

## Topic III

# Introduction to Structure and Bonding

### III.1 Module 11: Quantum Chemistry 101

1/27:

- We will have a normal class on Friday and hold review sessions at different times where we can ask questions.
- Suggested readings: Nocera Lecture 6, Nocera Lecture 7, MIT OCW quantum mechanics<sup>[1]</sup>.
- In chemistry, most problems are solved with the time-independent Schrödinger equation  $\hat{H}\Psi = E\Psi$ .
  - $\Psi$  is the wavefunction; it contains information on movement of the electron and its position.
  - $|\Psi(x, y, z)|^2 \propto P(x, y, z)$ .
  - $E$  is an eigenvalue of  $\hat{H}$ .
- If we are working with the time-dependent Schrödinger equation, we have another variable besides  $x, y, z$ , namely  $t$ . This allows us to calculate the probability that an electron is in a certain position at a given time.
- The Hamiltonian operator  $\hat{H} = \hat{T} + \hat{V}$  describes the total energy.
  - $\hat{T}$  is the kinetic energy operator.  $\hat{T} = \frac{\hat{p}^2}{2m}$ , where  $\hat{p}_x = -i\hbar \frac{d}{dx}$  is the momentum operator.
  - $\hat{V}$  is the potential energy operator. It typically describes the Coulombic attraction between the nucleus and the electron, which is approximately  $\frac{1}{r}$  where  $r$  is the distance from the nucleus to the electron.
- For a free electron in one dimension, the Schrödinger equation reduces to

$$\begin{aligned}-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} &= E\Psi \\ \frac{d^2\Psi}{dx^2} &= -\frac{2mE}{\hbar^2}\Psi\end{aligned}$$

- Dirac's bra-ket notation  $\langle \Psi | A | \Psi \rangle \equiv \int_V \Psi^* \hat{H} \Psi \, dx \, dy \, dz$ .
  - The **bra vector** (the first term inside the brackets) and **ket vector** (the last term inside the brackets) correspond to complex conjugates of the wave function.

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<sup>1</sup>Many chemistry courses go too deep into the math and physics of quantum mechanics, which obfuscates the chemistry and confuses us in Dr. Talapin's opinion.

- **LCAO method:** A way of finding the wavefunction of a molecule; of solving the Schrödinger equation after applying simplifications. Short for linear combination of atomic wavefunctions, i.e., the atomic orbitals  $\phi$ .

$$\Psi = \sum_i c_i \phi_i$$

- Each  $c_i$  is a coefficient, and the atomic orbitals form the basis set.
- Basically, we think of the wave function of a molecule as a linear combination of its atomic orbitals.
- $\phi$  is normalized, thus  $\int \phi_i^2 d\tau = 1$  where  $d\tau = dx dy dz$ .
- Continuing, we can calculate the expected value of  $\hat{H}$ , i.e., the ground state energy:

$$E = \frac{\int \Psi \hat{H} \Psi d\tau}{\int \Psi^2 d\tau}$$

- Shortcomings: Does not account for electron correlation and a few other things.

- Electronic structure of  $H_2$  molecule.

- $H_2$ 's structure is H–H.
- $\Psi = a\phi_1 + b\phi_2$ , where  $\phi_{1,2}$  are two atomic hydrogen  $1s$  orbitals.
- The electron density function is:  $\phi^2 = a^2\phi_1^2 + b^2\phi_2^2 + 2ab\phi_1\phi_2$ .
- By symmetry of H–H molecule,  $a = \pm b$ .
  - Symmetry of the coefficients should reflect symmetry of the atoms.
  - Hydrogen atoms are indistinguishable, so since the electron can't identify which atom it corresponds to, the math shouldn't either.
- If  $S = \int_{\tau} \phi_1 \phi_2 d\tau$  or  $\langle \phi_1 | \phi_2 \rangle$  is the overlap integral between two hydrogen  $1s$  orbitals, we have bonding and antibonding orbitals:

$$\Psi_b = \frac{1}{\sqrt{2(1+S)}}(\phi_1 + \phi_2) \quad \Psi_a = \frac{1}{\sqrt{2(1-S)}}(\phi_1 - \phi_2)$$

- The first orbital is  $\sigma_g$  bonding.
- The second orbital is  $\sigma_u^*$  antibonding.
- Introducing the normalizing requirement gives us the above coefficients.
- In the Hückel theory:

$$\alpha = \langle \phi_1 | \hat{H}_{\text{eff}} | \phi_1 \rangle = \langle \phi_2 | \hat{H}_{\text{eff}} | \phi_2 \rangle \quad \beta = \langle \phi_1 | \hat{H}_{\text{eff}} | \phi_2 \rangle$$

- If we calculate the expectation integrals, we will arrive at the above.
- $\hat{H}_{\text{eff}}$  is some effective Hamiltonian.
- The  $\alpha$  integral is the **Coulomb integral**.
- The  $\beta$  integral is the **interaction integral**.
- In the **Hückel approximation** (the simplest approximation of quantum mechanics), we define integrals as parameters that we can extract from empirical data:
  - $H_{ii} = \alpha$ .
  - $H_{ij} = 0$  for  $\phi_i$  not adjacent to  $\phi_j$ .
  - $H_{ij} = \beta$  for  $\phi_i$  adjacent to  $\phi_j$ .
  - $S_{ii} = 1$ .
  - $S_{ij} = 0$ .

- Expectation values for energy are

$$E_{a,b} = \frac{\langle \Psi_{a,b} | \hat{H}_{\text{eff}} | \Psi_{a,b} \rangle}{\langle \Psi_{a,b} | \Psi_{a,b} \rangle}$$

so

$$E_a = \frac{\alpha - \beta}{1 - S} \quad E_b = \frac{\alpha + \beta}{1 + S}$$

- Note that  $\beta < 0$  for atomic orbitals and  $\beta > 0$  for  $p$  orbitals in  $\sigma$  bonds.
- Also, in the Hückel one-electron model, the integrals  $\alpha$  and  $\beta$  remain unsolved.
- Note: As always, the bonding orbitals are less stabilized than the antibonding orbitals are destabilized.
  - This is a consequence of overlap, e.g., for a dimer, the  $1 \pm S$  term in  $E_{+/-} = \frac{\alpha \pm \beta}{1 \pm S}$ .
  - This is why  $\text{He}_2$  does not exist.

- **Overlap integral:** An integral proportional to the degree of spatial overlap between two orbitals. It is the product of wave functions centered on different lattice sites. Varies from 0 (no overlap) to 1 (perfect overlap). *Also known as  $S$ .*
- **Coulomb integral:** An integral giving the kinetic and potential energy of an electron in an atomic orbital experiencing interactions with all the other electrons and all the positive nuclei. *Also known as  $\alpha$ .*
- **Interaction integral** (on two orbitals 1,2): An integral giving the energy of an electron in the region of space where orbitals 1 and 2 overlap. The value is finite for orbitals on adjacent atoms, and assumed to be zero otherwise. *Also known as  $\beta_{12}$ , resonance integral, exchange integral.*
- Symmetry and quantum mechanics:

- Say we have  $\hat{H}\Psi = E\Psi$  where  $\hat{H}$  is the Hamiltonian and  $R$  is a symmetry operator (e.g.,  $C_2$  or  $\sigma_v$ ).
- Note that the Hamiltonian commutes with the symmetry operator:  $R\hat{H} = \hat{H}R$ .
- Since a symmetry operation does not change the energy of a molecule (it just moves it),  $\hat{H}R\Psi_i = E_i R\Psi_i$ .
- It follows that  $R$  does not change the form of the wave function, i.e.,  $R\Psi_i = \pm 1\Psi_i$ . This reflects the fact that  $R$  cannot change the probability  $P[e(x, y, z)] = |\Psi(x, y, z)|^2$  of finding an electron somewhere.
- Thus, the eigenfunctions of the Schrödinger equation generate a representation of the group.
- Non-degenerate wave functions are  $A$  or  $B$  type.
- Double-degenerate wave functions are  $E$  type.
- Triple-degenerate wave functions are  $T$  type.

- Back to the LCAO method:

$$E_i = \frac{\int \Psi_i^* H \Psi_i \, dV}{\int \Psi_i^* \Psi_i \, dV} \quad \Psi_i = \sum_i c_i \phi_i$$

- If we have a sizeable molecule with a couple dozen atoms, every molecular orbital (wave function) will be the sum of a couple dozen atomic orbitals.
- This generates a set of  $i$  linear homogenous equations, numbering in the hundreds or thousands that need to be solved.
- This is clearly too computationally expensive, so we need a trick.

- An example where symmetry arguments help a lot:
  - If  $f$  is odd ( $f(x) = -f(-x)$ ), then we know that  $\int_{-\infty}^{\infty} f(x) dx = 0$ .
- Group theory allows us to generalize this method to broader symmetry operations.
- Three important theorems:
  1. The characters of the representation of a direct product are equal to the products of the characters of the representations based on the individual sets of functions.
    - For example, in the  $T_d$  point group,  $T_1 = (3, 0, -1, 1, -1)$ , and  $T_2 = (3, 0, -1, -1, 1)$ . By the theorem,  $T_1 \times T_2 = (9, 0, 1, -1, -1)$ .
  2. A representation of a direct product,  $\Gamma_c = \Gamma_a \times \Gamma_b$ , will contain the totally symmetric representation only if the irreducible representations of  $a$  and  $b$  contain at least one common irreducible representation.
    - Continuing with the above example,  $T_1 \times T_2$  can be decomposed into  $A_2 + E + T_1 + T_2$ . Thus, by this theorem, if we take the product  $\Gamma_c = E \times T_1 \times T_2$ , the representation will contain the totally symmetric representation  $A_1$  (since  $\Gamma_b = E$  and  $\Gamma_a = T_1 \times T_2$  contains  $E$ ). Indeed, the decomposition  $E \times T_1 \times T_2 = (18, 0, 2, 0, 0) = A_1 + A_2 + 2E + 2T_1 + 2T_2$  contains  $A_1$ .
  3. The value of any integral relating to a molecule  $\int_V \Psi d\tau$  will be zero unless the integrand is invariant under all operations of the symmetry point group to which the molecule belongs. That is  $\Gamma_\Psi$  must contain the totally symmetric irreducible representation.
    - This example will concern the  $D_{4d}$  point group. We want to evaluate the integral  $\int_V \Psi_a \mu_z \Psi_b d\tau$  where  $\Gamma_{\Psi_a} = A_1$ ,  $\Gamma_{\mu_z} = B_2$ , and  $\Gamma_{\Psi_b} = E_1$ .
    - By Theorem 1, we can easily determine the representation  $\Psi_a \times \mu_z$ . We can then decompose it.
    - Noting that it does not contain the  $E_1$  irreducible representation (the only representation in  $\Psi_b$ ), we can learn from Theorem 2 that  $\Psi_a \mu_z \Psi_b$  does not contain the  $A_1$  irreducible representation.
    - Therefore, by Theorem 3,  $\int_V \Psi d\tau = \int_V \Psi_a \mu_z \Psi_b d\tau = 0$ .
- We use these three theorems to tell us what integrals will be zero in a much less computationally intensive fashion. We can then evaluate the remaining nonzero integrals.
- We can take direct products by hand, but there are also tables of direct products of irreducible representations.

