

Photoelectron Spectroscopy

- Empirically determine a.o. energies for use in M.O. theory

Verify predictions of M.O. theory by measuring M.O. energies.

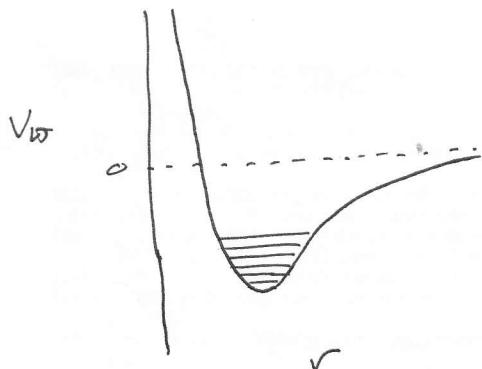
Physical Principle

Lennard-Jones / Morse potential to describe energy of bond (or collection of bonds) distortion(s).

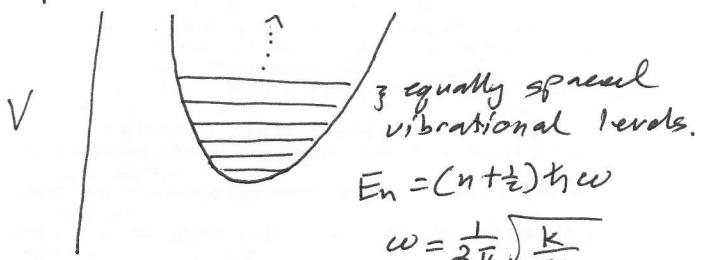
$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

ϵ = depth of potential well
 σ = r for which $V_{LJ} = 0$.

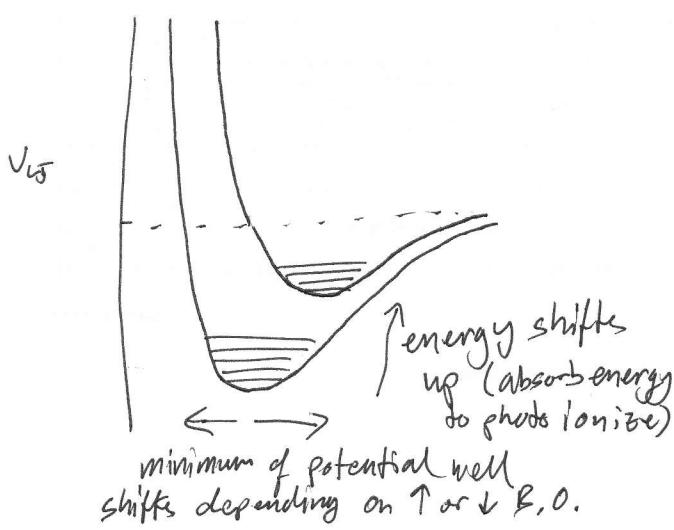
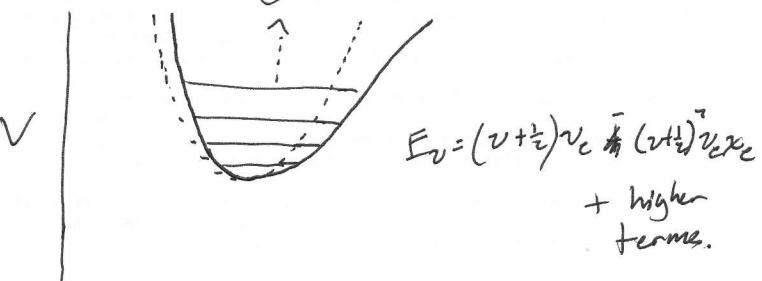
r = bond length, nuclear coordinates, etc.



For a given e^- configuration, approximate by harmonic / parabolic potential.

