8.67 Å$

4

For calculations

$(n_1^2 + n_2^2)$

(b)

- $(1,1) = 2$
- $(1,2)(2,1) = 5$
- $(1,3)(3,1) = 10$
- $(2,2) = 8$
- $(1,4)(4,1) = 17$
- $(2,3)(3,2) = 13$

Find E in eV

$$E_n = \frac{h^2}{8mL^2}(n_1^2 + n_2^2)$$

$C = 8.015 \times 10^{-20} J$

$$E_n = \frac{h^2}{8m(8.67 \times 10^{-10})^2}(n_1^2 + n_2^2)$$

n=17	(1,4)(4,1)	E= 8.51 eV
n=13	(2,3)(3,2)	E= 6.5 eV
n=10	(1,3)(3,1)	E= 5.0 eV
n=8	(2,2)	E= 4.0 eV
n=5	(1,2)(2,1)	E= 2.5 eV
n=2	(1,1)	E= 1 eV

$E_2 = C(1^2+1^2) = 2C = 1 eV$

$E_5 = C(1^2+2^2) = 5C = 2.5 eV$

$E_8 = C(2^2+2^2) = 8C = 4.00 eV$

$E_{10} = C(1^2+3^2) = 10C = 5.00 eV$

$E_{17} = C(1^2+4^2) = 17C = 8.51 eV$

$E_{18} = C(3^2+3^2) = 18C = 9.0 eV$

$E_{13} = C(2^2+3^2) = 13C = 6.5 eV$

+5

$2.659 \times 10^{39} - 1.33 \times 10^{18}$

c)

$L_x > L_y$

$$E_n = \frac{h^2}{8m}\left(\frac{n_1^2}{L_x^2} + \frac{n_2^2}{L_y^2}\right)$$

+2

$L = 8.67 Å$

longest wavelength
1×2

$E_n = 1 eV$

$n = 1, 1$

1.330×10^{18}

$$E_n = \frac{h^2}{8m}\left(\frac{n_1^2}{(8.67Å)^2} + \frac{n_2^2}{L_y^2}\right)$$

$$\frac{E_n 8m}{h^2} = \left(\frac{1}{(8.67Å)^2} + \frac{1}{(L_y)^2}\right)$$

$$\frac{(1.602\times10^{-19} J)(8)(9.109\times10^{-31})}{6.626\times10^{-34^2}} = \frac{1}{(8.67Å)^2} + \frac{1}{(L_y)^2}$$

For calculations

$$\sqrt{L_y{}^2} = \sqrt{\frac{h^2}{E_n 8m} - (8.67\text{\AA})^2}$$

$$L_y = \sqrt{\frac{h^2}{E_n 8m} - (8.67\text{\AA})^2}$$

$$L_y{}^2 = 2.65a \times 10^{39} -$$

$$2.66 \times 10^{-39} = \frac{1}{7.52 \times 10^{-19}} - \frac{1}{L_y{}^2}$$

$$2.667 \times 10^{-39} = 1.33 \times 10^{18} - \frac{1}{L_y{}^2}$$

is L_y 10% or more larger

10% = 9.537 × 10⁻¹⁰

need to find
L_y that works
then compare relation
ship with
$L_x = L = 8.67\text{\AA}$

6

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2. (25 points) **The electronic structure of Li**

This is a diagram of the electronic energy levels of an isolated Lithium atom.

Lithium energy level diagram

$\text{Li}: 1s^2 2s^1$
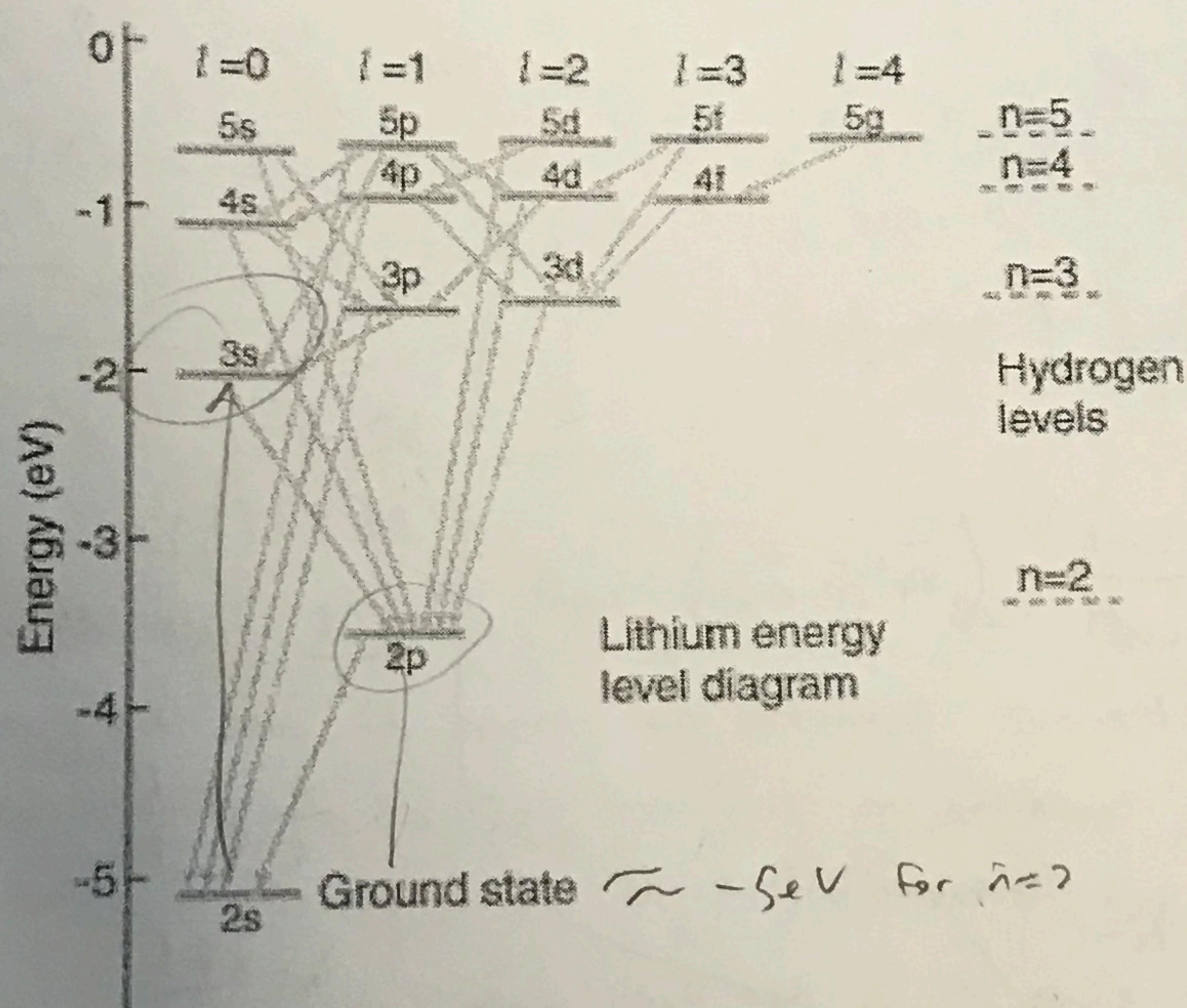
— -98eV

a) (5 points) Write down the electronic configurations of the ground state and the first two excited states of Li. Note that the energy of the 1s level (not shown in the figure) is approximately -98eV. For comparison, the ionization energy of hydrogen is 13.6eV. IE
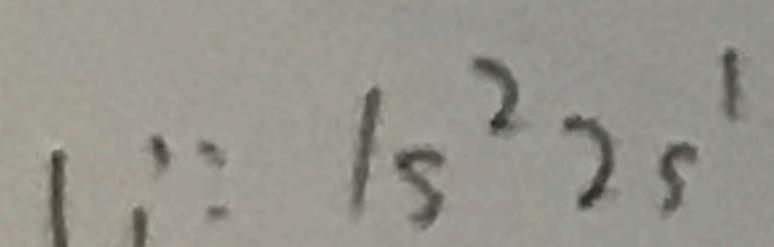
b) (5 points) Using this figure, estimate the two longest wavelengths of light that a Li atom in its ground state can absorb.