## III.2 Module 12: IR and Raman Active Vibrations (part 2)

- **Fermi's golden rule:** The rate of an optical transition from a single initial state to a final state is given by the transition rate for a single state.

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} E_0^2 | \langle f | H' | i \rangle |^2 \delta(E_f - E_i - h\nu)$$

- By state, we typically mean energy level.
- The transition rate is the probability of a transition happening.
- If it's an optical transition, conservation of energy implies that the energy difference between the initial and final state will equal the energy of the photon that the molecule absorbs or emits.
- $E_0^2$  is the light intensity.
- $h\nu$  is the photon energy.
- $\langle f | H' | i \rangle = \int \Psi_f^* H' \Psi_i d\tau$  is the square of the matrix element (the strength of the coupling between the states).

- $\delta(E_f - E_i - h\nu)$  is the resonance condition (energy conservation).
- In the dipole approximation,  $H' = -e\vec{r} \cdot \vec{E}$ .
- This is derived with time-dependent perturbation theory.
  - The matrix element  $M = \langle f | H' | i \rangle = \int \Psi_f^*(\vec{r}) H' \Psi_i(\vec{r}) d^3\vec{r}$ .
  - Perturbation:  $H' = -\vec{p}_e \cdot \vec{E}_{\text{photon}}$ . Dipole moment:  $\vec{p}_e = -e\vec{r}$ . Light wave:  $\vec{E}_{\text{photon}}(r) = \vec{E}_0 e^{\pm i\vec{k} \cdot \vec{r}}$ ,  $H'(\vec{r}) = e\vec{E}_0 \cdot \vec{r} e^{\pm i\vec{k} \cdot \vec{r}}$ .
  - This implies that in one dimension,  $|M| \propto \int \Psi_f^*(\vec{r}) x \Psi_i(\vec{r}) d^3\vec{r}$ .
  - We include other variables in higher dimensions.
- For IR absorption, the intensity  $I$  satisfies  $I \propto \int \Psi_{\text{e.s.}} \hat{\mu}_e \Psi_{\text{g.s.}} d\tau$ .
  - $\Psi_{\text{e.s.}}$  is the excited state wavefunction,  $\Psi_{\text{g.s.}}$  is the ground state wavefunction, and  $\hat{\mu}_e$  is the dipole operator.
  - We now apply the three theorems:
  - It is always true in vibration spectroscopy that  $\Gamma_{\text{g.s.}} = A_1$ . This is because in the ground state, the molecule is completely relaxed (nothing is perturbed).
  - Thus, we can already reduce to  $\Gamma_{\text{e.s.}} \cdot \Gamma_\mu \cdot \Gamma_{\text{g.s.}} = \Gamma_{\text{e.s.}} \cdot \Gamma_\mu \cdot 1$ .
  - Now  $\Gamma_\mu$  transforms as  $x, y, z$  unit vectors. In  $D_{3h}$ , this implies that  $\Gamma_\mu = E' + A''_2$ .
  - Therefore,  $I \propto \Gamma_{\text{vibs}} \cdot (E' + A''_2)$ .
  - For  $\text{PF}_5$ , since  $\Gamma_{\text{vibs}} = 2A'_1 + 3E' + 2A''_2 + E''$  has  $E'$  and  $A''_2$  in common with  $\Gamma_\mu$ , only  $3E'$  and  $2A''_2$  are IR active.
  - Additionally, with elements in common,  $\Gamma_{\text{vibs}} \cdot \Gamma_\mu$  will contain  $A_1$  by Theorem 2, and thus, the integrals  $\int \Psi_{\text{e.s.}} x \Psi_{\text{g.s.}} d\tau$ ,  $\int \Psi_{\text{e.s.}} y \Psi_{\text{g.s.}} d\tau$ , and  $\int \Psi_{\text{e.s.}} z \Psi_{\text{g.s.}} d\tau$  are all nonzero. Some linear combination of them will be proportional to  $I$ .
- The exam will include material from today's class, but not Friday's class.
- PSets 1 and 2 will cover all material on the exam?

### III.3 Nocera Lecture 6

*From Nocera (2008).*

1/29: • Solving the Schrödinger equation with the LCAO method for the  $k$ th molecular orbital  $\Psi_k$ :

$$\begin{aligned} \hat{H}\Psi_k &= E\Psi_k \\ |\hat{H} - E| \Psi_k \rangle &= 0 \\ |\hat{H} - E| c_a \phi_a + c_b \phi_b + \dots + c_i \phi_i \rangle &= 0 \end{aligned}$$

- Left-multiplying the above by each  $\phi_i$  yields a set of  $i$  linear homogenous equations.

$$\begin{aligned} c_a \langle \phi_a | \hat{H} - E | \phi_a \rangle + c_b \langle \phi_a | \hat{H} - E | \phi_b \rangle + \dots + c_i \langle \phi_a | \hat{H} - E | \phi_i \rangle &= 0 \\ c_a \langle \phi_b | \hat{H} - E | \phi_a \rangle + c_b \langle \phi_b | \hat{H} - E | \phi_b \rangle + \dots + c_i \langle \phi_b | \hat{H} - E | \phi_i \rangle &= 0 \\ &\vdots \\ c_a \langle \phi_i | \hat{H} - E | \phi_a \rangle + c_b \langle \phi_i | \hat{H} - E | \phi_b \rangle + \dots + c_i \langle \phi_i | \hat{H} - E | \phi_i \rangle &= 0 \end{aligned}$$

- We can then solve the **secular determinant**,

$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} & \cdots & H_{ai} - ES_{ai} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} & \cdots & H_{bi} - ES_{bi} \\ \vdots & \vdots & \ddots & \vdots \\ H_{ia} - ES_{ia} & H_{ib} - ES_{ib} & \cdots & H_{ii} - ES_{ii} \end{vmatrix} = 0$$

where  $H_{ij} = \int \phi_i \hat{H} \phi_j d\tau$  and  $S_{ij} = \int \phi_i \phi_j d\tau$ .

- To evaluate these integrals, see the notes in Module 11 concerning the Hückel approximation.

- **Extended Hückel theory:** An alternate integral approximation method that includes all valence orbitals in the basis (as opposed to just the highest energy atomic orbitals), calculates all  $S_{ij}$ s, estimates the  $H_{ii}$ s from spectroscopic data (as opposed to a constant  $\alpha$ ), and estimates  $H_{ij}$ s from a simple function of  $S_{ii}$ ,  $H_{ii}$ , and  $H_{ij}$ . This is a zero differential overlap approximation. *Also known as EHT.*

- A **semi-empirical** method.
- **Semi-empirical** (method): A method that relies on experimental data for the quantification of parameters.
- Other semi-empirical methods include CNDO, MINDO, and INDO.
- Hückel's method and LCAO example: Examine the frontier orbitals and their associated energies (i.e., determine eigenfunctions and eigenvalues, respectively) of benzene.

- We assume that the frontier MO's will be composed of LCAO of the  $2p\pi$  orbitals.
- Using orbitals as our basis and noting that benzene is of the  $D_{6h}$  point group, we can determine that  $\Gamma_{p\pi} = (6, 0, 0, 0, -2, 0, 0, 0, 0, -6, 2, 0)$ .
- Using the decomposition formula, we can reduce  $\Gamma_{p\pi}$  into  $\Gamma_{p\pi} = A_{2u} + B_{2g} + E_{1g} + E_{2u}$ . These are the symmetries of the MO's formed by the LCAO of  $p\pi$  orbitals in benzene.
- With symmetries established, LCAOs may be constructed by “projecting out” the appropriate linear combination with the following projection operator, which determines the linear combination of the  $i$ th irreducible representation.

$$P^{(i)} = \frac{\ell_i}{h} \sum_R [\chi^{(i)}(R)] \cdot R$$

- $\ell_i$  is the dimension of  $\Gamma_i$ .
- $h$  is the order.
- $\chi^{(i)}(R)$  is the character of  $\Gamma_i$  under operation  $R$ .
- $R$  is the corresponding operator.

- To actually apply the above projection operator, we will drop to the  $C_6$  subgroup of  $D_{6h}$  to simplify calculations. The full extent of mixing among  $\phi_1$ - $\phi_6$  is maintained within this subgroup, but the inversion centers are lost, meaning that in the final analysis, the  $\Gamma_i$ s in  $C_6$  will have to be correlated to those in  $D_{6h}$ .
- In  $C_6$ , we have  $\Gamma_{p\pi} = (6, 0, 0, 0, 0, 0) = A + B + E_1 + E_2$ .
- The projection of the Symmetry Adapted Linear Combination (SALC) that from  $\phi_1$  transforms as  $A$  is

$$\begin{aligned} P^{(A)} \phi_1 &= \frac{1}{6} [1E + 1C_6 + 1C_6^2 + 1C_6^3 + 1C_6^4 + 1C_6^5] \phi_1 \\ &= \frac{1}{6} [E\phi_1 + C_6\phi_1 + C_6^2\phi_1 + C_6^3\phi_1 + C_6^4\phi_1 + C_6^5\phi_1] \\ &= \frac{1}{6} [\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6] \\ &\cong \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \end{aligned}$$

where we make the last congruency (dropping the constant) because the LCAO will be normalized, which will change the constant, regardless.

