

### 3.1 Overlap Populations and Density of States etc.

#### Resonance Integral and Coulomb Parameter Revisited

**Expectation value** → mean or average quantity associated with some operator for a system described by a normalized wavefunction

$$E_{avg.} = \int \psi^* \hat{H} \psi d\tau = \langle \psi | \hat{H} | \psi \rangle$$

For some system  $\langle c_{1i}\phi_1 + c_{2i}\phi_2 + \dots | H_i^{eff} | c_{1i}\phi_1 + c_{2i}\phi_2 + \dots \rangle$

expanding this equation gives 2 kinds of integrals:

- 1)  $c_{\mu i} c_{\mu i} \langle \phi_\mu | H_i^{eff} | \phi_\mu \rangle = H_{\mu\mu} = \alpha$       **Coulomb parameter**  
numerically equivalent to VOIP!!
- 2)  $c_{\mu i} c_{\nu i} \langle \phi_\mu | H_i^{eff} | \phi_\nu \rangle = H_{\mu\nu} = \beta$       **Resonance integral**

NOTE: using Extended Hückel MO model, the Wolfsberg-Helmholtz formula estimates

$$\beta = \frac{1}{2} K S_{\mu\nu} (\alpha_\mu + \alpha_\nu)$$

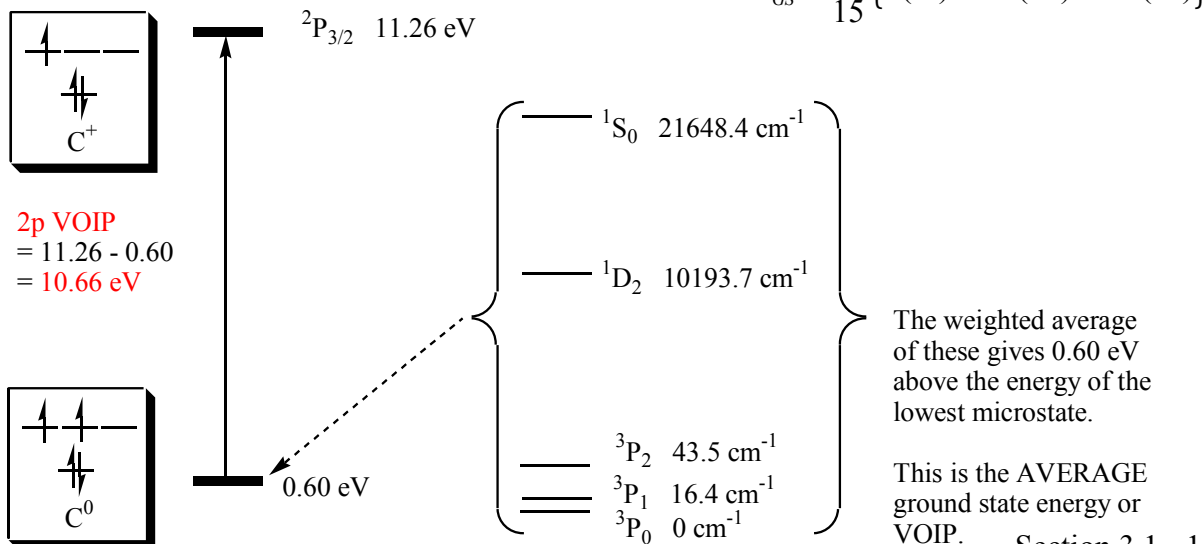
where  $K = 1.75 - 2.00$   
and  $S_{\mu\nu}$  is the **overlap integral**

Valence Orbital Ionization Potentials (VOIPs):      VOIPs are weighted potentials!

Recall: There are 15 microstates for 2 electrons in 3 degenerate orbitals

E.g. atomic C  $1s^2 2s^2 2p^2$

$$\bar{E}_{GS} = \frac{1}{15} \{ E(^1S) + 5E(^1D) + 9E(^3P) \}$$



Overlap Integral  $S_{ij}$

- Consider the plot of a wavefunction  $\chi$ , for an electron in a 1s orbital, as a function of distance from the nucleus (i.e., the radial part of the wavefunction):