$E = \frac{h^2}{8mL^2}\left(n_f^2 - n_i^2\right)$

$h\left(\frac{c}{\lambda}\right)$

c) (5 points) What is the energy of an electron in the ground state of an Li²⁺ ion?

$E = \frac{z^2}{n^2}(13.6)$

$\text{Li}^{2+}: 1s^1$
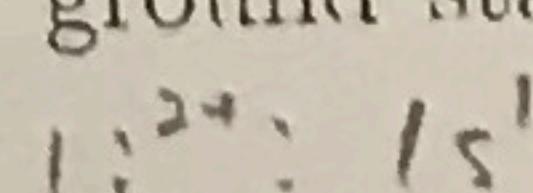
d) (5 points) Explain **in at most two sentences** why the 2s level of Li is significantly lower in energy than the 2p level. Comment in **one sentence** on how these two energy levels compare to the Hydrogen levels (shown on the right hand side of the figure). Be sure to be specific and quantitative.

e) (5 points) Write down the electronic configuration of the Li⁻.

$1s^2 2s^2$

$\text{Li}: (1s^2)(2s^1)$

$\text{Li}: 1s^2 2s^2$ +5

7
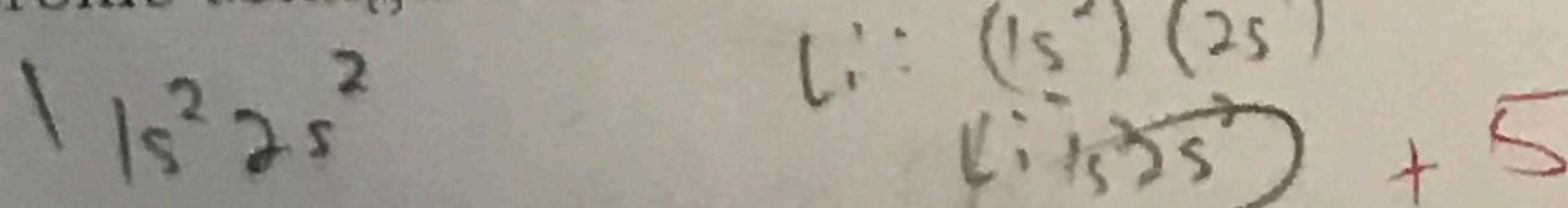
groundstate: $(1s^2)(2s^1)$ +5

(a) first excited: $(1s^2)(2p^1)$

Second excited: $(1s^2)(3s^1)$

(a) on first page

For calculations

$h\left(\frac{c}{\lambda}\right)$

n: 2→1

b) $E = \frac{h^2 n^2}{8mL^2}\left(n_f^2 - n_i^2\right)$

or

$IE = h\nu - \frac{1}{2}mv^2$

$IE = h\left(\frac{c}{\lambda}\right)$

$h\left(\frac{c}{\lambda}\right) = \frac{h^2 \cancel{n^2}}{8mL^2}\left(n_f^2 - n_i^2\right)$

$\frac{\lambda}{c} = \frac{8mL^2}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

$\Delta E = h\nu$

$\Delta E = h\left(\frac{c}{\lambda}\right)$

$\frac{\Delta E}{h} = \frac{c}{\lambda}$

$\lambda = \frac{8cmL^2}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

$\frac{\lambda}{c} = \frac{h}{\Delta E}$

$\lambda = \frac{hc}{\Delta E} \quad IE_1, IE_2$

$\lambda_1 = \frac{hc}{IE_1} \quad -9.8\text{eV}$

$\lambda_1 = (6.626\times10^{-34})($

$\lambda_2 = \frac{hc}{IE_2}$

b)
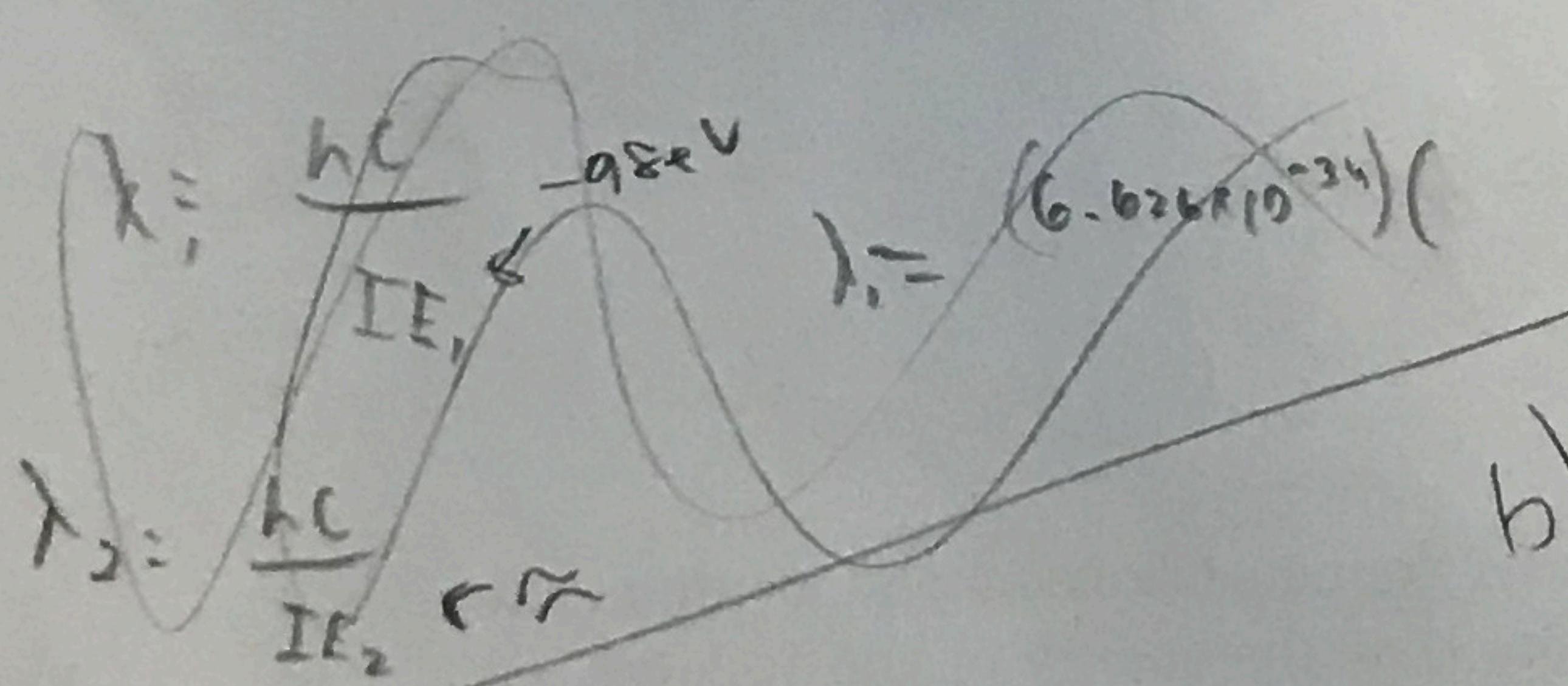
$1eV = 1.602\times10^{-19}\text{J}$

$\lambda_1 = \frac{hc}{-9.8\text{eV} \leftarrow \text{change to J}}$

$\lambda_1 = 1.265\times10^{-8}\text{m}$

+2

$\lambda_2 = \frac{hc}{-5\text{eV}}$

↑
change to
J

based on graph

$IE_2 \approx -5\text{eV}$

8

$\lambda_1 = 2.480\times10^{-7}\text{m}$

E

E=

E=

2=

For calculations

c) Find E of Li^{2+} $\quad$ $z = 3$ $\quad$ $n = 1$
$(1s^1)$

$E_n = \dfrac{z^2}{n^2}(ryd)$

$= \dfrac{3^2}{1}(ryd) = 9(2.18 \times 10^{-18}) = \boxed{1.962 \times 10^{-17} \, J}$ $\quad$ 0

d) The 2s level is lower than the 2p level because the 2s level does not have to access an additional sub-shell and is therefore _closer_ to the nucleus. The 2p level is an additional layer beyond the 2s level making it further away. The hydrogen levels are above the Li levels in $n = 2$ due to their single shell in the ground state as well as the weaker attraction between the nucleus and electrons because of having only 1 proton.