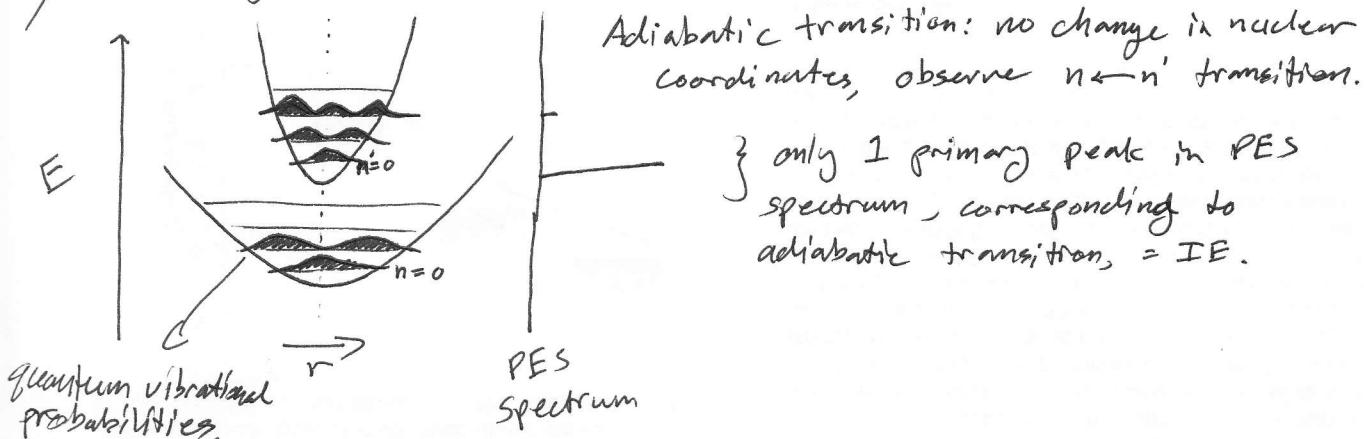


* In actuality, shape of potential well is not perfectly symmetric, has anharmonicity.



Three possibilities in PES (as far as we are concerned).

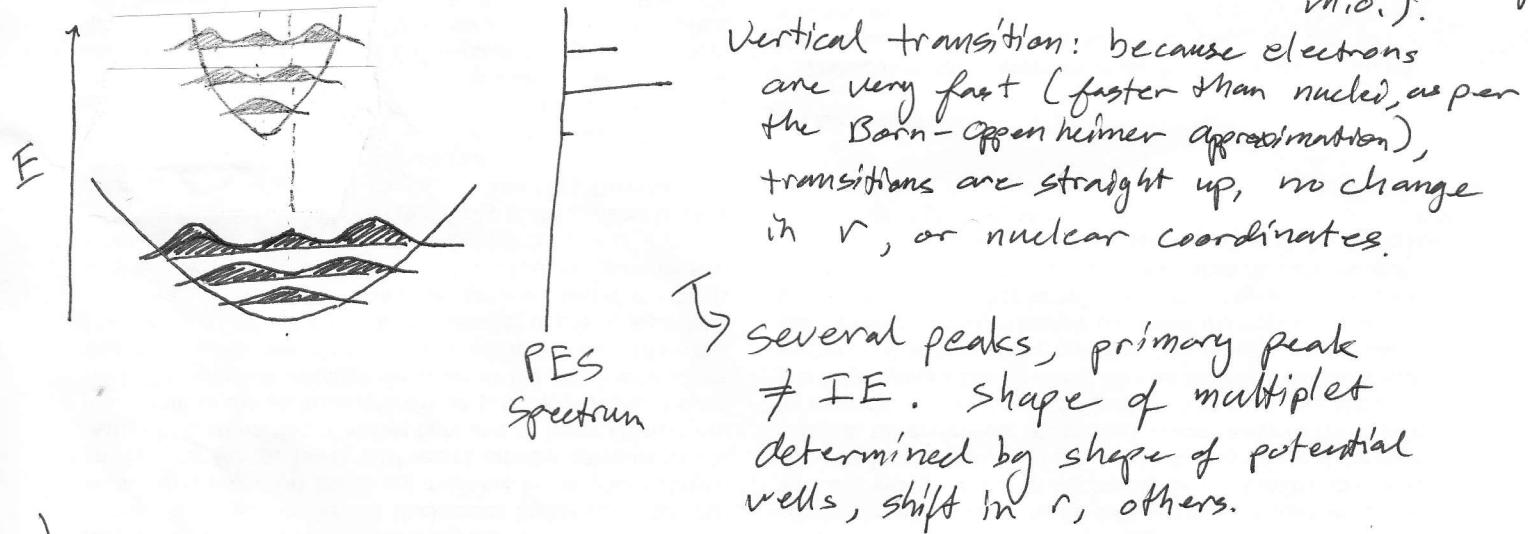
1) No change in bond order (upon ionization) (e^- taken from non-bonding m.o.)