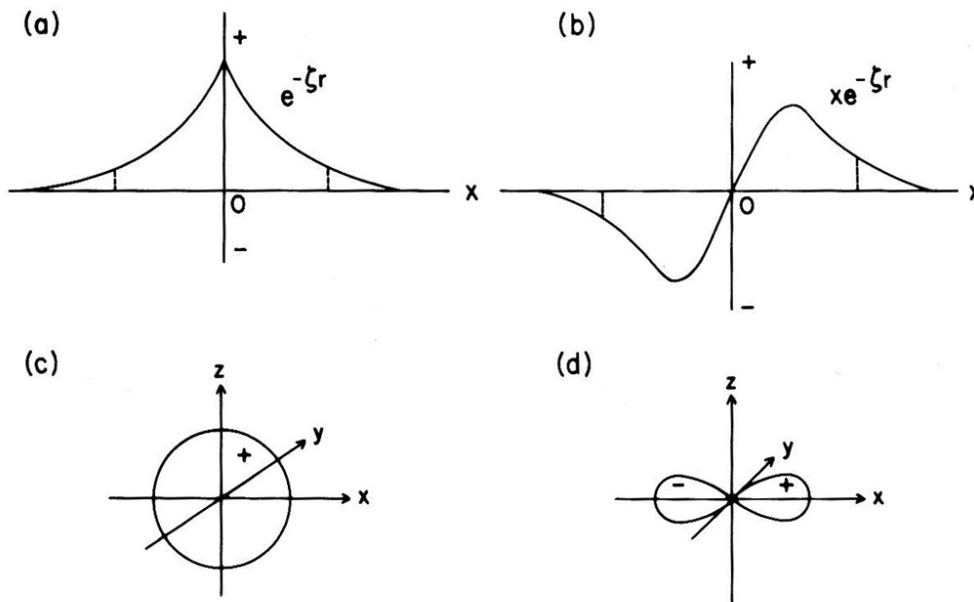
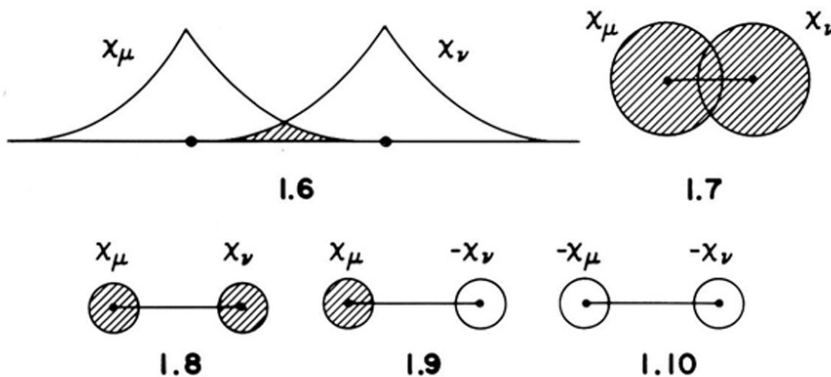


FIGURE 1.1. Radial part of the wavefunction for a 1s (a) and 2p (b) orbitals showing an arbitrary cutoff beyond which  $R(r)$  is less than some small value. The surface in three dimensions defined by this radial cutoff is shown in (c) for the 1s orbital and in (d) for the 2p orbital.

Source: "Orbital Interactions in Chemistry" Albright, Burdett, Whangbo, Wiley-Interscience, NY, 1985.

- Now consider the overlap of two such wavefunctions  $\chi_\mu$  and  $\chi_\nu$ :  $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \int \chi_\mu^* \chi_\nu dt$

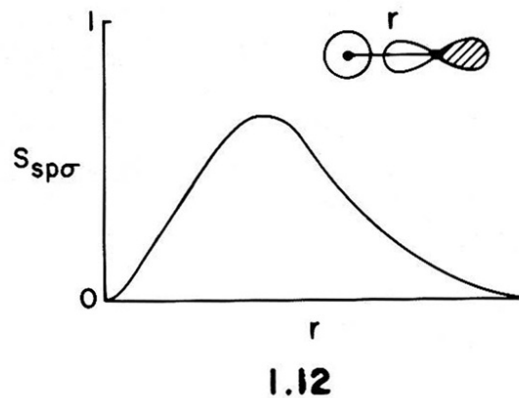
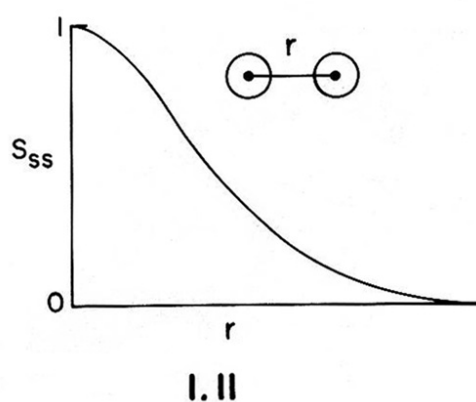


written as in 1.8. According to the sign convention of 1.1, the overlap integrals in 1.9 and 1.10 are given by equations 1.15 and 1.16, respectively. This simply shows

$$\langle \chi_\mu | -\chi_\nu \rangle = (-1) \langle \chi_\mu | \chi_\nu \rangle = -S_{\mu\nu} \quad (1.15)$$

$$\langle -\chi_\mu | -\chi_\nu \rangle = (-1)^2 \langle \chi_\mu | \chi_\nu \rangle = S_{\mu\nu} \quad (1.16)$$