$\sqrt{3}$

e) Li^-
configuration $\quad$ $\leftarrow$ $\quad +5$ $\quad$ 9
$\boxed{(1s^2)(2s^2)}$
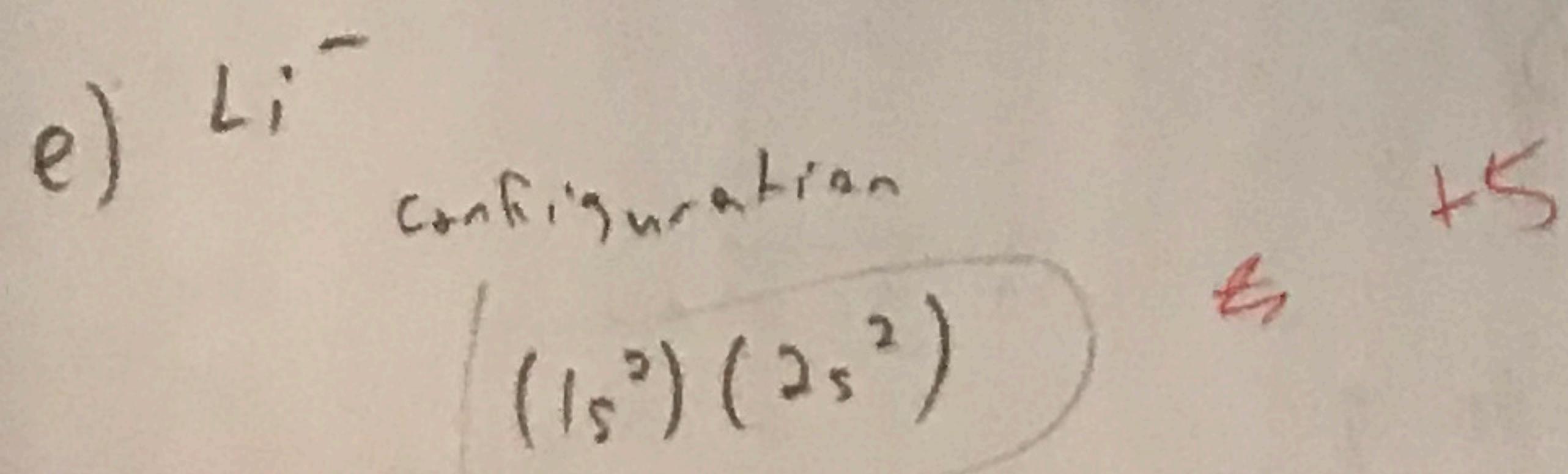
3. (25 points) **Molecular orbitals in diatomic molecules**

(a) (10 points) For each of the following valence electron configurations of a homonuclear diatomic molecule or molecular ion, identify the element X, Q, or Z, and determine the bond order.

- $X_2 : (\sigma_{g2s})^2(\sigma_{u2s}^*)^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi_{g2p}^*)^4$
- $Q_2^+ : (\sigma_{g2s})^2(\sigma_{u2s}^*)^2(\pi_{u2p})^4(\sigma_{g2p_z})^1$ — σ comes first
- $Z_2^- : (\sigma_{g2s})^2(\sigma_{u2s}^*)^2(\sigma_{g2p_z})^2(\pi_{u2p})^4(\pi_{g2p}^*)^3$

(b) (5 points) Consider molecular Fluorine F_2, and its ion F_2^+. Write down the molecular electronic configuration for both species.

(c) (5 points) Give the bond order of these two species and predict if either should be paramagnetic.

(d) (5 points) Which of these Fluorine species has the greater bond dissociation energy and why?

a)

$$\underline{\uparrow\downarrow} \; \underline{\uparrow\downarrow} \; \underline{\uparrow} \quad \overset{\sigma_{u2p}^*}{\uparrow\downarrow \; \uparrow\downarrow} \qquad \underline{\uparrow\downarrow} \; \underline{\uparrow} \; \underline{\uparrow}$$
$$2p \qquad \qquad \pi_{g2p}^* \qquad \qquad 2p$$

π_{u2p}

$\uparrow\downarrow \quad \sigma_{g2p}$

σ_{u2s}^*

$\underline{\uparrow\downarrow} \qquad \uparrow\downarrow \qquad \underline{\uparrow\downarrow}$
$2s \qquad \qquad 2s$

σ_{g2s}
$\uparrow\downarrow$

σ_{u1s}^*

$\underline{\uparrow\downarrow} \qquad \uparrow\downarrow \qquad \underline{\uparrow\downarrow}$
$1s \qquad \qquad 1s$

σ_{g1s}
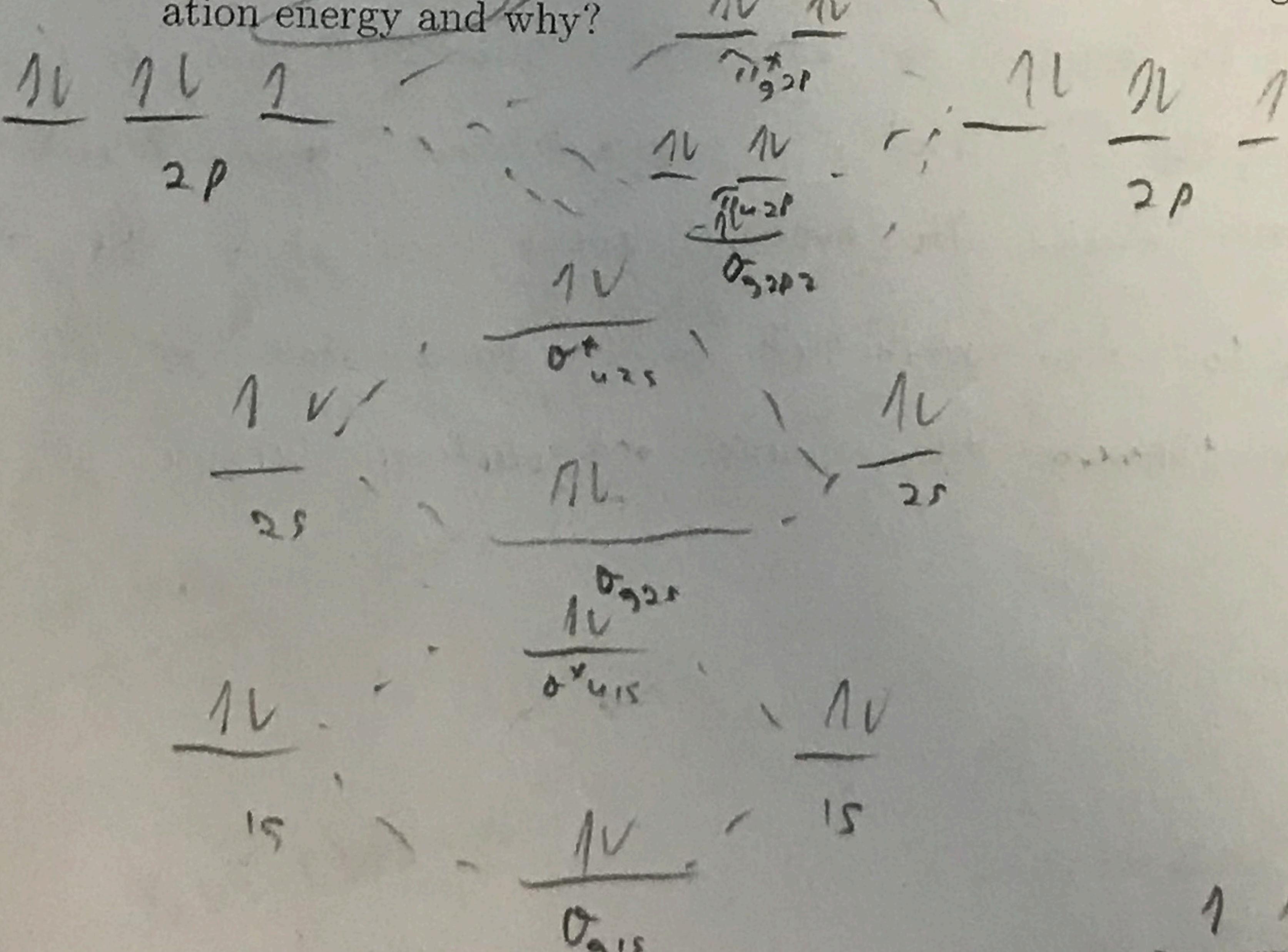
$BO: \frac{1}{2}[\text{bonding} - \text{antibonding}]$

