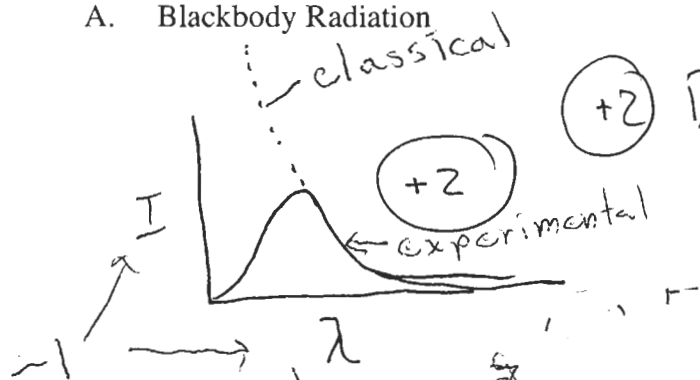**1.   (8+7 points)**   Briefly describe each of the following revolutionary 20th Century experiments and the important results obtained from its explanation. Sketch the results obtained and compare with "classical" predictions.
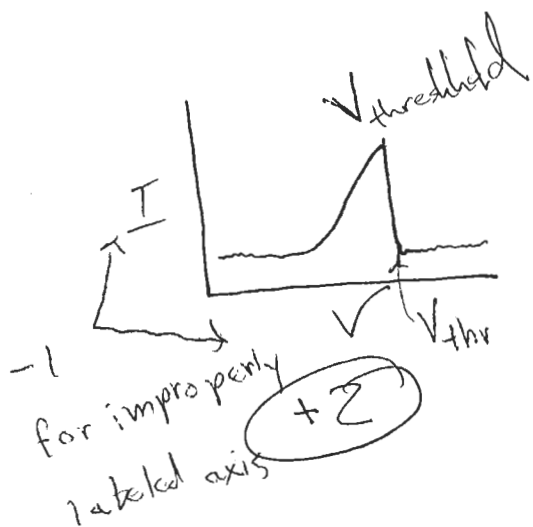
A.   Blackbody Radiation

classical

⊕ +2

experimental

I

~1

for improperly labeled axis

λ

(+2) Description: study of radiation given off by a hot body.

(light)

(+2) Classical wrong for short λ
goes off to ∞, ultraviolet catastrophe
not quantized

(+2) Light oscillations can only take on certain values
⟹ Energy is quantized $E = nh\nu$

B.   Franck-Hertz Experiment

$V_{threshold}$

(+2) e⁻ colliding with gaseous molecules in a N cathode, measure current

I

~1

for improperly labeled axis

(+2)

V_{thr}

through tube as you increase voltage

(+2) quantized E levels
in gas atoms → proves
Bohr's model for quantized
electronic transitions

(+1) no drop in classical

2.   **(5 points each)** Consider the (one-dimensional) Quantum Well (or Particle in a-Box) Model for a confined electron at 1000 K (Energy $\approx k_B T$):

A.   To what length (meters) must the electron be confined for quantum effects to be "appreciable?"

$$\lambda = \frac{h}{p} \qquad E = \frac{p^2}{2m}$$

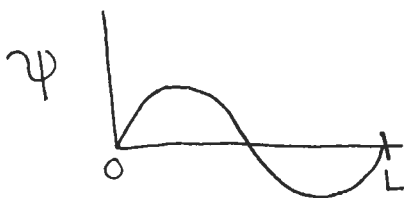$$\lambda = \frac{h}{(2mk_B T)^{1/2}} = 4.2 \times 10^{-9} \text{ m}$$

B.   What is the wavelength (m) for the lowest allowed transition for an electron in a 1.00×10^{-10} m well?

$$\Delta E = \frac{h^2}{8mL^2}\left(n_2^2 - n_1^2\right) = \frac{h^2}{8mL^2}\left(4-1\right)$$

$$= 1.81 \times 10^{-17}$$

$$\Delta E = \frac{hc}{\lambda} \qquad \lambda = \frac{hc}{\Delta E} = 1.10 \times 10^{-8} \text{ m}$$

C.   Sketch and properly label the <u>wave function</u> for the n = 2 states (for 0 < X < L).

D.   Why is a cosine function not an acceptable form for the electron wave function?

ψ must be 0 at X=0, however, cos(0) = 1 so it is unnacceptable.

