MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry I
Fall, 2017

Professor Robert W. Field

Lecture 25: Molecular Orbital Theory of Diatomic Molecules. II

In 5.111/5.112 we use orbital energies and *shielding* arguments to rationalize the Periodic Table. All properties, all atoms: IP, Electronegativity, size (via IP and modified Rydberg formula).

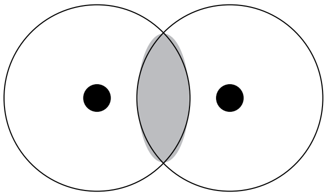
My personal vision has been to extend the periodicity of electronic properties from atoms to molecules. This lecture and a significant part of Exam III is constructed around that vision.

This lecture is intended to enable you to intuit the properties of H_2, AH, A_2, and AB diatomic molecules. Larger molecules would follow.

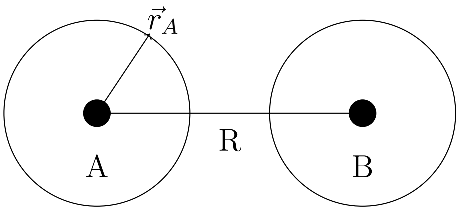
Toy Models — naive but SMART approximations

Semi–Empirical calculations — to calibrate the Toy Model based on *atomic energy levels*, *atomic sizes*, and *qualitative lessons learned from* the H_2^+ LCAO-MO model.

Orbitals: Pictures, Names, Bonding/Anti-bonding Properties



bonding is due to *constructive interference* that arises from overlap, S, in the region between the 2 nuclei

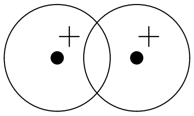


Bond strength is roughly proportional to overlap

$$S_{n\ell\lambda}(R) = \int n\ell\lambda_A(\vec{r}_A; R)n\ell\lambda_B(\vec{r}_B; R)d\tau.$$

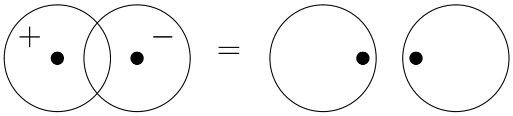
The molecular orbital is bonding if 2 atomic orbitals in the overlap region have same phase, anti-bonding if they have opposite phase.

$\sigma_g(ns)$ $ns_A + ns_B$



anti-bonding

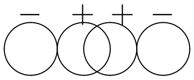
$\sigma_u^\star(ns)$ $ns_A - ns_B$



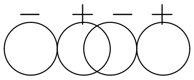
Body frame g, u inversion symmetry ($g =$ *gerade* or even, $u =$ *ungerade* or odd)

* is extra notation (optional) for anti-bonding

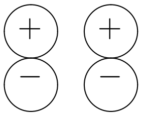
$\sigma_g(np)$ $np_{z,A} - np_{z,B}$



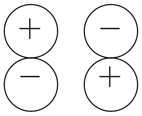
$\sigma_u^\star(np)$ $np_{z,A} + np_{z,B}$