$BO:$

$\underline{\uparrow}\,\underline{\uparrow}\,\underline{\uparrow} \qquad \qquad \underline{\uparrow}\,\underline{\uparrow}$
$2p \qquad \qquad \qquad 2p$

$\uparrow\downarrow \; \sigma_{g2p}$

π_{u2p}

$X_2 : \qquad X = F, \; \boxed{F_2} \qquad BO: \frac{1}{2}[6-4]=\frac{1}{2}(2)=1 \quad \boxed{1}$

$Q_2^+ : \quad Q = N, \; \boxed{N_2^+} \qquad BO: \frac{1}{2}(5-0) = \boxed{\frac{5}{2}} \quad \textcolor{red}{+8}$

$2_2^- := 2 \cdot O. \quad \boxed{O_2^-} \qquad BO: \frac{1}{2}[6-3] = \boxed{\frac{3}{2}}$

$\underline{\uparrow\downarrow} \; \underline{\uparrow} \; \underline{\uparrow}$
$2p$

$\underline{\uparrow\downarrow} \; \underline{\uparrow\downarrow} \; \underline{\uparrow}$
$2p$

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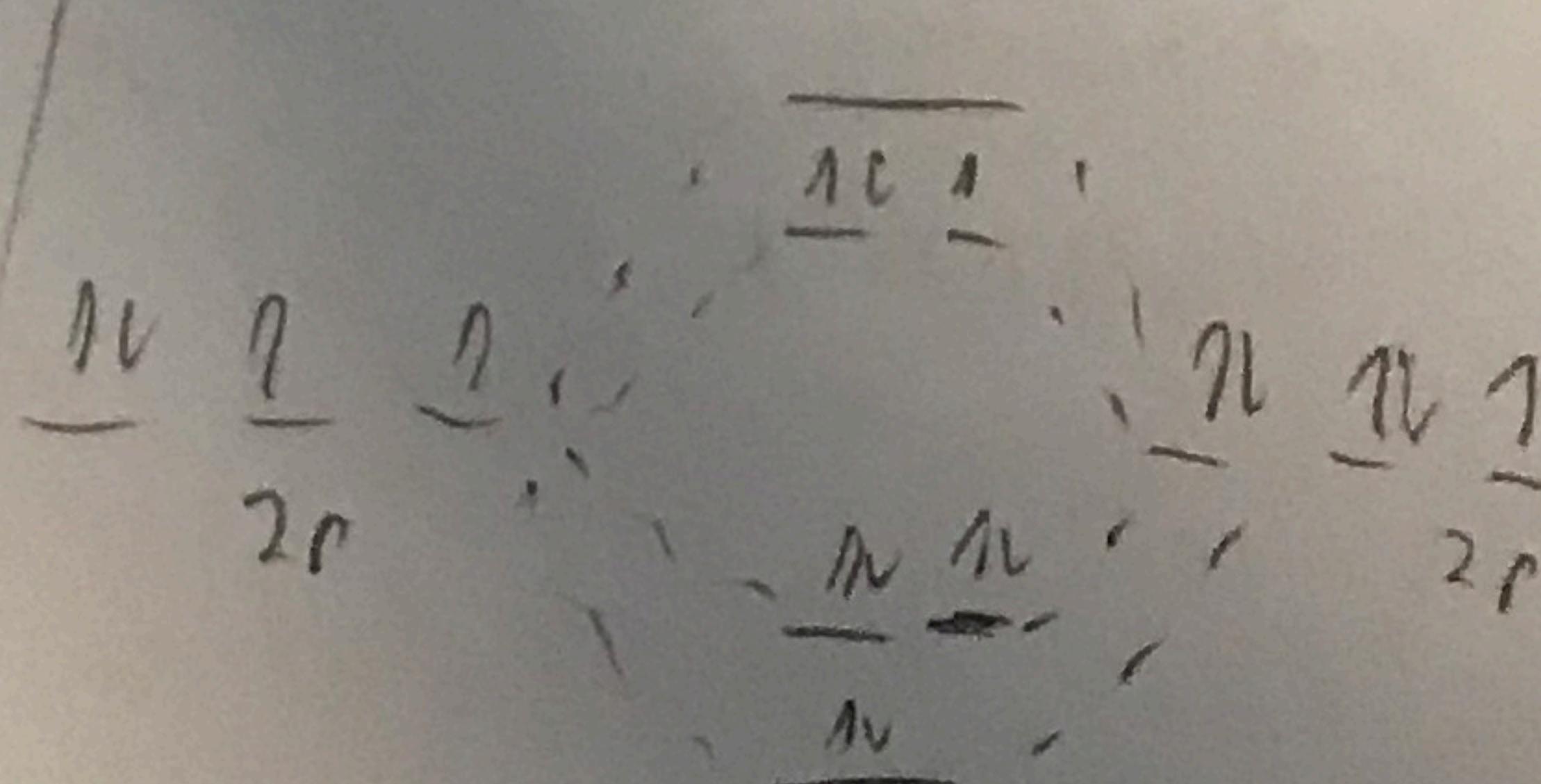
For calculations