- With a similar process, we can find that

$$\begin{aligned} P^{(B)}\phi_1 &= \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 \\ P^{(E_{1a})}\phi_1 &= \phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6 \\ P^{(E_{1b})}\phi_1 &= \phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6 \\ P^{(E_{2a})}\phi_1 &= \phi_1 - \varepsilon^*\phi_2 - \varepsilon\phi_3 + \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6 \\ P^{(E_{2b})}\phi_1 &= \phi_1 - \varepsilon^*\phi_2 - \varepsilon^*\phi_3 + \phi_4 - \varepsilon\phi_5 - \varepsilon^*\phi_6 \end{aligned}$$

- Since some of the projections contain imaginary components, we can obtain real components by taking  $\pm$  linear combinations and noting that  $\varepsilon = e^{2\pi i/6}$  in the  $C_6$  point group.

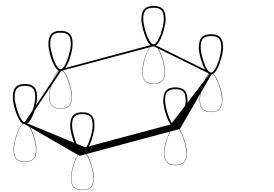
$$\begin{aligned} \Psi_3(E_1) &= \Psi'_3(E_{1a}) + \Psi'_4(E_{1b}) = 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6 \\ \Psi_4(E_1) &= \Psi'_3(E_{1a}) - \Psi'_4(E_{1b}) = \phi_2 + \phi_3 - \phi_5 - \phi_6 \\ \Psi_5(E_2) &= \Psi'_5(E_{2a}) + \Psi'_6(E_{2b}) = 2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6 \\ \Psi_6(E_2) &= \Psi'_5(E_{2a}) - \Psi'_6(E_{2b}) = \phi_2 - \phi_3 + \phi_5 - \phi_6 \end{aligned}$$

- We can now normalize: If  $\Psi_i = \sum_j c_j \phi_j$  where  $\text{gcd}(c_1, \dots, c_n) = 1$ , the normalizing constant is

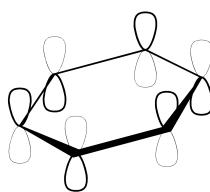
$$N = \frac{1}{\sqrt{\sum_j c_j^2}}$$

meaning that

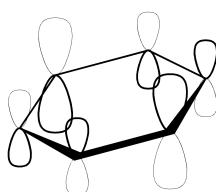
$$\begin{array}{ll} \Psi_1(A) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) & \Psi_2(B) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\ \Psi_3(E_1) = \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) & \Psi_4(E_1) = \frac{1}{2} (\phi_2 + \phi_3 - \phi_5 - \phi_6) \\ \Psi_5(E_2) = \frac{1}{\sqrt{12}} (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6) & \Psi_6(E_2) = \frac{1}{2} (\phi_2 - \phi_3 + \phi_5 - \phi_6) \end{array}$$



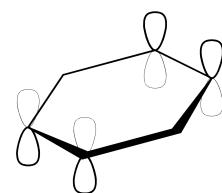
(a)  $\Psi_1(A) \sim \Psi(A_{2u})$ .



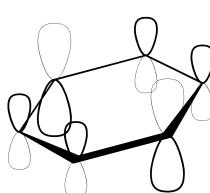
(b)  $\Psi_2(B) \sim \Psi(B_{2g})$ .



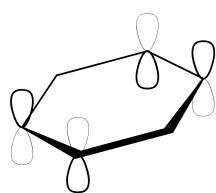
(c)  $\Psi_3(E_1) \sim \Psi(E_{1g}^a)$ .



(d)  $\Psi_4(E_1) \sim \Psi(E_{1g}^b)$ .



(e)  $\Psi_5(E_2) \sim \Psi(E_{2u}^a)$ .



(f)  $\Psi_6(E_2) \sim \Psi(E_{2u}^b)$ .

Figure III.1: Molecular orbitals of benzene.

- Figure III.1 shows pictorial representations of the SALCs.

### III.4 Nocera Lecture 7

*From Nocera (2008).*

- This lecture continues with the benzene example from Nocera Lecture 6.
- Finding the total energy of benzene:
  - The energies (eigenvalues of the individual wavefunctions) may be determined using the Hückel approximation as follows.

$$\begin{aligned}
 E(\Psi_{A_{1g}}) &= \int \Psi_{A_{1g}} \hat{H} \Psi_{A_{1g}} d\tau \\
 &= \langle \Psi_{A_{1g}} | \hat{H} | \Psi_{A_{1g}} \rangle \\
 &= \left\langle \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \middle| \hat{H} \middle| \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \right\rangle \\
 &= \frac{1}{6} \left( (H_{11} + H_{12} + H_{13} + H_{14} + H_{15} + H_{16}) + (H_{21} + H_{22} + H_{23} + H_{24} + H_{25} + H_{26}) + \sum_{i=3}^6 \sum_{j=1}^6 H_{ij} \right) \\
 &= \frac{1}{6} \left( (\alpha + \beta + 0 + 0 + 0 + \beta) + (\beta + \alpha + \beta + 0 + 0 + 0) + \sum_{i=3}^6 (\alpha + 2\beta) \right) \\
 &= \frac{1}{6}(6)(\alpha + 2\beta) \\
 &= \alpha + 2\beta
 \end{aligned}$$

- Similarly, we can determine that

$$\begin{aligned}
 E(\Psi_{B_{2g}}) &= \alpha - 2\beta \\
 E(\Psi_{E_{1g}^a}) &= E(\Psi_{E_{1g}^b}) = \alpha + \beta \\
 E(\Psi_{E_{2u}^a}) &= E(\Psi_{E_{2u}^b}) = \alpha - \beta
 \end{aligned}$$

- We can now construct an energy level diagram (Figure III.2). We set  $\alpha = 0$  and let  $\beta$  be the energy parameter (a negative quantity; thus, a MO whose energy is positive in units of  $\beta$  has an absolute energy that is negative).

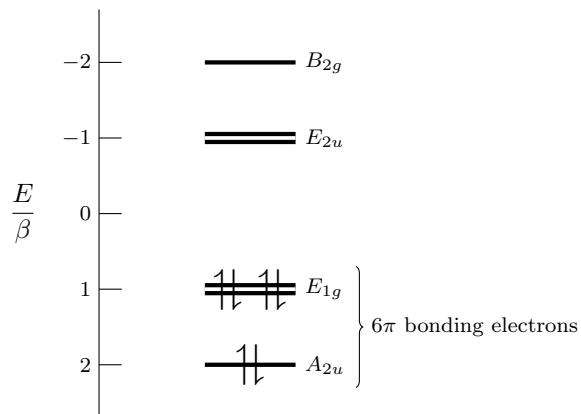


Figure III.2: Energy level diagram of benzene.

- From Figure III.2, we can determine that the energy of benzene based on the Hückel approximation is

$$E_{\text{total}} = 2(2\beta) + 4(\beta) = 8\beta$$

- **Delocalization energy:** The difference in energy between a molecule that delocalizes electron density in a delocalized state versus a localized state. *Also known as resonance energy.*

- Finding the delocalization energy of benzene:

- Consider cyclohexatriene, a molecule equivalent to benzene except that it has 3 *localized*  $\pi$  bonds. Cyclohexatriene is the product of three condensed ethene molecules.

- Ethene has 2  $\pi$  bonds  $\phi_1$  and  $\phi_2$ .

- Following the procedure of Nocera Lecture 6, we can determine that

$$\Psi_1(A) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \quad \Psi_2(B) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

- Thus,

$$E(\Psi_1) = \left\langle \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \middle| \hat{H} \middle| \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \right\rangle = \frac{1}{2}(2\alpha + 2\beta) = \beta$$

$$E(\Psi_2) = \left\langle \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \middle| \hat{H} \middle| \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \right\rangle = \frac{1}{2}(2\alpha - 2\beta) = -\beta$$

- Correlating the above calculations (performed within  $C_2 \subset D_{2h}$ ) to the  $D_{2h}$  point group gives  $A \rightarrow B_{1u}$  and  $B \rightarrow B_{2g}$ .

- We can now construct an energy level diagram.

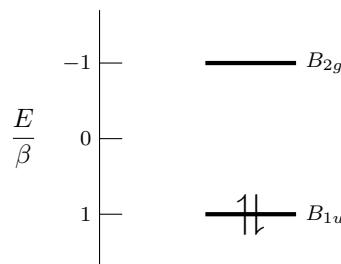


Figure III.3: Energy level diagram of ethene.

- Figure III.3 tells us that  $E_{\text{total}} = 2(\beta) = 2\beta$ . Consequently, the total energy of cyclohexatriene is  $3(2\beta) = 6\beta$ .
- Therefore, the resonance energy of benzene based on the Hückel approximation is

$$E_{\text{res}} = 8\beta - 6\beta = 2\beta$$

- **Bond order:** A quantity defined for a given bond as

$$\text{B.O.} = \sum_{i,j} n_e c_i c_j$$

where  $n_e$  is the orbital  $e^-$  occupancy and  $c_{i,j}$  are the coefficients of the electrons  $i, j$  in a given bond.