Adiabatic transition: no change in nuclear coordinates, observe $n \leftarrow n'$ transition.

only 1 primary peak in PES spectrum, corresponding to adiabatic transition, = IE.

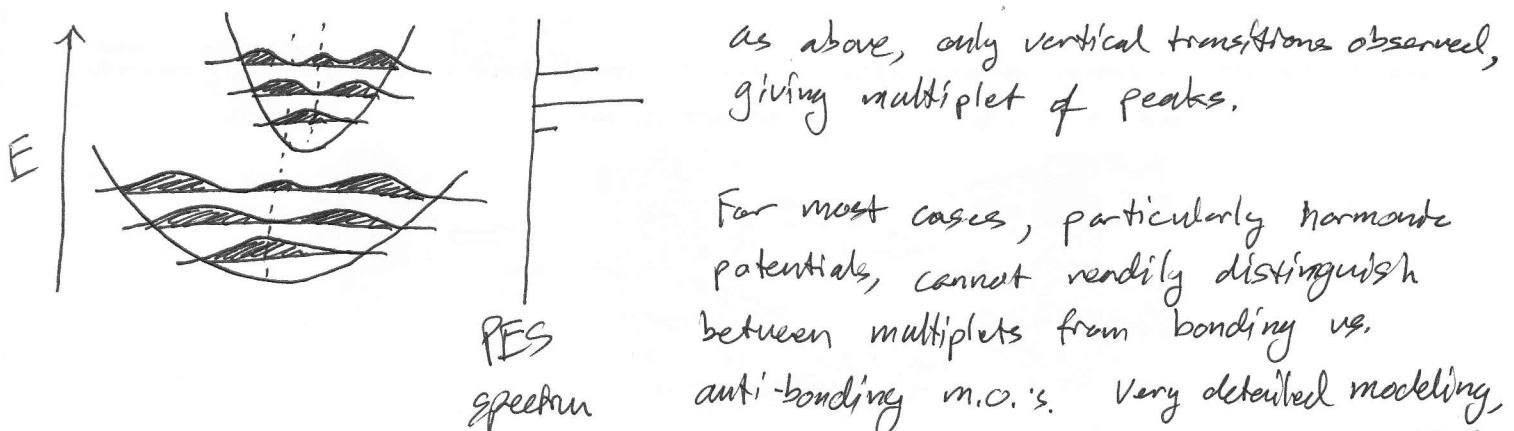
2) Increasing bond order (upon ionization) (e^- taken from anti-bonding m.o.).



Vertical transition: because electrons are very fast (faster than nuclei, as per the Born-Oppenheimer approximation), transitions are straight up, no change in r , or nuclear coordinates.

Several peaks, primary peak \neq IE. Shape of multiplet determined by shape of potential wells, shift in r , others.

3) Decreasing bond order (upon ionization) (e^- taken from bonding m.o.).