b) F_2
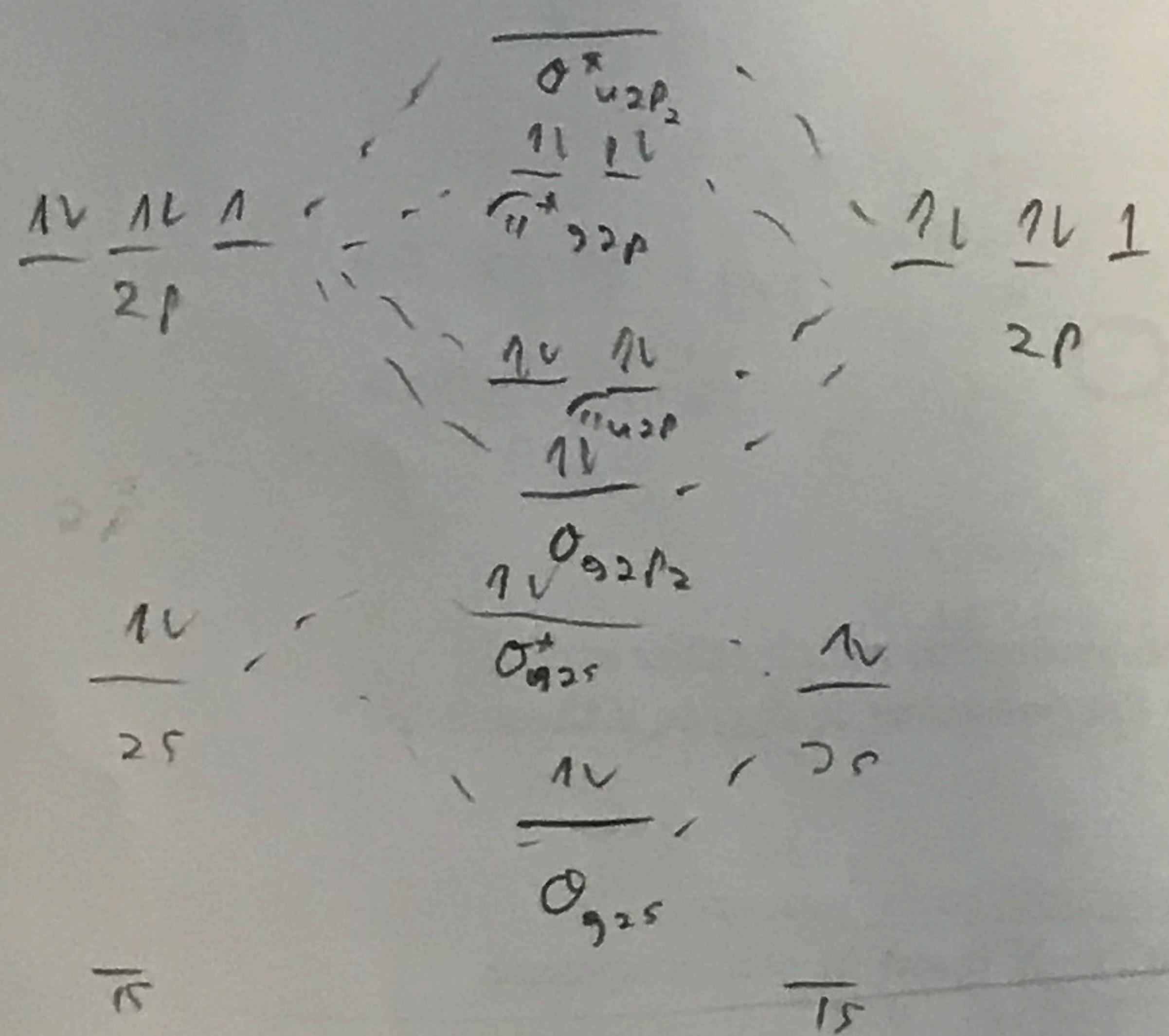
$$F_2: (\sigma_{g1s})^2 (\sigma^*_{u1s})^2 (\sigma_{g2s})^2 (\sigma^*_{u2s})^2 (\sigma_{g2p})^2 (\pi_{u2p})^4 (\pi^*_{g2p})^4$$

$$F_2^+: (\sigma_{g1s})^2 (\sigma^*_{u1s})^2 (\sigma_{g2s})^2 (\sigma^*_{u2s})^2 (\sigma_{g2p})^2 (\pi_{u2p})^4 (\pi^*_{g2p})^3$$

+5

c) $BO_{F_2}: \frac{1}{2}(6-4) = \frac{2}{2} = 1$

$BO_{F_2^+}: \frac{1}{2}(6-3) = \frac{3}{2}$

+5

F_2: diamagnetic (not paramagnetic)

F_2^+: paramagnetic

d) F_2^+ +5 would have a greater bond dissociation energy because it has a stronger bond due to a higher bond order. There is a stronger energy holding the electrons to the nucleus because there are less antibonding orbitals

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4.(25 points) **Nitroamide**

NH_2NO_2

H

H — N — N

O

O

NH_2 NO_2

$1+1+10+12 = 24$

$36-24: 12/2 = 6$
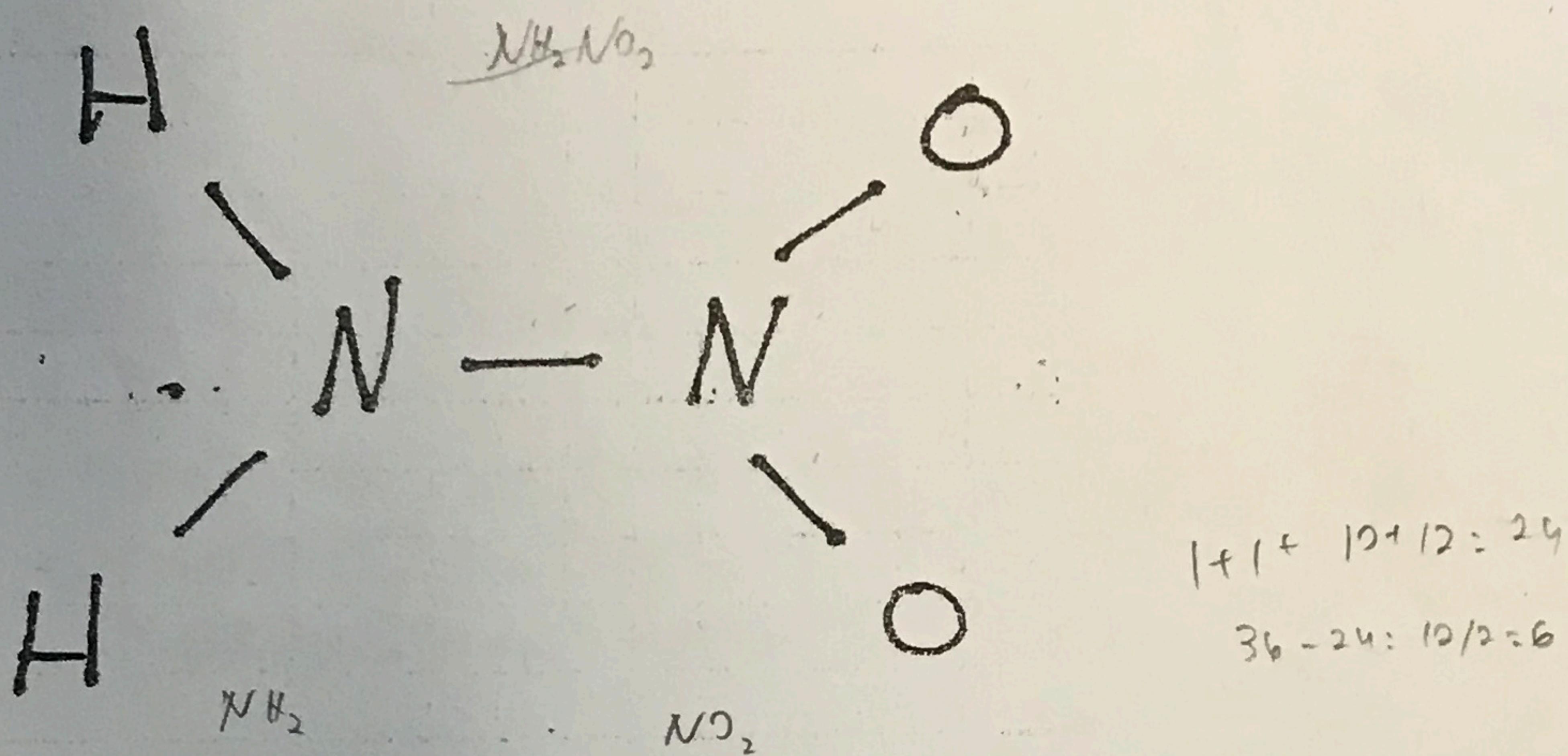
Figure 1: The above figure shows which atoms are bonded to which other atoms in the molecule. It will be up to you in answering the questions to decide if these are single or double bonds.

is a **nonplanar** molecule. It was previously thought to be planar.