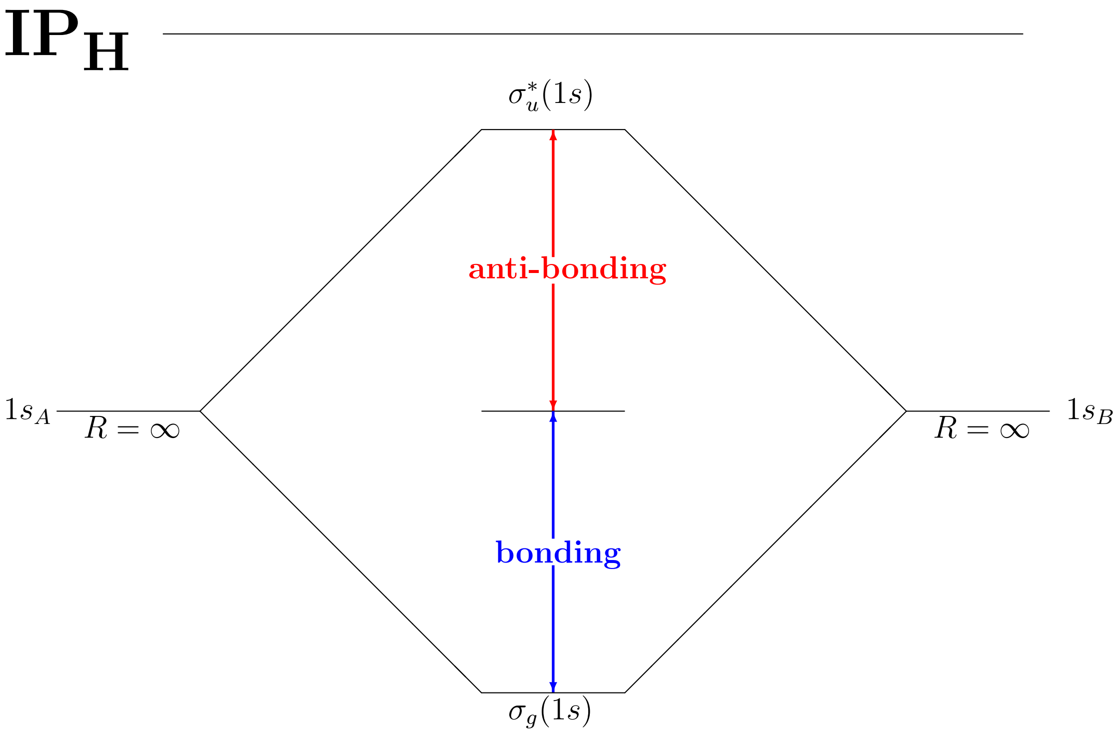
$\pi_u(np)$ $np_{y,A} + np_{y,B}$



$\pi_g^\star(np)$ $np_{x,A} - np_{x,B}$



What did we learn from H_2^+?



σ_g(1s) less bonding than $\sigma_u^\star$(1s) is anti-bonding

IP (H_2^+) $X^2\Sigma_g^+ \sim$ IP (H) plus bonding (D_e^e) stabilization due to one e^- in σ_g(1s)

Electronic Ground state in σ_g(1s) $X^2\Sigma_g^+$ is bound!

Excited state $A^2\ \Sigma_u^+$ is repulsive

$$R_e(H_2^+) < 2\langle r \rangle_{H\ 1s}$$

Minimal Basis Set Variational Calculation

(what is the Variational Theorem?)

2 AO's → 2 MO's

minimize E_{avg}

determine ground state $E(R)$ and R_e (equilibrium internuclear distance)

more variational functions would give more accurate values. Requires computer.

Trust our model for qualitative insights

Extrapolate from H_2^+ to H_2. What happens to molecular properties if we add another e^-

- get R_e decrease by $\sim 30\%$
- get ω_e increase by $\sim 90\%$ (vibrational frequency)
- get D_e^e (dissociation energy) increase by $\sim 70\%$

concept of "bond". Go from 1/2 bond to full bond.

In chemistry we think of a bond as involving $2e^-$. Why not 1 or 3? You can put $2e^-$ into one orbital $(\alpha\beta - \beta\alpha)$ but not $3e^-$.

More on H_2^+

The $1s_A, 1s_B$ basis set gave (McQuarrie)

$$
\begin{aligned}
S(R) &= e^{-R}\left(\underbrace{1 + R + \frac{1}{3}R^2}\right) \\
H_{12}(R) &= e^{-R}\left(\frac{1}{R}\overbrace{-\frac{1}{2} - \frac{1}{6}R - \frac{1}{6}R^2}\right) \qquad \text{at large } R,\ S \text{ is driving force for bonding} \\
\varepsilon(R) &= \underset{\substack{\uparrow \\ E_{\mathrm{H}(1s)}}}{-\frac{1}{2}} + \underbrace{e^{-2R}\left(1 + \frac{1}{R}\right)}_{\substack{\text{bare H}^+\text{ penetrates inside H atom. Sees} \\ \text{repulsion by progressively less-shielded nu-} \\ \text{cleus as } R\text{–decreases.}}}
\end{aligned}
$$

Everything is atom-like at large–R

Bonding begins as R decreases, initially $\underset{\sim}{\propto} S$

Bonding turns around and is cancelled by overlap repulsion at short R [at what R would you expect this to begin to be important?]

$$R < 2\left\langle r \right\rangle_{n\ell} \qquad (z \text{ direction})$$

Short step from H_2^+ to H_2 to A_2

How many e^-?