- Chemists talk in terms of classes of overlap:  $\sigma$ ,  $\pi$ ,  $\delta$ , ...
- Consider the  $\sigma$ - bonding between two s-orbitals. Compare to the  $\sigma$ - bonding between an s- and a p- orbital:



### Angular Dependence of $S_{ij}$

- In general, the overlap integral between any two orbitals can be defined as the sum of three components ...

$$S_{AB} = S_{\sigma} F(\sigma, \theta, \varphi) + S_{\pi} F(\pi, \theta, \varphi) + S_{\delta} F(\delta, \theta, \varphi)$$

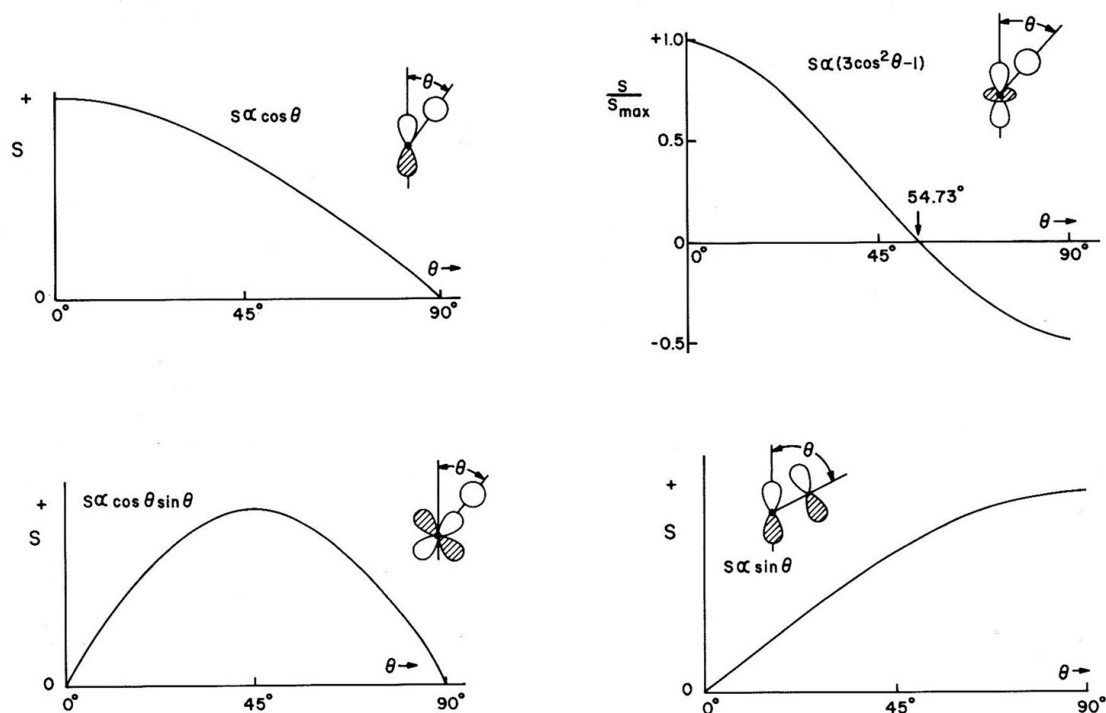


FIGURE 1.4. Angular dependence of the overlap integral for some commonly encountered pairs of atomic orbitals.

## Orbital Overlap Populations - MOOPs and COOPs

- For a polyatomic molecule with ORTHONORMAL molecular orbitals  $\psi_i$  derived from atomic orbitals  $\phi_\mu$ :

$$\psi_i = \sum_{\mu} c_{i\mu} \phi_{\mu}$$

- If the orbital contains  $n_i$  electrons ( $n_i = 0, 1, 2$ ):

$$1. \quad P_{\mu\mu} = \sum_i n_i c_{i\mu}^2$$

gives the net electron population of an atomic orbital  $\phi_{\mu}$ .