(a) (15 points) Predict the bond order of the N–N bond in the nonplanar structure

N–N

(b) 10 points) If the molecule were planar after all, what would be the bond order of the N–N bond?
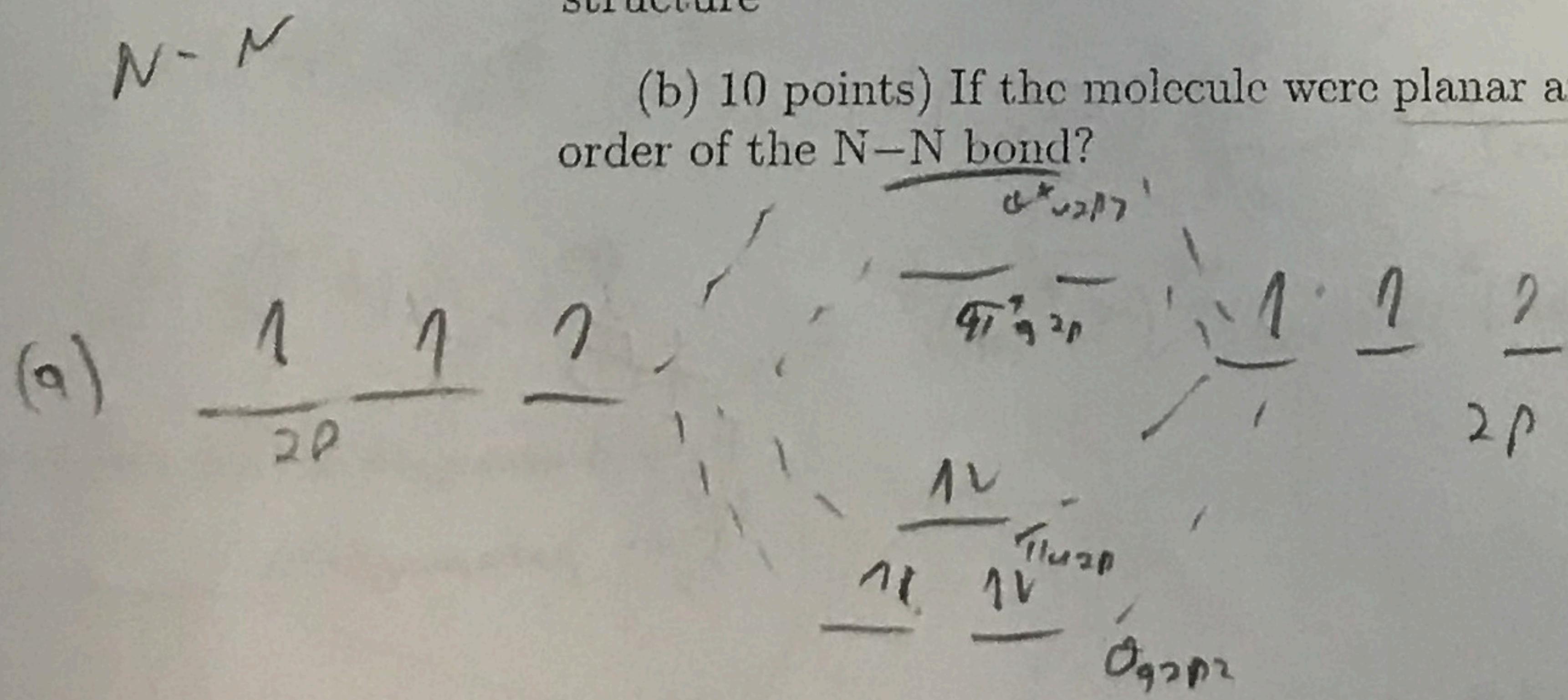
σ^*_{2p}