Feed e^- into lowest orbitals following "exclusion principle"

Configuration: list of occupied orbitals

Excited configurations too → excited states

Configurations can give rise to several electronic states, as for He(1s 2s) : ^{1}S + ^{3}S

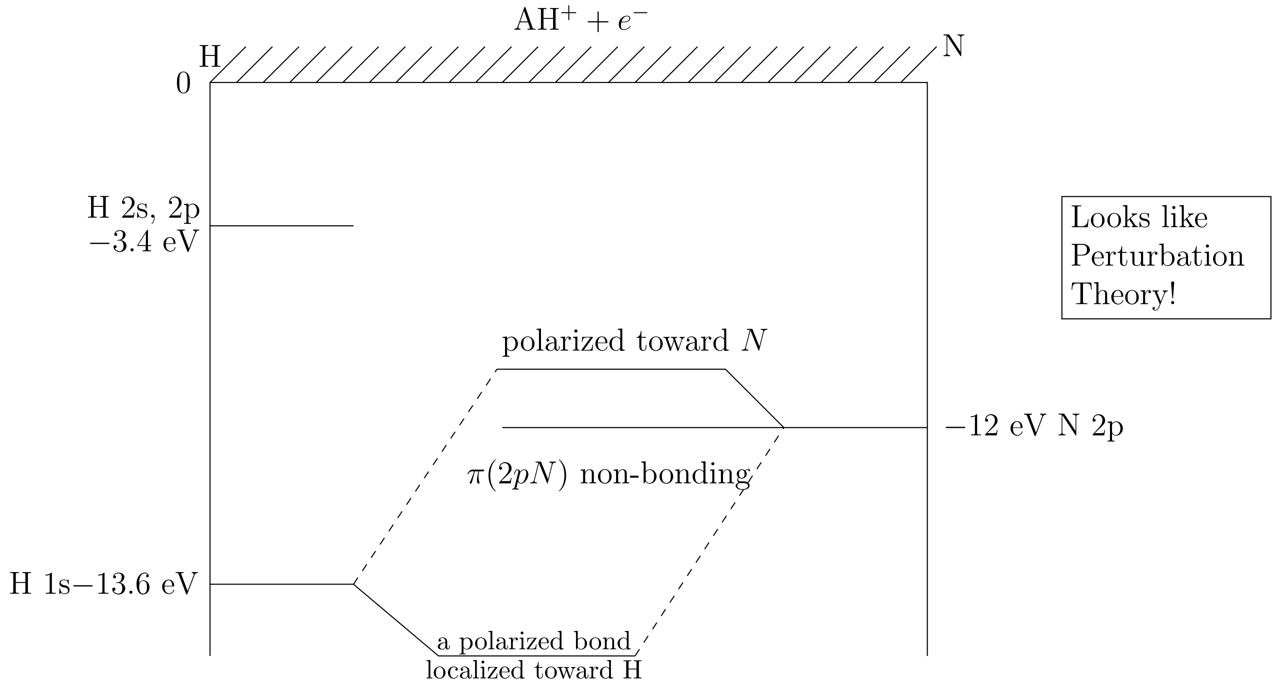
$$\begin{array}{llll} \text{for H}_2 & X^1\Sigma_g^+ & \sigma_g(1s)^2 & \text{bound} \\ & a^3\Sigma_u^+ & \sigma_g(1s)\sigma_u^\star(1s) & \text{repulsive} \end{array}$$