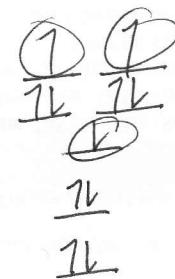
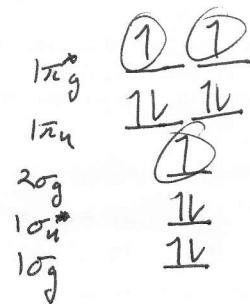
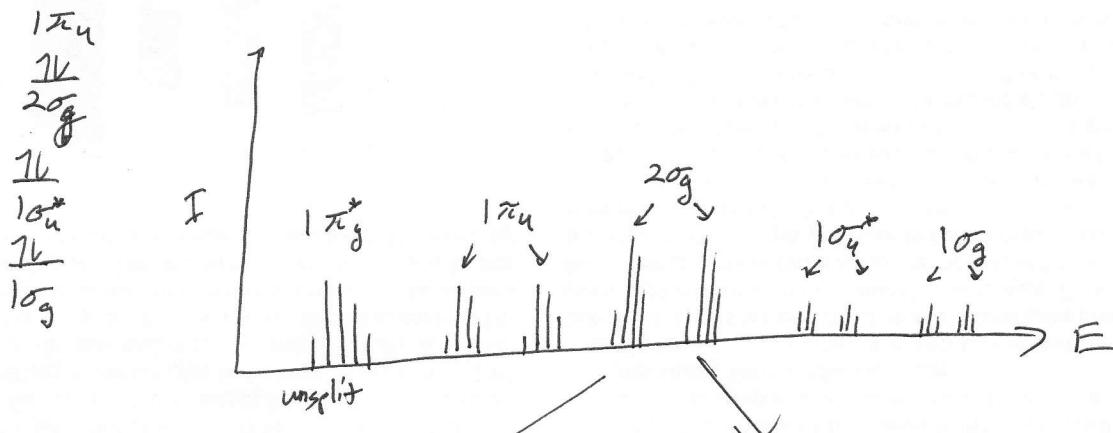
as above, only vertical transitions observed, giving multiplet of peaks.

For most cases, particularly harmonic potentials, cannot readily distinguish between multiplets from bonding vs. anti-bonding m.o.'s. Very detailed modeling, taking into account anharmonicity could help but beyond the scope of this course.

(4.) Special case for paramagnetic molecules, i.e. w/ unpaired e⁻.

For O₂: $\frac{1}{1} \frac{1}{1}$ → paramagnetic,
unpaired e⁻.

Ideal, perfectly resolved spectrum.



electron spin-spin
coupling splits
the PES multiplet,
for all e⁻ (in theory).

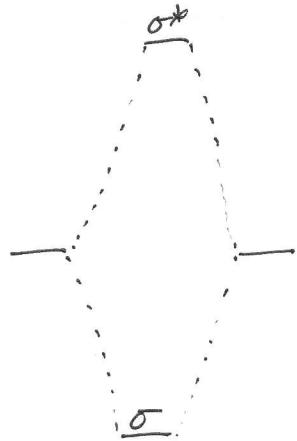
Molecular Orbital Theory

- Mix atomic orbitals from different atoms (compare to VBT, same atom) to get bonding (stabilized) and antibonding (destabilized) orbitals.
 - \downarrow build up of e^- density between nuclei = bond (add symmetry matched orbitals)
 - \downarrow node, depletion of e^- density between nuclei. (subtract symmetry matched orbitals).
- Can also combine M.O.'s w/ each other. (for more complicated molecules, coming next week).
- Energies and spatial distribution of resulting M.O.'s predict chemical properties. (i.e. reactivity, magnetism, spectra, etc.).