3.   **(5 points each)** The wave function of an electron in the ground state of the hydrogen atom is

$$\varphi(r) = \left(\frac{1}{\pi\alpha_0^3}\right)^{1/2} \exp\left(-\frac{r}{\alpha_0}\right)$$
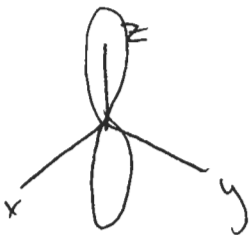
$$\alpha_0 = 0.529 \times 10^{-10}\,\text{m}$$

A.   What is the probability of finding the electron in a volume of 1.0 pm^3 at a distance of 52.9 pm from the nucleus, in a fixed but arbitrary direction?

$$\psi^2(r = 52.9 \times 10^{-12}) = \frac{1}{\left(\pi\,(.529\times10^{-10})^3\right)}\,\exp\left[\frac{-2\,(52.9\times10^{-12})}{.529\times10^{-10}}\right]$$
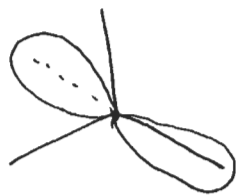
(+3) $= 2.91 \times 10^{29}\,m^{-3}$

(+2) $P = \psi^2 \Delta V = \left(2.91 \times 10^{29}\,m^{-3}\right)\left(1 \times 10^{-36}\,m^3\right)$

$$= 2.91 \times 10^{-7}$$
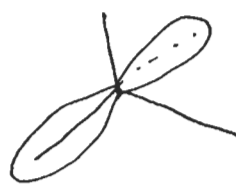
B.   Sketch and label the atomic orbitals corresponding to n = 2, ℓ =1, showing radial and/or angular nodes.
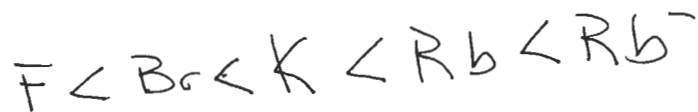

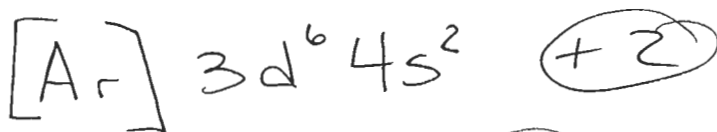P_z P_y P_z (+3)

(+2)

C.   Arrange the following five atoms or ions in order of size, from the smallest to the largest: K, Rb, Br, F, Rb⁻.

$$F < Br < K < Rb < Rb^-$$
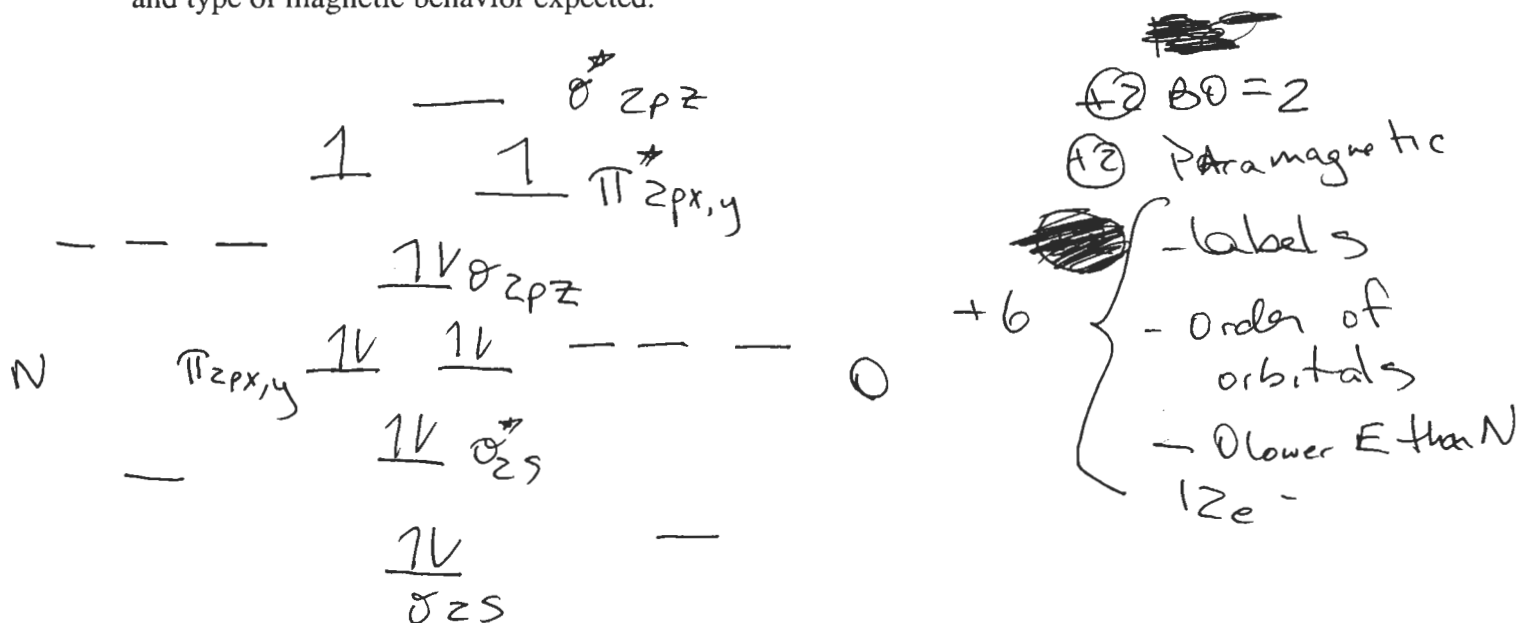
(+5)