There could also be σ_g, σ_u, π_g, π_u orbitals arising from 2s, 2p

These $n = 2$ orbitals are much less bonding/anti-bonding: WHY?

orbital size, much smaller S at R_e of $X^1\Sigma_g^+$ ground electronic state

H_2 →AH (NH as example)



AO Energies (from Atomic Spectra) [Semi-Empirical]

	IE
H (1s)	13.6 eV
H(2s, 2p)	3.4 eV
N(1s)	$>$ 100 eV
N(2s)	$\sim$ 18 eV
N(2p)	$\sim$ 12 eV
NH $X^3\Sigma_g^-$	$\sim$ 13.6 eV

bonding

Total number of $e^- = 8$. Look at order of IE to guide the order in which orbitals are filled. $2e^-$ in N(1s), $2e^-$ in N(2s), $2e^-$ in H–N $1s\sigma - 2p\sigma$ strong covalent bond, $2e^-$ in Non-BONDING N($2p\pi$)

We have

$$\underbrace{\sigma^2\sigma^2}_{\text{atom-localized}}\underbrace{\sigma^2}_{\text{bonding}}\underbrace{\pi^2}_{\text{non-bonding}} \qquad \pi^2 : {}^3\Sigma^-, {}^1\Delta, {}^1\Sigma^+ \text{ electronic states}$$