- Finding the bond order of benzene between carbons 1 and 2:

- Just apply the formula:

$$\begin{aligned} \text{B.O.} &= [\Psi_1(A_2)] + [\Psi_3(E_{1g}^a)] + [\Psi_4(E_{1g}^b)] \\ &= (2) \left( \frac{1}{\sqrt{6}} \right) \left( \frac{1}{\sqrt{6}} \right) + (2) \left( \frac{2}{\sqrt{12}} \right) \left( \frac{1}{\sqrt{12}} \right) + (2)(0) \left( \frac{1}{2} \right) \\ &= \frac{1}{3} + \frac{1}{3} + 0 \\ &= \frac{2}{3} \end{aligned}$$

### III.5 Module 13: Why Molecular Orbitals?

- Note that in the point group flow chart, there is no  $D_{nv}$ ; only  $D_{nd}$ .
- We will not need LCAO for the exam tomorrow.
- The exam covers Modules 1-12.
- Lewis (1916) first proposed that bonds came from interpenetrability of electron density.
- The next step came from Linus Pauling, who proposed valence bond theory.
  - In order to account for polarity of the bond, he created a term that described the probability that both electrons bond to one atom.
- A new approach then emerged from Robert Mulliken, Friedrich Hund, and Clemens C.J. Roothaan. All three men worked at UChicago!
  - Mulliken is mainly credited for the development of MO theory.
  - Roothaan retired, found retirement boring, moved to Palo Alto and was key in the development of computer processors.
- Molecular orbital theory:
  - Atomic orbitals of different atoms combine to create molecular orbitals.
  - The number of atomic orbitals equals the number of molecular orbitals.
  - Electrons in these molecular orbitals are shared by the molecule as a whole.
  - Molecular orbitals can be constructed from LCAO.
    - For diatomic molecules:  $\Psi = c_a \Psi_a + c_b \Psi_b$ .
- There is no such thing as a chemical bond (this model is only intuitively helpful), only molecular orbitals!
- **Bonding** (orbital): An orbital that has most of the electron density between the two nuclei.
- **Anti-bonding** (orbital): An orbital that has a node between the two nuclei.
- **Nonbonding** (orbital): An orbital that is essentially the same as if it was only one nucleus.
- We find the energy of electronic states using theoretical calculations that we test with photoelectron spectroscopy<sup>[2]</sup>.
- **Photoelectron spectroscopy**: A photo-ionization and energy-dispersive analysis of the emitted photoelectrons to study the composition and electronic state of a sample. *Also known as PES.*
  - A sample (solid, liquid, or gas) is impinged upon by a focused beam of X-rays (say of 1.5 kV).
  - When the sample is exposed to the X-rays, electrons fly out of the sample. The KE of these electrons can be measured.
  - Essentially,  $h\nu$  takes an electron from the core level to above the vacuum level. We know  $h\nu$  and we measure  $KE_{\text{electron}}$ , allowing us to calculate the bonding energy of the electron:  $h\nu = I_{\text{BE}} + E_{\text{kinetic}}$  (see Figure III.4).
- **X-ray photoelectron spectroscopy**: Using soft (200-2000 eV) X-ray excitation (photons in the X-ray energy range) to examine core levels. *Also known as XPS.*
- **Ultraviolet photoelectron spectroscopy**: Using vacuum UV (10-45 eV) radiation (photon is in UV energy range) from discharge lamps to examine valence levels. *Also known as UPS.*

<sup>2</sup>Refer to Labalme (2020), specifically Figure 7.20 and the accompanying discussion.

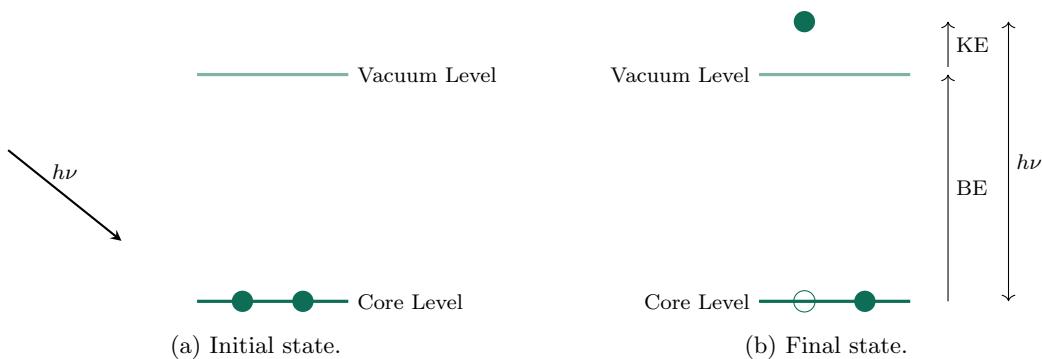


Figure III.4: Photoelectron spectroscopy at an atomic level.

- If we apply PES to O<sub>2</sub>, we get counts that correspond to molecular orbitals  $\pi_g^*$ ,  $\pi_u$ ,  $\sigma_g$ , and  $\sigma_u^*$ .
- Photoelectron spectrum of H<sub>2</sub>O:
  - Pauling's theory suggest that the lone pairs should have equal energy greater than the equal energy of the bonds.
  - However, PES reveals that the lone pairs have two different energies. This is a nail in the coffin of Pauling's valence bond theory.
- PES of CH<sub>4</sub>:
  - There are two states; one with degeneracy 3 and one with degeneracy 1.
  - We have 3 bonds of one energy and 1 with another.
  - Another nail in the coffin.

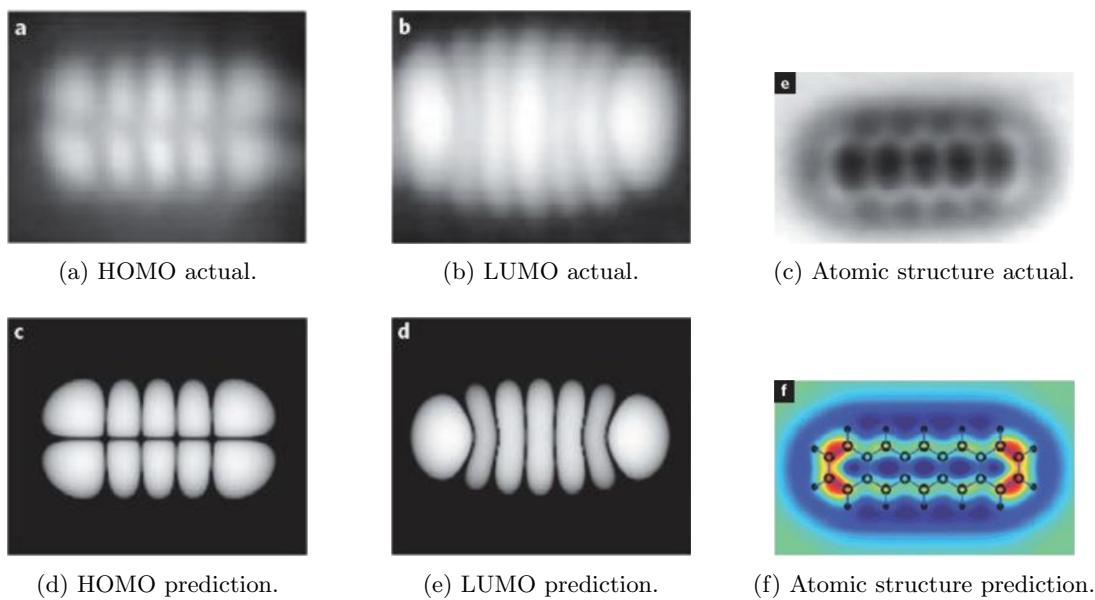


Figure III.5: Correspondence between MO predictions and scanning tunnelling microscopy.

- Can one “see” molecular orbitals? With a scanning tunneling microscope, we can “see” pentatene (5 linearly fused benzene rings). The correspondence between the pictures and MO theory’s predictions is impressive (see Figure III.5).

### III.6 Module 14: Constructing Molecular Orbitals (Part 1)

- Bonding:  $\Psi_\sigma = \Psi_+ = \frac{1}{\sqrt{2}}(\psi_{1s_a} + \psi_{1s_b})$ .
- Anti-bonding:  $\Psi_{\sigma^*} = \Psi_- = \frac{1}{\sqrt{2}}(\psi_{1s_a} - \psi_{1s_b})$ .
  - Addition doesn't necessarily correlate to bonding and subtraction to anti-bonding.
- With simple orbitals, we can combine orbitals by inspection.
  - However, we will learn to build molecular orbitals for much more complicated molecular orbitals, such as those of ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ).
- Degree of orbital overlap/mixing depends on:
  1. Energy of the orbitals (the closer the energy, the more mixing; when the energies differ greatly, the reduction energy due to bonding is insignificant).
  2. Spatial proximity (the atoms must be close enough that there is *reasonable* orbital overlap, but not so close that repulsive forces interfere).
  3. Symmetry (atomic orbitals mix if they have similar symmetries; regions with the same sign of  $\Psi$  overlap).
- The strength of the bond depends upon the degree of orbital overlap.
- For heteronuclear molecules:

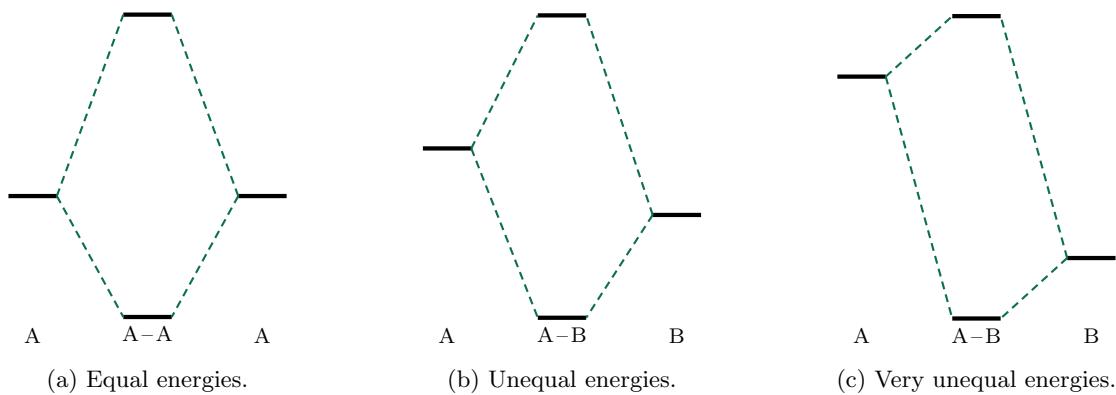


Figure III.6: Combining orbitals of varying energies.