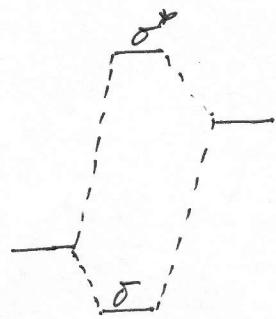
Orbital Interaction Diagram

- 1) Plot energy level of a.o.'s (or fragment M.O.'s).
 - From PES ~~spectroscopy~~ (directly for a.o.'s)
(deduced for fragment M.O.'s).
- 2) Determine which orbitals will mix.
 - Energies $\leq 15\text{eV}$
 - Same symmetry.
- 3) Determine magnitude of interaction:
 - overlap (shape of orbital, nuclear distance),
 - energy difference
- 4) Plot MOs and draw resulting orbital shapes.
 - for every orbital pair, get one bonding and one antibonding M.O.
- 5) Fill in w/ electrons (Aufbau principle).

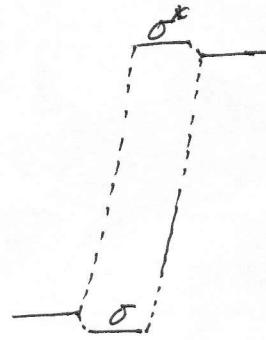
Generally: Energy matching



Strong covalent bond

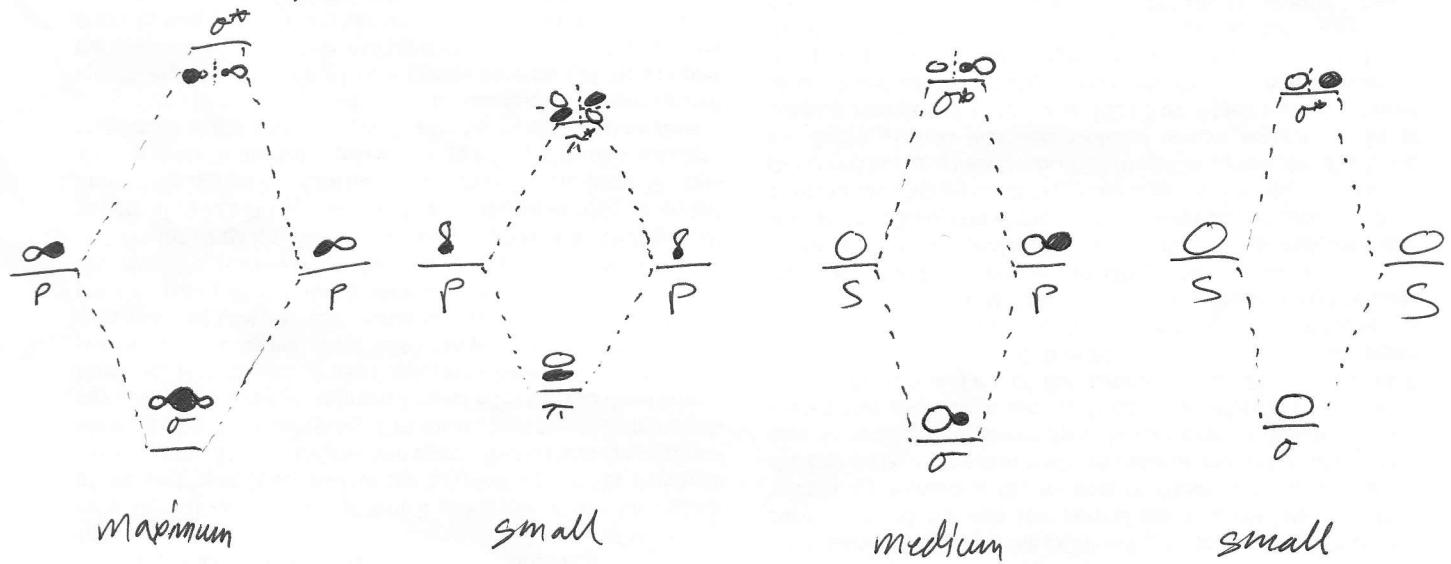


polar-covalent



ionic, nonbonding

Overlap



maximum

small

medium

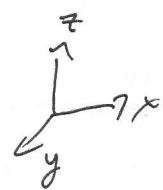
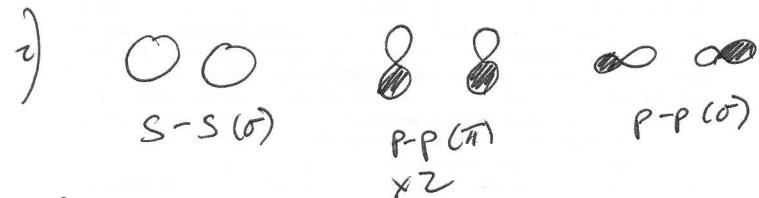
small

*delta bond (δ - δ overlap) smallest.