$$2. \quad P_{\mu\nu} = \sum_i 2n_i c_{i\mu} c_{i\nu} S_{\mu\nu}$$

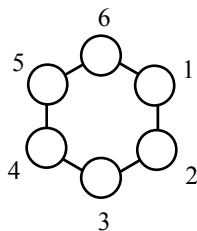
gives the **overlap population** between two atomic orbitals  $\phi_{\mu}$  and  $\phi_{\nu}$  located on two atoms A and B in the molecule.

$$3. \quad q_{\mu} = P_{\mu\mu} + \frac{1}{2} \sum_{\nu(\neq\mu)} P_{\mu\nu}$$

gives the gross electron population of  $\phi_{\mu}$

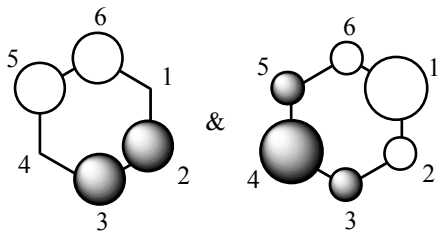
- Overlap populations are a useful device to describe total electronic interactions between a given pair of atoms:

For example: **Molecular Orbital Overlap Population (MOOP)** for benzene



$$\psi_{(a_{2u})} = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$P_{12(a_{2u})} = (2)(2) \left( \frac{1}{\sqrt{6}} \right) \left( \frac{1}{\sqrt{6}} \right) S_{\pi} = \frac{2}{3} S_{\pi}$$



$$\psi_{(e_{1g})} = \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

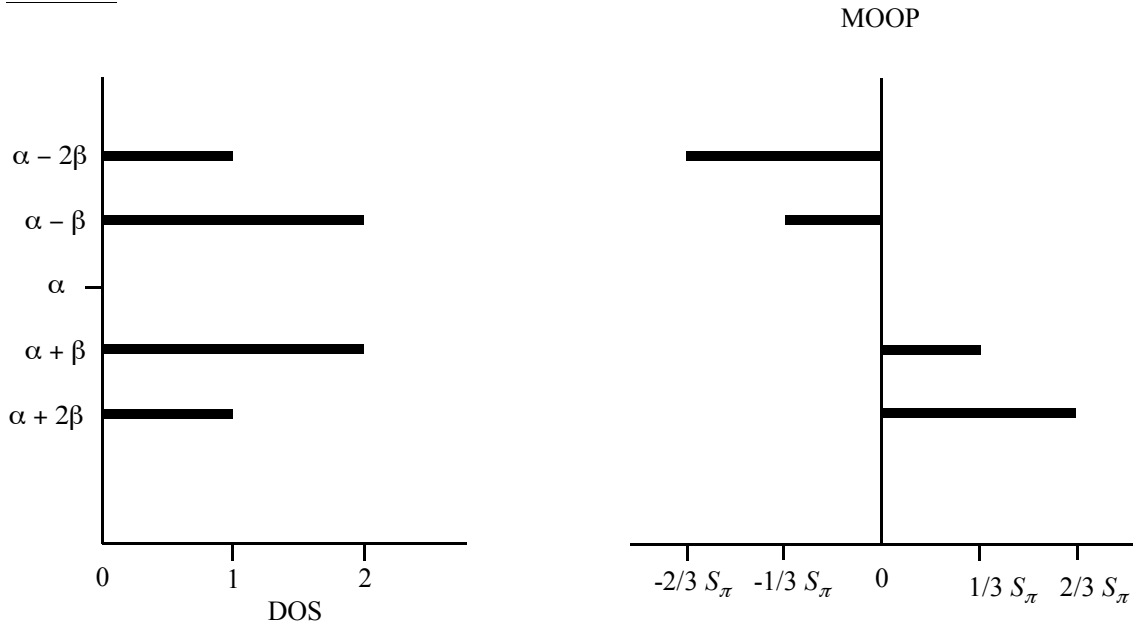
$$P_{16(e_{1g})} = 0 + (2)(2) \left( \frac{2}{\sqrt{12}} \right) \left( \frac{1}{\sqrt{12}} \right) S_{\pi} = \frac{2}{3} S_{\pi}$$