- The bonding orbital(s) will reside predominantly on the atom of lower orbital energy (the more electronegative atom).
- The anti-bonding orbital(s) will reside predominantly on the atom with greater orbital energy (the less electronegative atom).
- The energies of atomic orbitals (measured by PES) have been tabulated (see Figure III.7).
- If you want to measure orbital energies in the range of -10 eV (i.e., upper valence orbitals; see Table 5.2 in Miessler et al. (2014)), use UPS. If you want to look at energy states that are very deep, very core (i.e., 1s in Fe), use XPS.
- **State conservation principle:** The number of molecular orbitals is equal to the number of incipient (atomic) orbitals.
- Symmetry and orbital diagrams (suggested reading Cass and Hollingsworth (2004)):

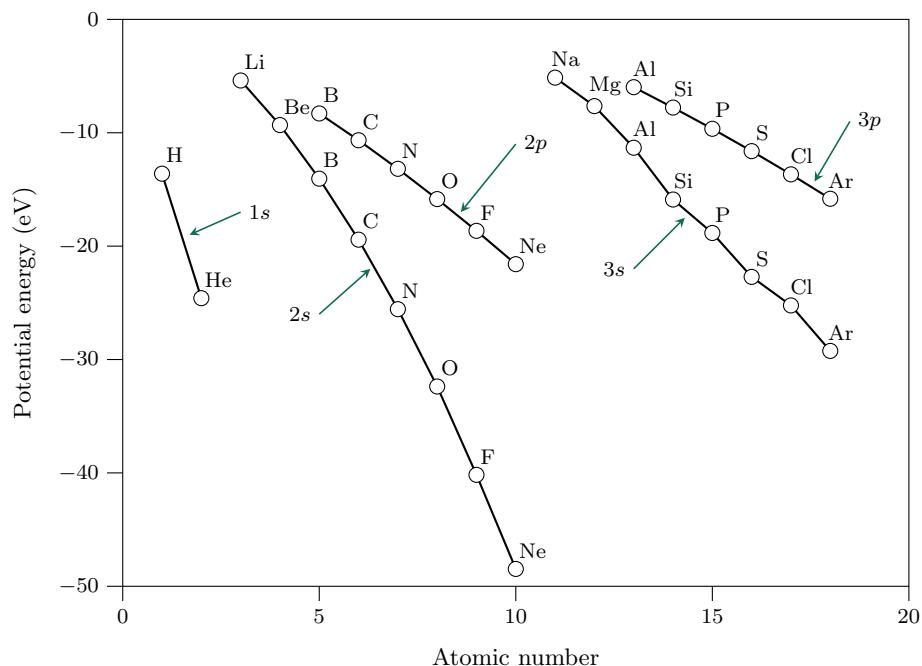
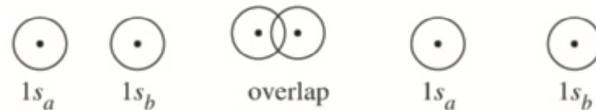
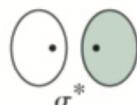


Figure III.7: Orbital potential energies.

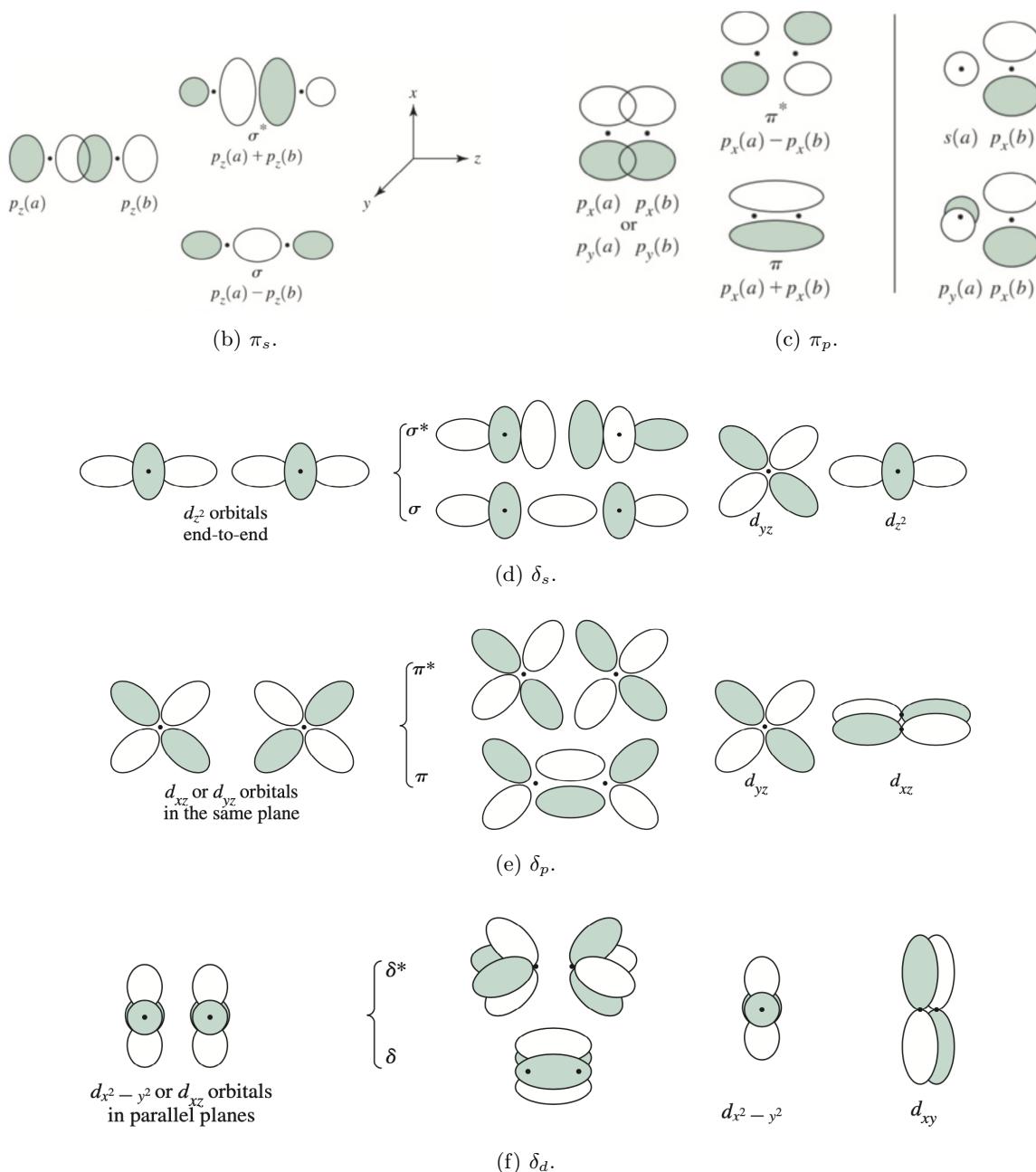
- Orbitals of the same symmetry mix.
- Orbital interactions can be bonding, nonbonding, or antibonding.
- There are three basic types of orbital overlap:  $\sigma$  (end-on interaction),  $\pi$  (side-by-side approach) and  $\delta$  (off-axis approach).
  - $\sigma$  orbitals are symmetric to rotation about the line connecting nuclei.
  - $\pi$  orbitals change sign of the wave function with  $C_2$  rotation about the bond axis.
  - Orbitals also denoted  $g$  are symmetric to inversion.
  - Orbitals also denoted  $u$  are antisymmetric to inversion.
- Orbitals with the correct symmetry and most similar energy mix to the greatest extent.

$$\sigma^* = \frac{1}{\sqrt{2}}[\psi(1s_a) - \psi(1s_b)]$$



$$\sigma = \frac{1}{\sqrt{2}}[\psi(1s_a) + \psi(1s_b)]$$

(a)  $\sigma_s$ .

Figure III.8: Constructing  $s$ ,  $p$ , and  $d$  molecular orbitals.

- There are six MO constructions to be aware of:  $s-s$ ,  $p-p$  ( $\sigma$  and  $\pi$ ), and  $d-d$  ( $\sigma$ ,  $\pi$ , and  $\delta$ ). See Figure III.8.
  - There are similar orbitals in simple diatomic molecules.
- As the mixing of  $\sigma_g$  orbitals gets stronger, the  $2p$  state drops in energy faster than the  $2s$  state, causing the  $2p$  state to have lower energy than the  $2s$  state after a while.

### III.7 Office Hours (Wang)

- Quantum mechanics will not be included on tomorrow's exam.
- Hybridization was developed (1931 by Pauling) earlier than VSEPR theory (1940 by Sidgwick and Powell).
- What *is* a direct product of representations?
  - The direct product generates an  $n \times m$  matrix?
  - Di doesn't have a great explanation, but he's gonna give me a link to his Advanced Inorganic Chemistry textbook.
- Can you go over how to do problems IV and VI with direct product analysis?
  - The IR absorption way from Module 12?
  - $\Gamma_{\text{g.s.}} = A_1$  always.
  - $\Gamma_\mu$  is the sum of the  $x, y, z$  linear irreducible representations.
  - $\Gamma_{\text{e.s.}} = \Gamma_{\text{vibs}}$ .
  - We need to calculate the direct product of every representation in  $\Gamma_{\text{vibs}}$  with every term in  $\Gamma_\mu$ . Products that contain  $A_1$  are IR active?
  - Example:  

$$A_1 \times (A_1 + B_1 + B_1) = A_1 \times A_1 + A_1 \times B_1 + A_1 \times B_2$$
    - Since  $A_1 \times A_1 = A_1$ , we already know after taking only this product that  $A_1$  is IR active.
    - Things aren't IR active because they're linear. Things are IR active because their direct product with the sum of the linear groups contains the totally symmetric representation.
- You can only take the direct product of irreducible representations?

### III.8 Office Hours (Talapin)

- To what extent do we need to know term symbols (they appeared briefly in Module 1)?
- How do we identify the  $T_h$  point group?