See slides for depiction of possible bonding combinations.

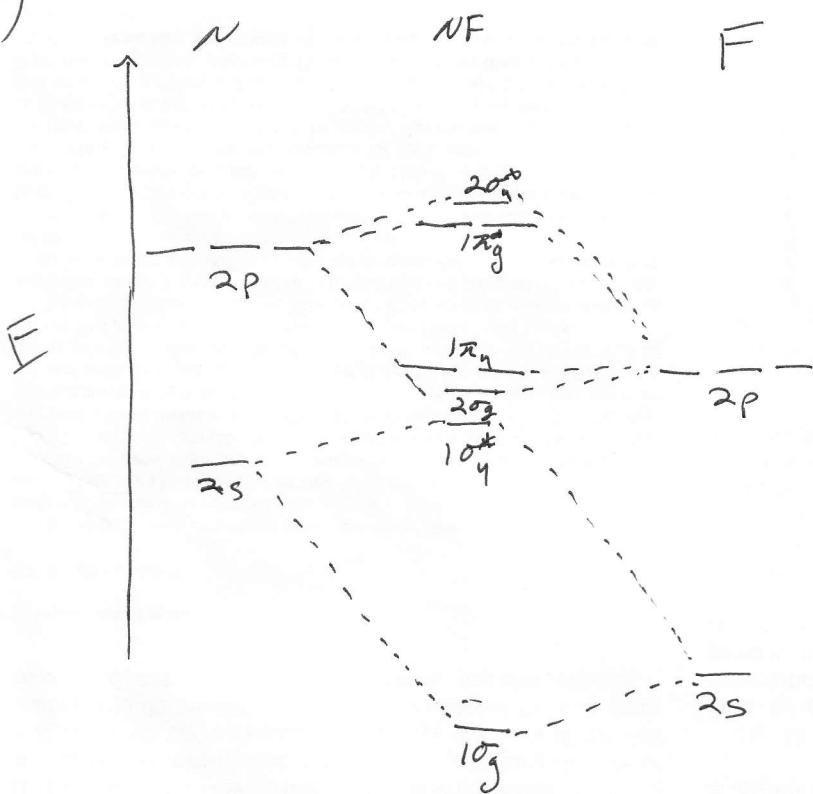
Example: NF , NF^+ , NF^-

$$\begin{array}{ll} 1) 2s(N) = -25.6 \text{ eV} & 2s(F) = -40.2 \text{ eV} \\ 2p(N) = -13.2 \text{ eV} & 2p(F) = -18.6 \text{ eV} \end{array}$$