therefore  $1/3 S_{\pi}$  per orbital of the  $e_{1g}$  set

likewise  $P_{(e2u)} = -1/3 S_\pi$  and  $P_{(b2g)} = -2/3 S_\pi$

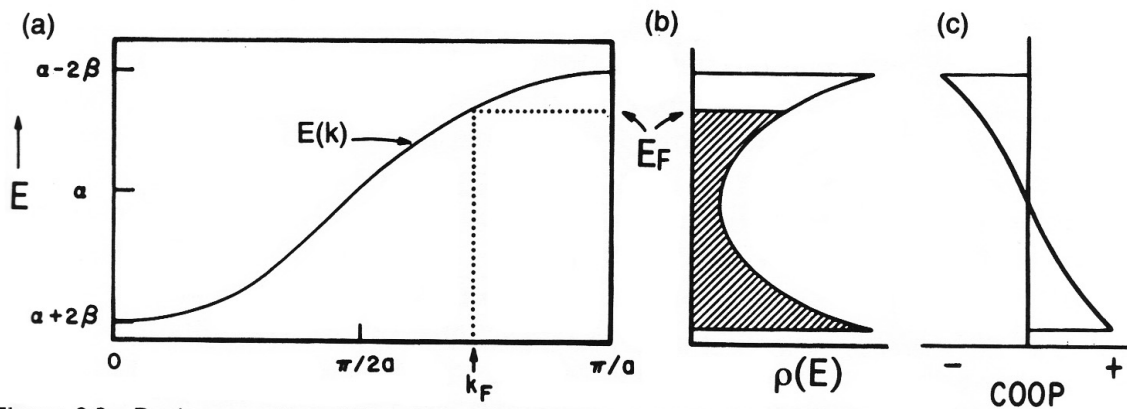
**\*\*HOMEWORK: Prove this to yourself! \*\***

Benzene:



Crystal Orbital Overlap Potential

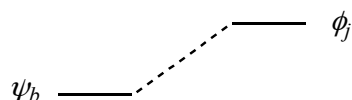
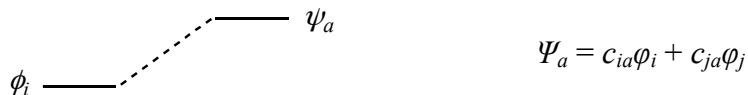
- The COOP is intended to show more clearly the bonding character of the orbitals at different energy levels.



**Figure 2.3** Basic properties of the electronic structure of the  $\pi$  orbitals of the infinite one-dimensional chain  $(-\text{CH}-)_n$ . Shown in (a) is the dispersion of the band, the variation in the energy with  $k$ . (b) The density of states,  $\rho(E)$ . (c) The crystal orbital overlap population (COOP) curve for this density of states. (b) and (c) should be compared with that for benzene in Figure 1.8.

## Orbital Overlap Populations Revisited

- Consider a 2-orbital problem:



- If there are  $N$  electrons in  $\psi_a$ , we can write the **charge distribution** as:

$$N\psi_a^2 = Nc_{ia}^2\phi_i^2 + Nc_{ja}^2\phi_j^2 + 2Nc_{ia}c_{ja}\underbrace{\phi_i\phi_j}_{\downarrow}$$

recall  $\langle \phi_i | \phi_j \rangle = S_{ij}$

- If the atomic and molecular orbitals are normalized:

Then:

$$\begin{aligned} \langle \psi_a | \psi_a \rangle &= 1 \\ \langle \phi_i | \phi_i \rangle &= 1 \\ \langle \phi_j | \phi_j \rangle &= 1 \end{aligned}$$

Therefore, if we integrate the above charge distributions equation over all space:

$$N = \underbrace{Nc_{ia}^2}_{\text{charge on } \phi_i} + \underbrace{Nc_{ja}^2}_{\text{charge on } \phi_j} + \underbrace{2Nc_{ia}c_{ja}S_{ij}}_{\text{MULLIKEN OVERLAP POPULATION!}}$$

## Normalization

Since 
$$\langle \psi_a | \psi_a \rangle = \int (c_{ia}^2 \overbrace{\phi_i^2}^{\langle \phi_i | \phi_i \rangle = 1} + c_{ja}^2 \overbrace{\phi_j^2}^{\langle \phi_j | \phi_j \rangle = 1} + 2c_{ia}c_{ja} \underbrace{\phi_i\phi_j}_{S_{ij} = \langle \phi_i | \phi_j \rangle}) d\tau = 1$$

THEN 
$$c_{ia}^2 + c_{ja}^2 + 2c_{ia}c_{ja}S_{ij} = 1$$

In a bonding orbital  $S_{ij} > 0$

$$\text{and } c_{ia}^2 + c_{ja}^2 = 1 - 2c_{ia}c_{ja}S_{ij} < 1$$

In an antibonding orbital  $S_{ij} < 0$

$$\text{and } c_{ia}^2 + c_{ja}^2 = 1 - 2c_{ia}c_{ja}S_{ij} > 1$$

## Conclusion:

In EHMO theory, it is possible to have orbital coefficients greater than unity!

These will appear in higher lying (empty) antibonding combinations.