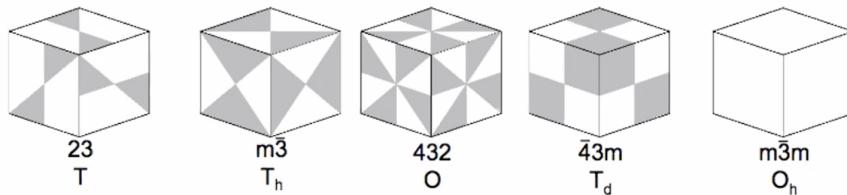


Figure III.9: Tetrahedral point groups.

- It's a very rare point group. It has no dihedral planes.
- What is the point of conjugate elements?
  - Conjugate elements allow us to group symmetry elements into classes — conjugate elements are in the same class!
- Will we need to be able to work with infinite character tables?
- What was that whole thing you did with a symmetry operation  $R$  and the Schrödinger equation?

- What level of familiarity do we need with Dirac's bra-ket notation?
  - Just know that it represents an integral.
- Do we need to evaluate/what do we need to know about those integrals from Wednesday's class?
  - It will be sufficient to write down representations.
- Why does  $\Gamma_\mu$ , the representation of the dipole moment, transform with  $x, y, z$ ?
  - $n$ -degree perturbation theory.
- The problems will be similar to homework problems.

### III.9 Module 15: Constructing Molecular Orbitals (Part 2, HF Molecule)

- 2/1:
- MO Diagrams from Group Theory:
    1. Assign a point group.
    2. Choose basis functions (orbitals).
    3. Apply operations.
    4. Generate (a) reducible representation(s) and SALCs (the latter if applicable).
    5. Reduce to irreducible representations.
    6. Combine central and peripheral orbitals by their symmetry.
    7. Fill MOs with  $e^-$ 's. Draw orbitals.
    8. Generate SALCs of peripheral atoms (if applicable).
    9. Draw peripheral atom SALC with central atom orbital to generate bonding/antibonding MOs (if applicable).
  - We will not need SALCs here.
  - H–F example:
    - Point group:  $C_{\infty v}$ . However, we will work within the  $C_{2v}$  subgroup (knowing why to choose this specific subgroup will come later; just accept it for now).
    - Choose basis functions ( $H_{1s}$ ,  $F_{1s}$ ,  $F_{2p_x}$ ,  $F_{2p_y}$ , and  $F_{2p_z}$ ).
    - Applying operations, we get

$$\begin{aligned}\Gamma_{H_{1s}} &= (1, 1, 1, 1) = A_1 \\ \Gamma_{F_{1s}} &= (1, 1, 1, 1) = A_1 \\ \Gamma_{F_{2p_z}} &= (1, 1, 1, 1) = A_1 \\ \Gamma_{F_{2p_x}} &= (1, -1, 1, -1) = B_1 \\ \Gamma_{F_{2p_y}} &= (1, -1, -1, 1) = B_2\end{aligned}$$

- Therefore, the  $H_{1s}$ ,  $F_{1s}$ ,  $F_{2p_x}$ ,  $F_{2p_y}$ , and  $F_{2p_z}$  orbitals transform with the  $A_1$ ,  $A_1$ ,  $A_1$ ,  $B_1$ , and  $B_2$  irreducible representations, respectively.
- Note that we can also extract  $p$ -orbital information from the corresponding linear functions in the character table.
- Also note that one orbital  $\Rightarrow$  one degree of freedom. We do not have  $x, y, z$ -DOFs as before.

- When we bring the atoms together, those orbitals with similar symmetry (in this case, all the  $A_1$  orbitals) will start mixing. However, from Figure III.7, the  $F_{1s}$  orbital has a very different energy (much lower) than the  $H_{1s}$  orbital, meaning that it has negligible mixing with  $H_{1s}$ . On the other hand,  $H_{1s}$  along with the  $2p$ -orbitals in fluorine have comparable energies, so they will have significant mixing.
- We will get a low energy MO from  $F_{1s}$ , a higher bonding MO from  $H_{1s}$  and  $F_{2p_z}$ , two higher nonbonding MOs from  $F_{2p_x}$  and  $F_{2p_y}$ , and a higher anti-bonding MO from  $H_{1s}$  and  $F_{2p_z}$ .

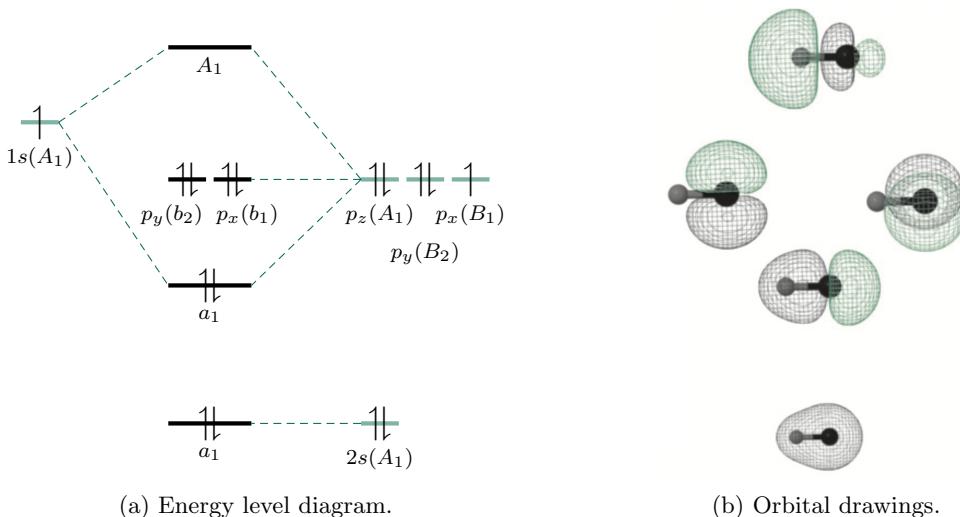


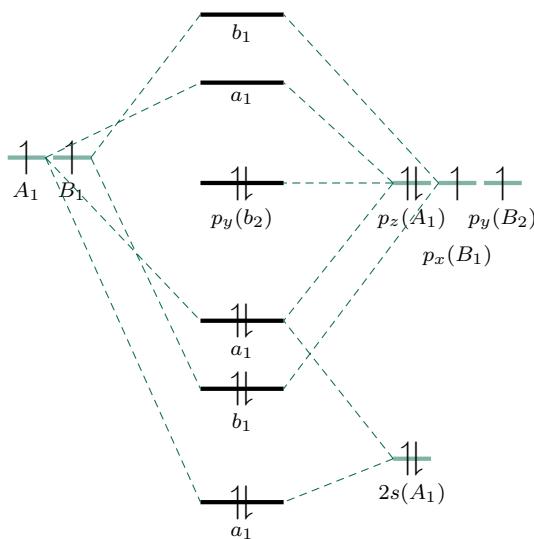
Figure III.10: HF orbital diagram.

- We can now fill the MOs with the atomic electrons using the Aufbau principle, the Pauli exclusion principle, and Hund's rule. We can also draw these orbitals.
- Orbital energies can be found in Table 5.2 of Miessler et al. (2014).
- If the energy difference between orbitals is more than 10 eV, then we can *probably* (not always) ignore mixing.
  - The approximate scaling is that the stabilization energy (or energy gain) is inversely proportional to the energy gap.
  - The magnitude of the interaction integral will be approximately inversely proportional to the energy gap between the atomic orbitals participating.
- Organic chemists can go a long way with a hybridization approach even though it is not reflected in inorganic chemistry.

### III.10 Module 16: Constructing Molecular Orbitals (Part 3, $\text{H}_2\text{O}$ Molecule)

- Beware: Orientation of the point groups  $C_{2v}$  and  $D_{2h}$ .
  - Unlike all other groups,  $C_{2v}$  and  $D_{2h}$  present problems in assigning the irreducible representations. For most groups, the symmetry axis is obvious, or if there are several axes, the principal axis is obvious. For  $C_{2v}$  and  $D_{2h}$ , an ambiguity exists. The commonly (but not unanimously) used convention is the following:
  - If there are three  $C_2$  axes, the one with the largest number of atoms unmoved by a  $C_2$  operation is  $z$ . If there is only one  $C_2$  axis, that is  $z$ .

- Once  $z$  is defined, the  $y$ -axis is defined as the axis of the remaining two axes which has the largest number of atoms unmoved by the  $\sigma$  symmetry operation.
- The  $x$ -axis is the remaining axis.
- The overall result is that the symmetry axes in ethylene are defined as:  $z$  - along the C=C bond;  $y$  - in the molecular plane, perpendicular to the C=C bond; and  $x$  - out of the plane.
- Similar approaches apply to the  $C_{2v}$  point group.
- We will need SALCs here.
  - Since the hydrogen atoms do not lie on the principal rotation axis, they will not individually obey the symmetry operations.
  - Thus, we need **Symmetry Adapted Linear Combinations**.
- **Symmetry Adapted Linear Combination** (of atomic orbitals): The linear combination of multiple atomic orbitals corresponding to peripheral atoms (atoms that do not lie on the principal axis). This linear combination will obey the symmetry modes. *Also known as SALC.*
- To generate SALCs, the steps are:
  - Group the atomic orbitals in the molecule into sets which are equivalent by symmetry.
  - Generate and reduce the reducible representation for each set.
  - Use the projection operator for one basis.
- $H_2O$  example:
  - Point group:  $C_{2v}$ .
  - Choose basis functions (both  $H_{1s}$  orbitals, O the same as F in the last example).
  - Applying operations, we get
 
$$\Gamma_H = (2, 0, 2, 0) = A_1 + B_1$$
    - For the hydrogens, it makes sense that we need two irreducible representations to describe two atoms. More formally, the number of basis functions should match the number of irreducible representations to account for possible degeneracy of irreducible representations.
    - The O orbitals are the same as the F orbitals in the last example.
  - Combining orbitals by their symmetry and energy again, we get the following MOs.

Figure III.11:  $H_2O$  orbital diagram.

- We can now compare this with the results from photoelectron spectroscopy and see that our predictions are correct.