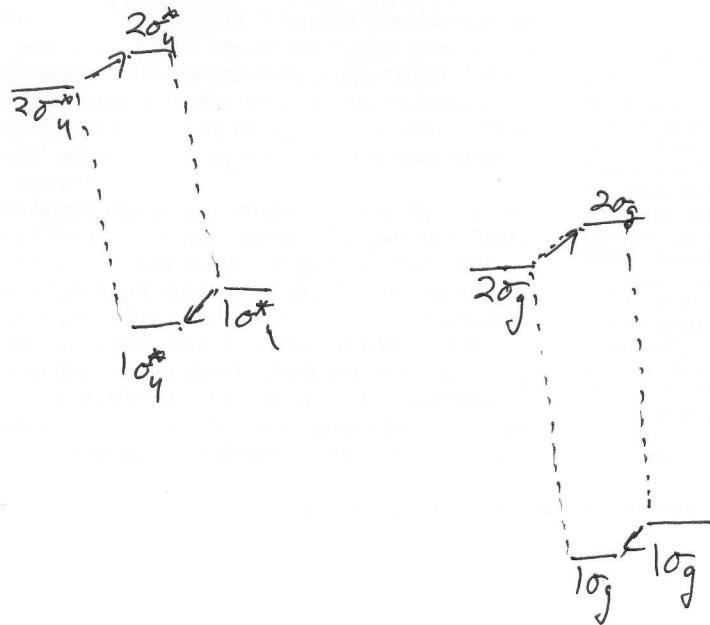


S-P (σ) Maybe?
 all energies within ≈ 15 eV from each other. S-S, P-P and SP mixing.

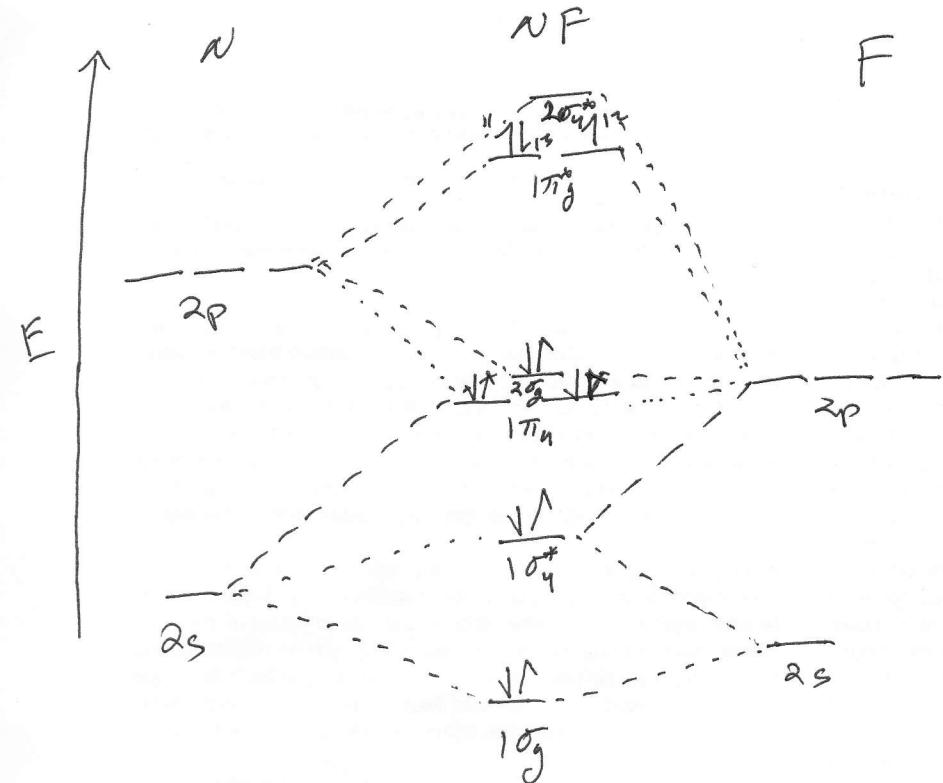
(3,4)



First consider no mixing of S-P.



Then mix S-P m.o.'s



5) for NF , $7e^- + 5e^- = 12e^-$
 NF^+ , $11e^-$
 NF^- , $13e^-$

Bond orders: NF^+ : $\frac{5}{2}$ ($\frac{8 \text{ bonding } e^- - 3 \text{ anti-bonding } e^-}{2}$)

NF : 2 I

NF^- : $\frac{7}{2}$ filled $1\pi_g + 1\pi_u^*$
 give net B.O. = 0.

Para magnetism? all exhibit paramagnetism (unpaired e^-).

$\overline{\delta}$ splits each peak in the ~~paramagnetic~~ PES, except for $1\pi_g^*$.
 In NF , NF^+