Predict IP(NH) = IP[N 2p] + D_e^e

LCAO-MO for A$_2$

Li$_2$. . . F$_2$

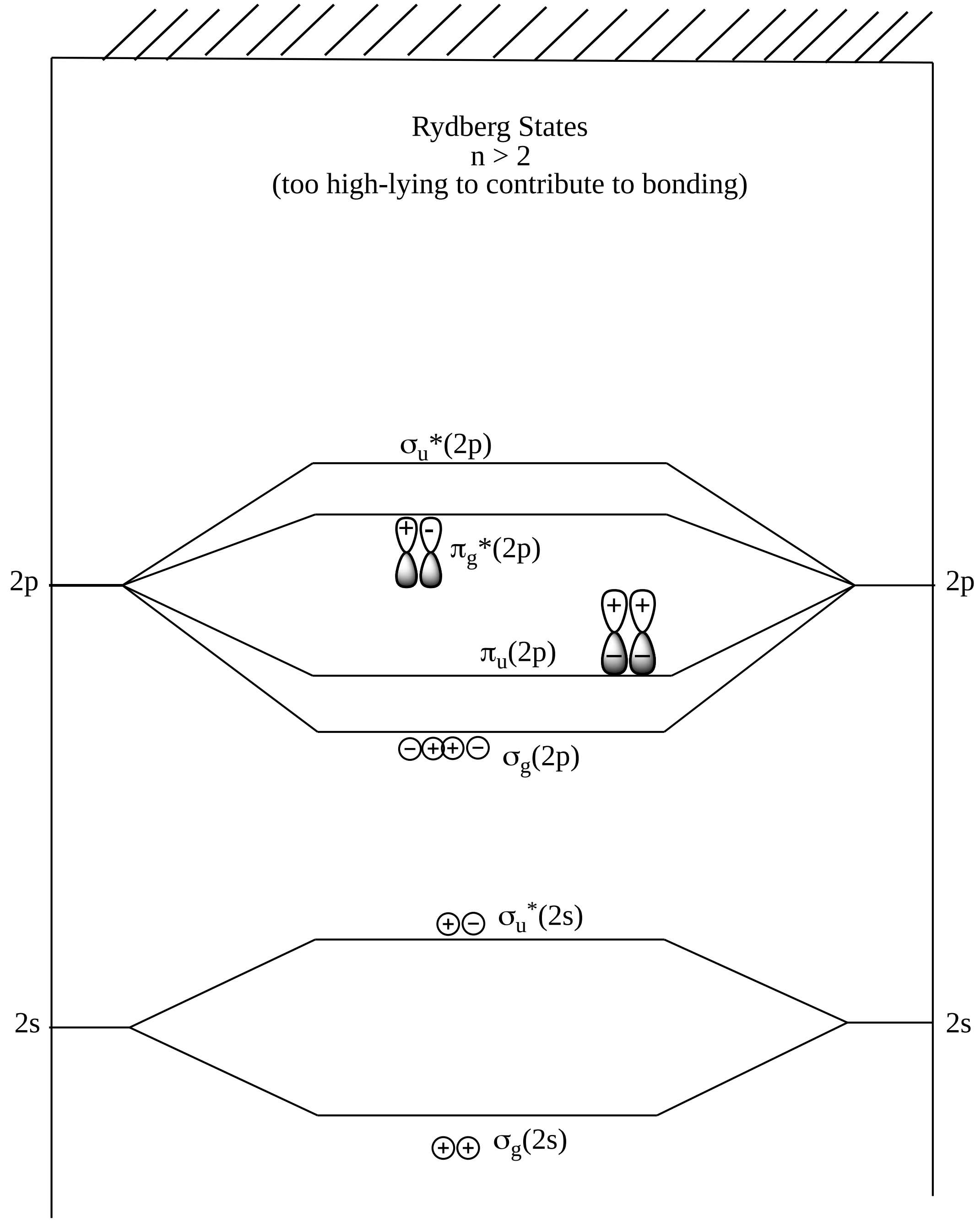
Always in textbooks

To begin — look up (from atomic spectra)

Atom A 2p,2s AO energies relative to A$^+$

Now to build a PRIMITIVE LCAO-MO diagram.

This is intentionally naive because it requires addition of extra effects, based on some empirical observations on a few systems generalized to many systems.



Facts: 2s smaller than 2p because of higher Ionization Energy, hence smaller size. Overlap starts at smaller R. σ_g(2p) more bound than π_u(2p) overlap because p orbital is extended along z.

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See Fig. 11.4 in McQuarrie, Donald A. *Quantum Chemistry, 2nd Edition*. University Science Books, 2007. ISBN: 9781891389504.

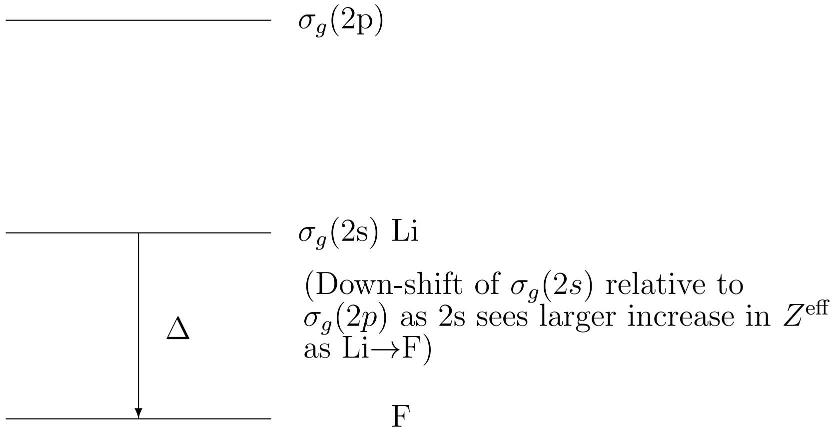
σ_g(2s) and σ_g(2p) have same σ_g symmetry so they can interact. Also true for

$$\sigma_u^\star(2s) \text{ and } \sigma_u^\star(2p).$$

Also π_u, $\pi_g^\star$ have no π orbital below — no upward shift due to repulsion from below.

Why does $\sigma(2s) \sim \sigma(2p)$ interaction change as we go across period Li→F?

Atom ion-core shielding effects cause an increase in s, p energy gap.