D.   Write the electron configuration for iron. Is it paramagnetic?

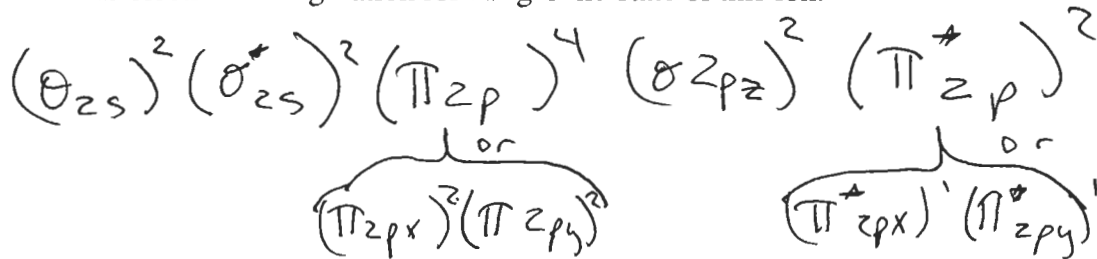$$[Ar]\ 3d^6\ 4s^2 \quad (+2)$$

paramagnetic (+3)

4.   **(10+5+5+5 points)**   Consider the bonding in the NO⁻ anion.

A.   Draw and label the appropriate molecular orbital correlation diagram and predict the bond order and type of magnetic behavior expected.
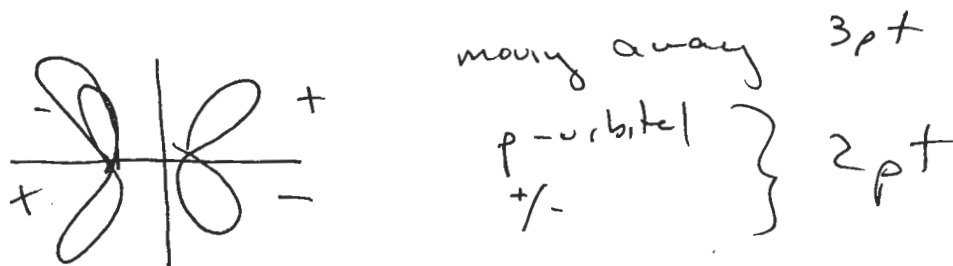

B.   Write the electron configuration for the ground state of this ion.

$$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma 2p_z)^2 (\pi_{2p}^*)^2$$

or

$$(\pi_{2p_x})^2 (\pi_{2p_y})^2$$

or

$$(\pi_{2p_x}^*)^1 (\pi_{2p_y}^*)^1$$

C.   Write the expression (no explicit functions needed) for the 2p σ* antibonding wave function in terms of atomic wave functions.