(a) ↑ ↑ ↑ π^*_{2p} ↑ ↑ ↑

$\overline{2p}$ $2p$

↑↓   BO: $\frac{1}{2}(bonding - antibonding)$

↑↓ ↑↓ π_{2p}

σ_{2p} $= \frac{1}{2}(6-0) = \boxed{3}$

↑↓

↑↓   ↑↓

$2s$ $2s$

↑↓

↑↓   ↑↓

$1s$ $1s$

12
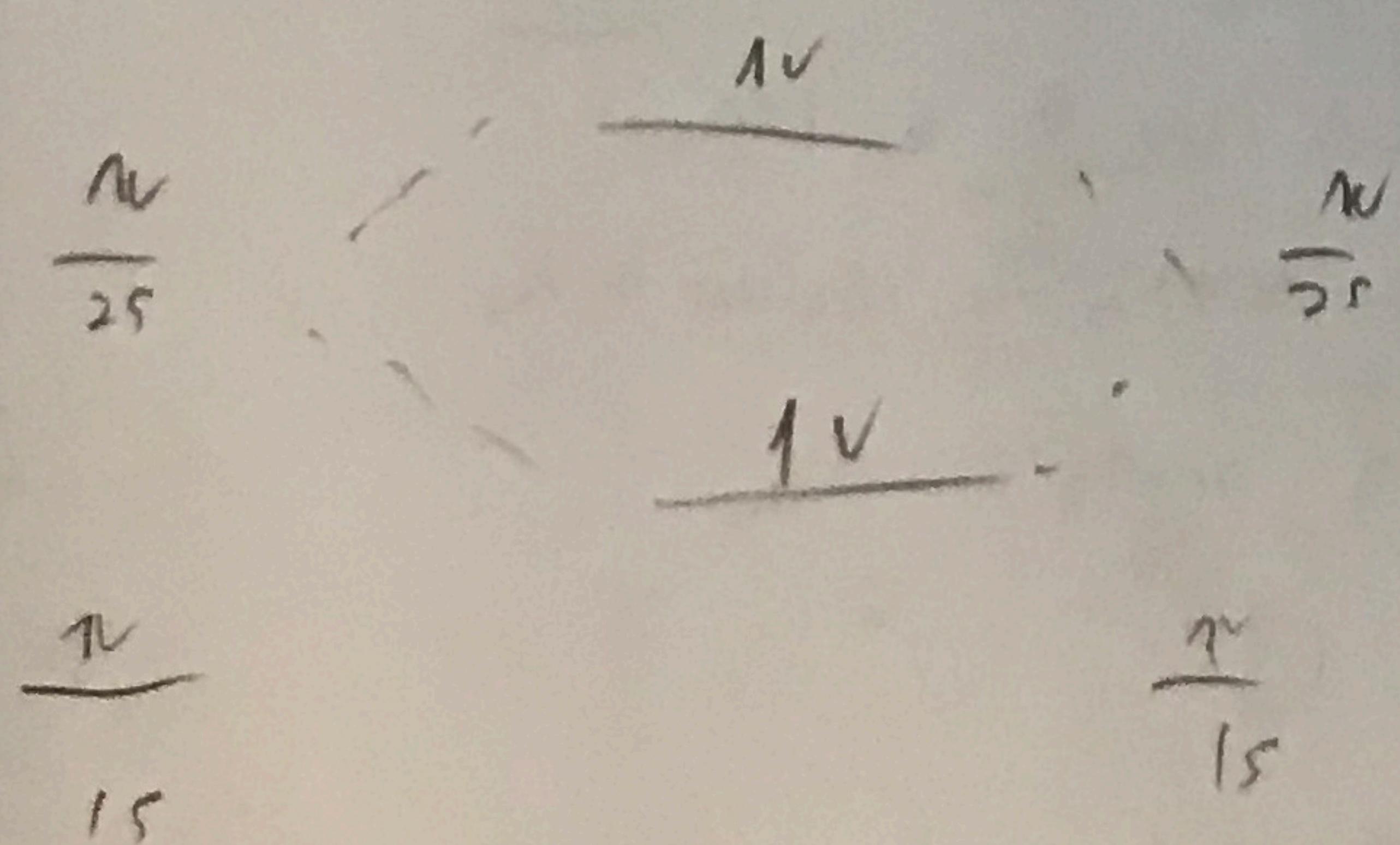
(b) If were planar

$$2 + 2(5) + 2(6) = 24$$

$$32 + 4 = 36$$

$$36 - 24 = 12/2 = 6 \text{ bonds}$$

bond order = 2

Lec 1
Public Affairs Building 1246

MECH&AE 103
Lec 1
Public Affairs Building 1246

MECH&AE 105A
Dis 1A
Boelter Hall 2444
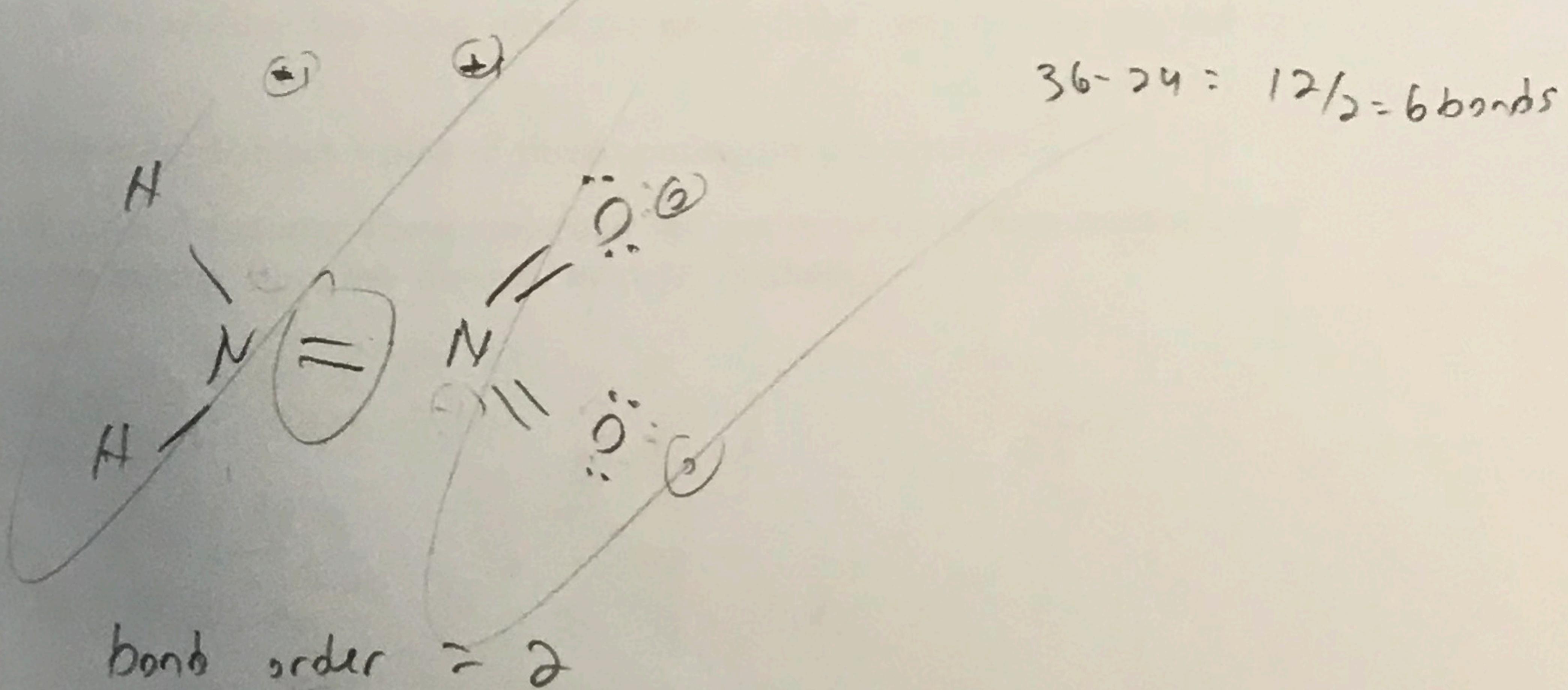
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Scott Hoppes

5.(25 points) **Molecular Oxygen and its ions**
When one electron is added to an oxygen molecule, a superoxide ion O_2^- is formed. The addition of two electrons leads to a peroxide ion O_2^{2-}. The removal of an electron from molecular oxygen generates a positive ion O_2^+

(a) (5 points) Construct a correlation diagram for O_2^-.

(b) (5 points) Give the valence electron configuration for each of the species: O_2^+, O_2, O_2^-, O_2^{2-}.

(c) (5 points) Give the bond order for each of the species from the list in part b.

(d) (5 points) Predict which of these species are paramagnetic.

(e) (5 points) Arrange these molecular species in order of **increasing** bond dissociation energy from left (lowest) to right (highest).

(a) O_2^-

b) O_2^+: $(\sigma_{g\,2s})^2 (\sigma^*_{u\,2s})^2 (\sigma_{g\,2p})^2 (\pi_{u\,2p})^4 (\pi^*_{g\,2p})^1$

O_2: $(\sigma_{g\,2s})^2 (\sigma^*_{u\,2s})^2 (\sigma_{g\,2p})^2 (\pi_{u\,2p})^4 (\pi^*_{g\,2p})^2$

O_2^-: $(\sigma_{g\,2s})^2 (\sigma^*_{u\,2s})^2 (\sigma_{g\,2p})^2 (\pi_{u\,2p})^4 (\pi^*_{g\,2p})^3$