(Down-shift of $\sigma_g(2s)$ relative to $\sigma_g(2p)$ as 2s sees larger increase in Z^{eff} as Li→F)

$$\mathbf{H} = \begin{pmatrix} \varepsilon_p & V_{ps} \\ V_{ps} & \varepsilon_s \end{pmatrix}$$

$$\begin{aligned} \varepsilon &= \frac{\varepsilon_p + \varepsilon_s}{2} \pm \left[\Delta\varepsilon^2 + V_{ps}^2\right]^{1/2} \\ \Delta\varepsilon &= \frac{\varepsilon_p - \varepsilon_s}{2} \\ \varepsilon &= \frac{\varepsilon_p + (\varepsilon_s - \Delta)}{2} \pm \left[(\Delta\varepsilon + \Delta)^2 + V_{ps}^2\right]^{1/2} \end{aligned}$$

Repulsion shift from nominal pattern decreases Li→F

toward nominal	$\sigma_g < \pi_u$	O,F
starts out inverted	$\pi_u < \sigma_g$	Li … N

Crude interpretive use of non-degenerate perturbation theory:

$$\begin{aligned} \text{for A-A } \varepsilon^\circ_{n\ell\lambda_A} &= \varepsilon^\circ_{n\ell\lambda_A} \\ V^{AA}_{n\ell\lambda} &= \frac{1}{2}(n\ell\lambda^* - n\ell\lambda). \end{aligned}$$

R-dependent energy difference between anti-bonding and bonding orbital.

For A-B $\varepsilon^\circ_{n\ell\lambda_A} \neq \varepsilon^\circ_{n\ell\lambda_B}$.

Use this $V^{AA}_{n\ell\lambda}$ to guess value of $V^{AB}_{n\ell\lambda}$

$$V^{AB}_{n\ell\lambda} = \int \psi^\circ_{n\ell\lambda_A} \mathbf{H}^{(1)} \psi^\circ_{n\ell\lambda_B} d\tau$$

Alternatively, could estimate $V^{AB}_{n\ell\lambda}$ from

$$\left[\left(V^{AA}_{n\ell\lambda}\right)\left(V^{BB}_{n\ell\lambda}\right)\right]^{1/2}$$