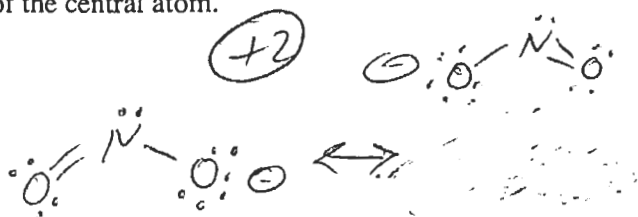$$\sigma_{2p}^* = C_1 \Psi_{2p_z} - C_2 \Psi_{2p_z}$$

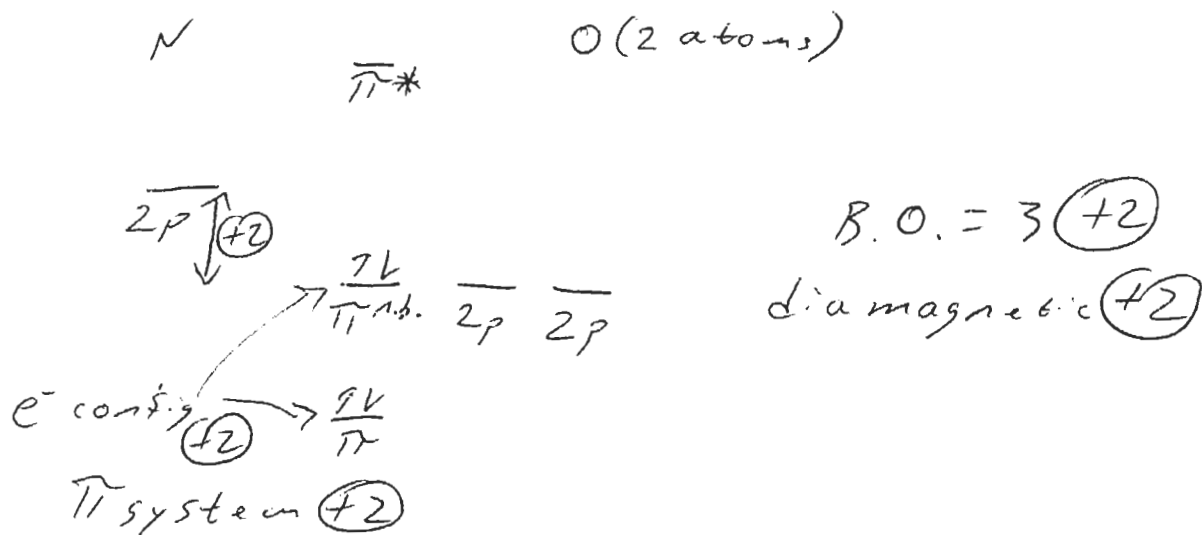D.   Sketch and label the 2p π* antibonding orbital.

moving away   3p t

p - orbital   } 2p t

+/-

5.   **(5+10+5 points)**   Consider the nitrite ion $\left(NO_2^-\right)$.

A.   Draw an approximate Lewis structure and predict the steric number, geometry, and hybridization of the central atom.
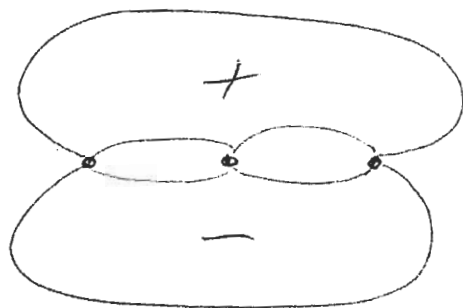

$SN = 3$ (+1)
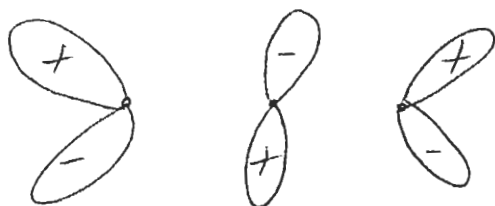
geometry = bent (+1)

hybridization = sp^2 (+1)

B.   Draw and label the molecular orbital correlation diagram for the pi electrons, and predict the bond order and magnetic behavior.

N   π*   O (2 atoms)

2p (+2)

π n.b.   2p   2p

B.O. = 3 (+2)

diamagnetic (+2)

e⁻ config (+2) → π

π system (+2)

C.   Sketch and label the π-bonding, π-antibonding, and π-nonbonding orbitals formed from the atomic p-orbitals.

π bonding (+1)

π-antibonding (+2)

π-nonbonding (+2)