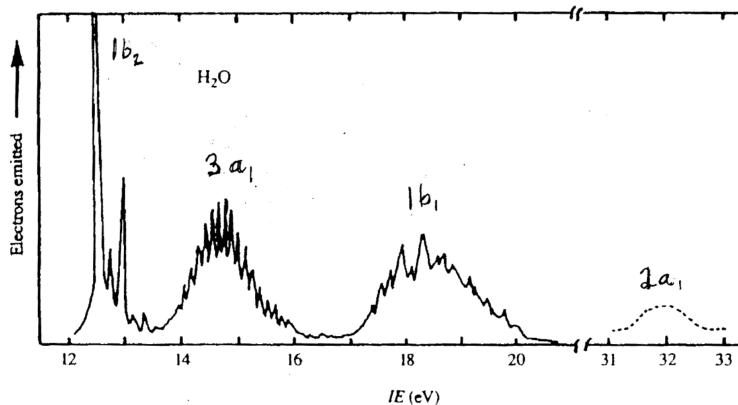


Figure III.12: Photoelectron spectrum for  $\text{H}_2\text{O}$ .

- We see four different states, which matches the prediction of Figure III.11.
- The lowest state is called  $2a_1$  because it is the second state that transforms as  $A_1$  going out from the core (the first is  $1a_1$  corresponding to oxygen's  $1s$  electrons [this state is not shown in Figure III.11 because it is so core as to not be significantly relevant to the chemistry of  $\text{H}_2\text{O}$ ]).
- Then  $1b_1$  is the first  $B_1$  state going out from the core,  $3a_1$  is the third  $A_1$  state, and  $1b_2$  is the first  $B_2$  state.
- There are no  $4a_1$  and  $2b_1$  electrons (see Figure III.11); hence, there are no such PES peaks (see Figure III.12).
- Note that the numbers along the bottom axis correspond to the orbital potential energies of the corresponding molecular orbitals.
- For  $\text{H}_2\text{O}$ , hybridization is qualitatively wrong.
- To generate SALCs:
  - Use the projection operator. See Nocera Lecture 6 for how to mathematically apply it.
  - Projection operators constitute a method of generating the symmetry allowed combinations.
  - Taking one AO and projecting it out using symmetry.
- Using the projection operator method to reconstruct SALC orbitals ( $\text{NH}_3$  example):

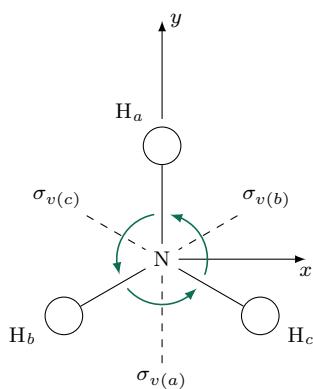


Figure III.13: Coordinate system for  $\text{NH}_3$ .

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$	linear	quadratic
$A_1$	1	1	1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	
$E$	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Table III.1: Character table for the  $C_{3v}$  point group.

- Ungroup the operations in the classes in Table III.1. Choose  $H_a$  and see into which  $H$  it projects under each operation. If we order the operations  $E, C_3, C_3^2, \sigma_{v(a)}, \sigma_{v(b)}, \sigma_{v(c)}$ , then  $H_a$  becomes  $H_a, H_b, H_c, H_a, H_c, H_b$ , respectively.
- Multiply each projected atom by the corresponding character and sum. Thus, for the three representations, we have

$$\begin{aligned} A_1 &= H_a + H_b + H_c + H_a + H_c + H_b = 2H_a + 2H_b + 2H_c \\ A_2 &= H_a + H_b + H_c - H_a - H_c - H_b = 0 \\ E &= 2H_a - H_b - H_c + 0 + 0 + 0 = 2H_a - H_b - H_c \end{aligned}$$

- We have essentially just done what the projection operator would enable us to do.

- Continuing with the  $\text{H}_2\text{O}$  example:

- Using the projection operator, we get

$$\begin{aligned} P^{A_1} &= \frac{1}{4}[1E\phi_1 + 1C_2\phi_1 + 1\sigma_{xz}\phi_1 + 1\sigma_{yz}\phi_1] = \frac{1}{2}(\phi_1 + \phi_2) \\ P^{B_1} &= \frac{1}{4}[1E\phi_1 - 1C_2\phi_1 + 1\sigma_{xz}\phi_1 - 1\sigma_{yz}\phi_1] = \frac{1}{2}(\phi_1 - \phi_2) \end{aligned}$$

- $P^{A_1}$  is a sum of the two hydrogen 1s orbitals.
- $P^{B_1}$  is a difference of the two hydrogen 1s orbitals.
- This step allows us to construct electron density maps for the SALCs of the hydrogen's atomic orbitals.
- We can now see if the symmetry of various orbitals matches up or doesn't match up and use this information to sketch molecular orbitals.
- Oxygen atomic orbital coefficients can only be analytically derived with quantum mechanical calculations.
- How can we predict the shape of molecules from MO theory (i.e., without VSEPR theory)?
- **Walsh diagrams** help understand the molecular shapes (bond angles).
  - If  $\text{H}_2\text{O}$  is linear, it is part of the  $D_{\infty h}$  point group (which can be reduced to  $D_{2h}$  for further mysterious reasons).
  - $1\sigma_g^+$ : If we slowly decrease the bond angle, the hydrogen orbital overlap will increase, meaning that  $1\sigma_g^+$  energy decreases.
  - $1\sigma_u^+$ : If we slowly decrease the bond angle, the  $s$  and  $p$  orbitals will become less aligned, meaning that  $1\sigma_u^+$  energy increases.
  - $\pi_u, 2a_1$ : Energy decreases as hydrogen orbitals get closer to the appropriately signed region of the  $\text{O}_p$  orbital.
  - $\pi_u, b_2$ : Energy is constant.
  - Now all orbitals with electrons have been accounted for. Since 2 energies go down, 1 goes up, and 1 stays the same as bond angle decreases, we know that bond angle will decrease to an equilibrium.

### III.11 Module 17: Constructing Molecular Orbitals (Part 4, NH<sub>3</sub> Molecule)

2/3: • NH<sub>3</sub> example:

- Point group: C<sub>3v</sub>.
- Basis functions: H<sub>1s</sub>, N<sub>2s</sub>, N<sub>2p<sub>x</sub></sub>, N<sub>2p<sub>y</sub></sub>, and N<sub>2p<sub>z</sub></sub>.
- Apply operations (pick any one operation from each class)/construct reducible representations:

$$\Gamma_H = (3, 0, 1) = A_1 + E$$

$$\Gamma_{N_{2s}} = A_1$$

$$\Gamma_{N_{2p_x}} = E$$

$$\Gamma_{N_{2p_y}} = E$$

$$\Gamma_{N_{2p_z}} = A_1$$

- N<sub>2p<sub>x</sub></sub> and N<sub>2p<sub>y</sub></sub> are doubly degenerate — their transformation cannot be decoupled and they transform together.
- Look at the relevant energies and plot them against each other.
- 3 A<sub>1</sub> type atomic orbitals form 3 a<sub>1</sub> type MOs.

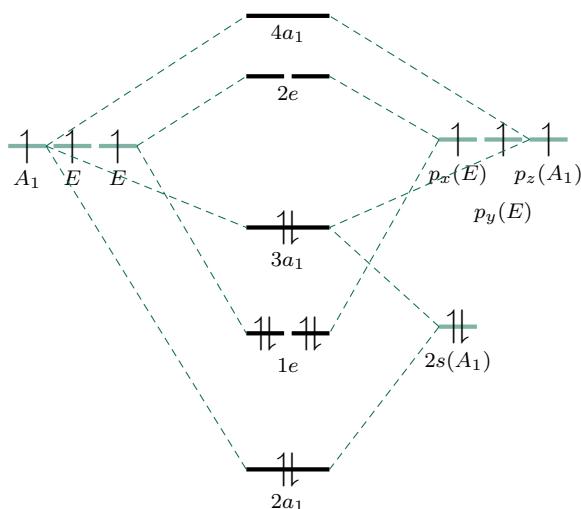


Figure III.14: NH<sub>3</sub> orbital diagram.

- Since 2s(A<sub>1</sub>) and 1s(A<sub>1</sub>) are so far away energetically, their combination will have very low energy.
- On the other hand, since the 2s(A<sub>1</sub>) and p<sub>z</sub>(A<sub>1</sub>) are close in energy, they have a lot of overlap.
- We can't analytically calculate orbital energies at this level. Take an educated guess on the homework and explain your reasoning. Note that here, e orbitals are more stabilizing because they are bigger and have larger overlap. Also, σ bonds are stronger than π bonds because there is a higher degree of overlap.
- To see what these orbitals look like, we need to apply the projection operator.
- We need to construct one A<sub>1</sub> orbital and two E orbitals.
- Modifying from the example from last time, we have  $P^{A_1} \approx \phi_1 + \phi_2 + \phi_3$  and  $P^E \approx 2\phi_1 - \phi_2 - \phi_3$ .

- For the last  $E$  SALC, we apply the projection to each hydrogen atom (we can choose any basis function) giving us, in addition to the other projections,  $P^E \approx 2\phi_2 - \phi_3 - \phi_1$  and  $P^E \approx 2\phi_3 - \phi_1 - \phi_2$ . By subtracting these two, we get  $\Psi_E = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$ . Do we choose this linear combination because it's orthogonal to the other two? Because its structure is different and simple (you *can* do it with any linear combination, but it will make the analysis much more complicated if you do it with a trickier linear combination).
- We need to renormalize our SALCs so that the integral of their square over all space is 1. To normalize, we must guarantee that the sum of the squares of the coefficients is 1. For  $P^{A_1}$  for example,  $1^2 + 1^2 + 1^2 = 3$ , so we must scale the whole thing by  $\frac{1}{\sqrt{3}}$ .
- In the PES spectrum, we see three peaks, one being approximately twice as wide as the others (corresponding to the double degenerate state).
- Walsh diagrams (rely on the pictures that we draw of orbitals):
  - $1a'_1$  energy decreases,  $1e'$  energy increases,  $a''_2$  energy decreases rather dramatically.
  - If we promote electrons to the excited state, the relevant Walsh diagrams will change, and this will cause the molecule to change shape.
- Also try to sketch the MOs in the homework.