O_2^{2-}: $(\sigma_{g\,2s})^2 (\sigma^*_{u\,2s})^2 (\sigma_{g\,2p})^2 (\pi_{u\,2p})^4 (\pi^*_{g\,2p})^4$
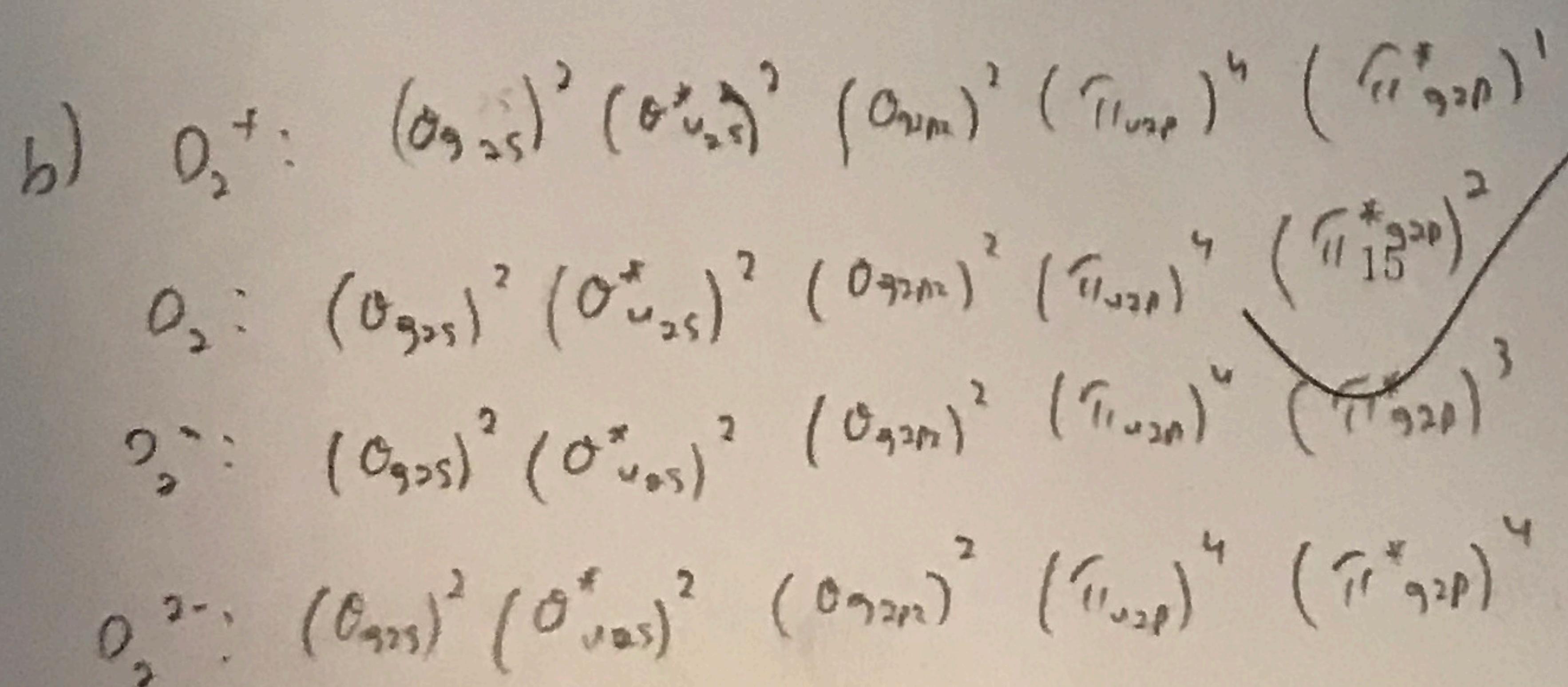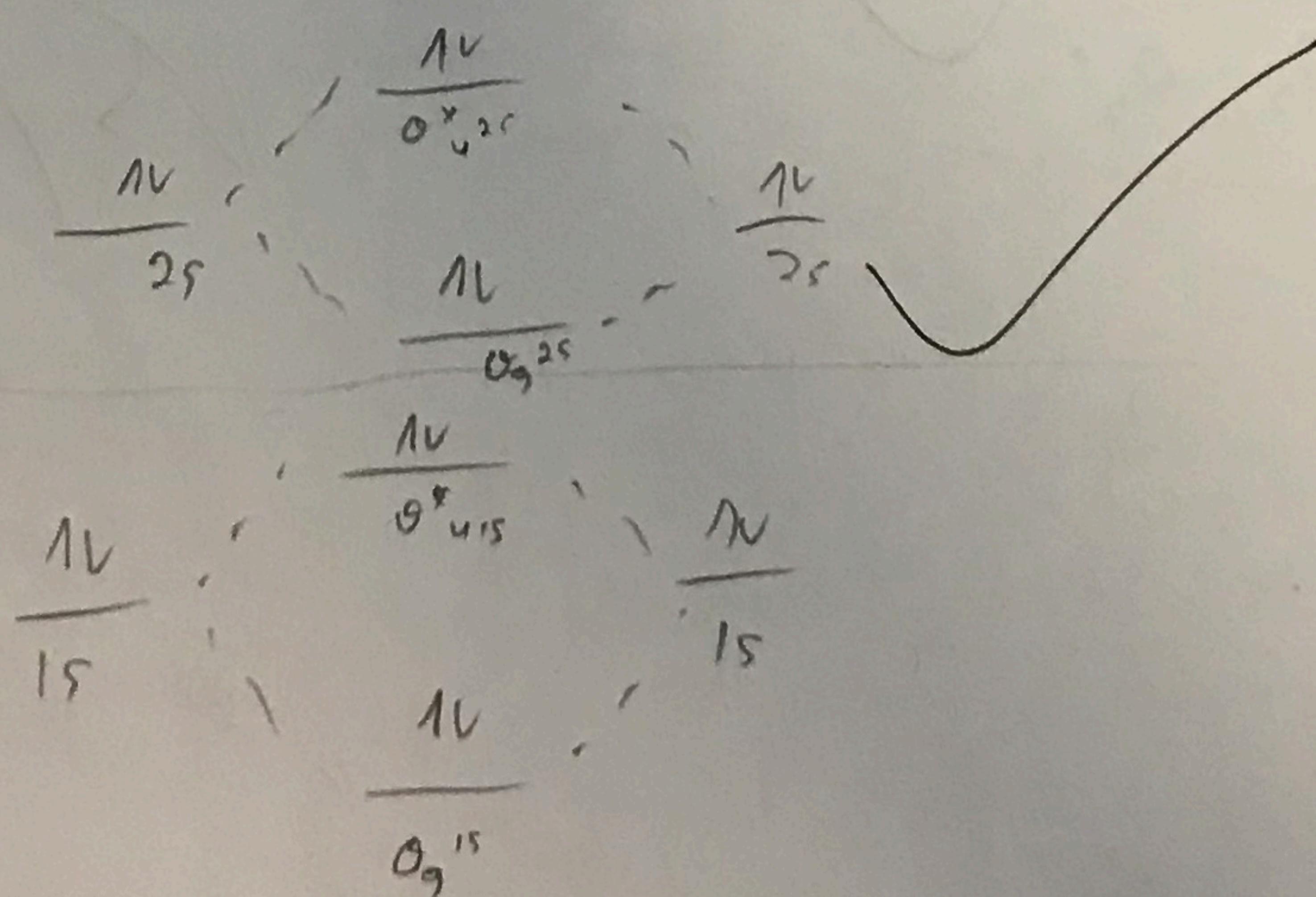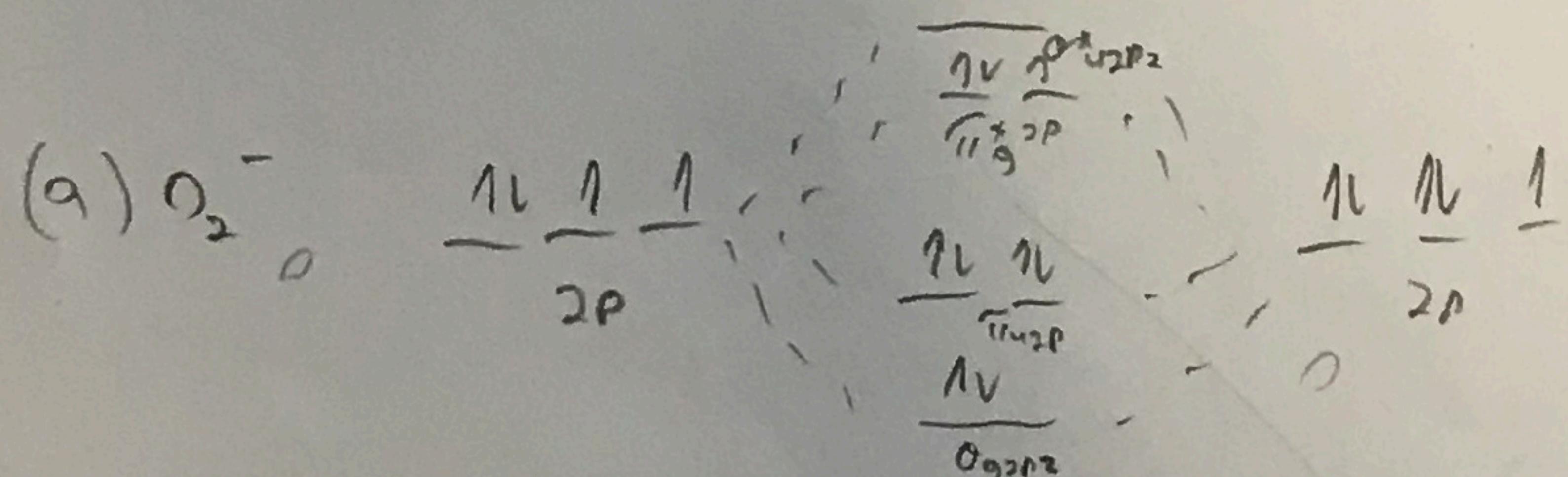
c) O_2^+: $BO = \frac{1}{2}(6-1) = \frac{5}{2}$

O_2: $BO = \frac{1}{2}(6-2) = \frac{4}{2} = 2$

O_2^-: $BO = \frac{1}{2}(6-3) = \frac{3}{2}$

O_2^{2-}: $BO = \frac{1}{2}(6-4) = \frac{2}{2} = 1$

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For Calculations

d) O_2^+ : paramagnetic

O_2 : paramagnetic

O_2^- : paramagnetic

O_2^{2-} : not paramagnetic ✓

e) increasing bond dissociation energy

lowest BO → highest BO

O_2^{2-} , O_2^- , O_2 , O_2^+ ✓

25/25