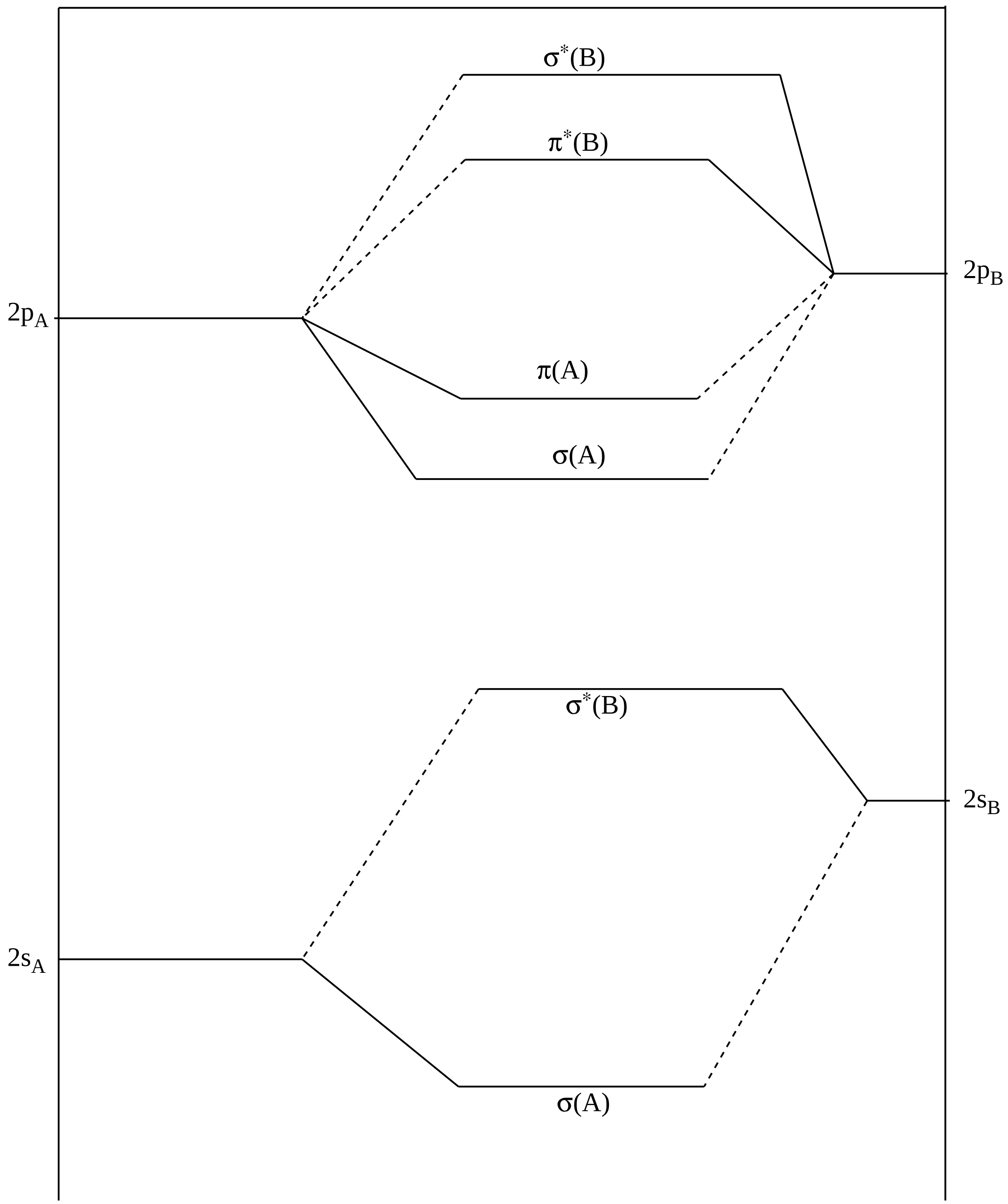
So from $\varepsilon_{n\ell\lambda^*} - \varepsilon_{n\ell\lambda} = 2V^{AB}_{n\ell\lambda}$ now we can use this semi-empirical value of $V^{AB}_{n\ell\lambda}$ to predict $V^{AB}_{n\ell'\lambda'}$ for some molecule guided by orbital size (orbital ionization energy) or $S(R)$ overlap or for neighboring AB molecules where

$$\varepsilon^{(0)}_{n\ell\lambda_A} \neq \varepsilon^{(0)}_{n\ell\lambda_B}$$

$$\begin{pmatrix} \varepsilon^{(0)}_{n\ell\lambda_A} & V \\ V & \varepsilon^{(0)}_{n\ell\lambda_B} \end{pmatrix}$$

Orbital Energy Order		$\varepsilon_{\sigma_g(2p)} > \varepsilon_{\pi_u(2p)}$	Li,. . . , C	
		$\varepsilon_{\pi_u(2p)} > \varepsilon_{\sigma_g(2p)}$	N, O, F	
8 valence e^-	C$_2$	$X^1\Sigma_g^+$	$\sigma_g^2\sigma_u^2\pi_u^4$	$\pi_u(2p) < \sigma_g(2p)$
		$a^3\Pi_u$	$\sigma_g^2\sigma_u^2\pi_u^3\sigma_g$	
10 valence e^-	N$_2$	$X^1\Sigma_g^+$	$\sigma_g^2\sigma_u^2\sigma_g^2\pi_u^4$	
		$A^3\Sigma^+$	$\sigma_g^2\sigma_u^2\sigma_g^2\pi_u^3\pi_g^\star$	$\}\sigma_g(2p) < \pi_u(2p)$
		$B^3\Pi_g$	$\sigma_g^2\sigma_u^2\sigma_g\pi_u^4\pi_g^*$	

So we can explain, anticipate, and exploit predicted "anomalies".



Unequal sharing of orbitals from A vs. B

Use non-degenerate perturbation theory to estimate:

- fractional A, B character in orbital

- polar bonding
- sign of polarity depends on number of e^-
- vs. equal sharing for A_2 molecules
- how does a molecule bind to a metal surface? positive end down, negative end down, lying down?

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