### III.12 Module 18: Constructing Molecular Orbitals (Part 5, $\text{H}_2\text{C}=\text{CH}_2$ Molecule)

- $\text{H}_2\text{C}=\text{CH}_2$  example:

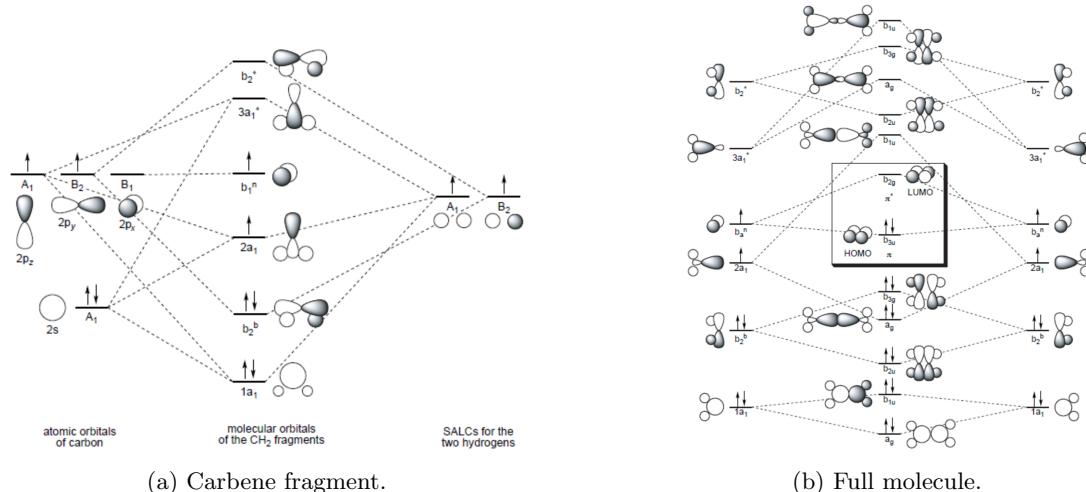


Figure III.15:  $\text{H}_2\text{C}=\text{CH}_2$  orbital diagram.

- Two different approaches ( $D_{2h}$ ):  $\text{C}_1 + \text{C}_2$  then  $\text{H}_{1-4}$ , or two carbene fragments ( $\text{CH}_2$ ).
  - We can read about the first approach in the linked JCE article (Cass & Hollingsworth, 2004).
- $C_{2v}$  for the  $\text{CH}_2$  fragment.
- When we make the MO diagram, we have two unpaired electrons, one in each of the upper two orbitals. These will be used for bonding to the other carbene fragment.
- We will then combine the MO diagrams and will need to reassign orbital names because ethene isn't  $C_{2v}$ ; it's  $D_{2h}$ .

### III.13 Module 19: Isolobal Principle

- **Isolobal** (fragment): A fragment with similar (not identical) numbers, symmetry properties, approximate energies, and shapes of the frontier orbitals and the number of electrons in them.
- This allows us to show, for example, that a carbene fragment and a  $d^7$  metal complex have similar properties.
- Two  $\text{CH}_3$  fragments will tend to couple into ethane. But so will two isolobal  $\text{Mn}(\text{CO})_5$  fragments!

### III.14 Module 20: Orbital Hybridization

- **Hybridization:** The concept of mixing atomic orbitals into new hybrid orbitals (with different energies, shapes, etc. than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds.
- Hybridization accomplishes the work of MO theory in steps: Creating new orbitals and then bonding atoms with them, as opposed to defining new orbitals and filling them.
- This was the dominant approach in chemistry before MO theory, and is still widely used in organic chemistry.
- For light elements, the energy gaps between orbitals aren't very large and this method is legitimate to some degree.
  - For carbon, it's acceptable.
  - For silicon and lead (in the same group), this is not a good approach; it will give you incorrect predictions (e.g., around bond angles and lengths).
- Steps to determine the hybridization of a bond:
  1. Assign a point group.
  2. Choose basis function ( $\sigma$  bonds).
  3. Apply operations.
  4. Reduce to irreducible representations.
  5. Compare symmetry of irreducible representations to central atom MOs.
- $\text{BF}_3$  example:
  - Point group:  $D_{3h}$ .
  - $\Gamma_\sigma = (3, 0, 1, 3, 0, 1)$ .
  - $\Gamma_\sigma = A'_1 + E'$ .
  - For boron,  $\text{B}(s) = A'_1$ ,  $\text{B}(p_x) = E'$ ,  $\text{B}(p_y) = E'$ , and  $\text{B}(p_z) = A''_2$ . Thus, since one orbital matches up on  $s$  and two match up on  $p$  (specifically,  $p_x, p_y$ ), the hybrid orbitals will be  $sp^2$  (hybrid of  $s, p_x, p_y$ ).
- It is not generally justifiable to say that atomic orbitals in *individual* atoms mix before bonding.

### III.15 Chapter 5: Molecular Orbitals

*From Miessler et al. (2014).*

- 1/29: • MO theory uses group theory to describe molecular bonding, complementing and extending Chapter 3.

- “In molecular orbital theory the symmetry properties and relative energies of atomic orbitals determine how these orbitals interact to form molecular orbitals” (Miessler et al., 2014, p. 117).
  - The molecular orbitals are filled according to the same rules discussed in Chapter 2.
  - If the total energy of the electrons in the molecular orbitals is less than that of them in the atomic orbitals, the molecule is stable relative to the separate atoms (and forms). If the total energy of the electrons in the molecular orbitals exceeds that of them in the atomic orbitals, the molecule is unstable (and does not form).
  - Homonuclear** (molecule): A molecule in which all constituent atoms have the same atomic number.
  - Heteronuclear** (molecule): A molecule that is not homonuclear, i.e., one in which at least two atoms differ in atomic number.
  - A less rigorous pictorial approach can describe bonding in many small molecules and help us to build a more rigorous one, based on symmetry and employing group theory, that will be needed to understand orbital interactions in more complex molecular structures.
  - Schrödinger equations can be written for electrons in molecules as they can for electrons in atoms. Approximate solutions can be constructed from the LCAO method.
    - In diatomic molecules for example,  $\Psi = c_a\psi_a + c_b\psi_b$  where  $\Psi$  is the molecular wave function,  $\psi_{a,b}$  are the atomic wave functions for atoms  $a$  and  $b$ , and  $c_{a,b}$  are adjustable coefficients that quantify the contribution of each atomic orbital to the molecular orbital.
  - “As the distance between two atoms is decreased, their orbitals overlap, with significant probability for electrons from both atoms being found in the region of overlap” (Miessler et al., 2014, p. 117).
  - Electrostatic forces between nuclei and electrons in bonding molecular orbitals hold atoms together.
- 2/5:
- Precise calculations show that the coefficient of the  $\sigma^*$  hydrogen antibonding orbital is slightly larger than that of the  $\sigma$  orbital, but we typically neglect this distinction.
    - This technically implies that  $\Delta E_{\sigma^*} > \Delta E_{\sigma}$ , i.e., that the increase in energy from electrons in atomic orbitals moving into the  $\sigma^*$  antibonding molecular orbital is greater in magnitude than the decrease in energy from electrons in atomic orbitals moving into the  $\sigma$  bonding molecular orbital.
  - $\sigma$  orbital:** A molecular orbital that is symmetric to rotation about the line connecting the nuclei.
  - Orbital asterisk:** Denotes antibonding orbitals for those molecules where bonding and antibonding orbital descriptions are unambiguous (i.e., smaller molecules).
  - When two regions of like sign overlap, the sum of the orbitals exhibits increased electron probability in the overlap region, and vice versa for regions of opposite sign.
  - When the  $z$ -axes are drawn pointing in the same direction, their difference is  $\sigma$  and their sum is  $\sigma^*$ .



(a) Same direction.

(b) Opposite directions.

Figure III.16: Choice of  $z$ -axis direction.

- Notice how in Figure III.16b, we can simply push the orbitals together (add them) to have regions of like sign overlap and form a bonding orbital.

- However, in Figure III.16a, with a more standard coordinate system, we have to flip the signs of one of the orbitals before merging them (multiply it by  $-1$  and add it to the other orbital/subtract it from the other orbital) to create a bonding orbital. If we add them as they are, we will get an antibonding orbital.
- **$\pi$  orbital:** A molecular orbital with a change in sign of the wave function under  $C_2$  rotation about the  $z$ -axis (the bond axis).
  - $\pi$  and  $\pi^*$  orbitals arise from the interactions between  $p_x$  and  $p_y$  atomic orbitals.
- MOs that form from  $p_z$  orbitals are  $\sigma$  and  $\sigma^*$  orbitals.
- “When orbitals overlap equally with both the same and opposite signs... the bonding and antibonding effects cancel, and no molecular orbital results” (Miessler et al., 2014, p. 121).
- $d$  orbitals can also be involved in bonding in heavier elements such as the transition metals.
  - Two  $d_{z^2}$  orbitals participate in  $\sigma$  bonding.
  - Two  $d_{xz}$  or  $d_{yz}$  orbitals participate in  $\pi$  bonding.
  - Two  $d_{x^2-y^2}$  or  $d_{xz}$  orbitals participate in  **$\delta$  bonding**.
- **$\delta$  orbital:** A molecular orbital with a change in sign of the wave function under  $C_4$  rotation about that  $z$ -axis.
  - $\delta$  and  $\delta^*$  orbitals arise from the interactions of atomic orbitals meeting in parallel planes and combining side to side.
- “Sigma orbitals have no nodes that include the line connecting the nuclei, pi orbitals have one node that includes the line connecting the nuclei, and delta orbitals have two nodes that include the line connecting the nuclei” (Miessler et al., 2014, p. 121).
- Note that  $p_x$  and  $d_{xz}$  orbitals (for example) could, in theory, interact.
- Additional thoughts on Figure III.6:
  - Similarity in energy is correlated with similarity in structure.
  - When orbital energies are similar (Figure III.6a), there is a large difference between the atomic orbitals and the molecular orbitals, resulting in a great potential for stabilization through bonding.
- Molecular orbitals help us understand the structure of  $\text{Li}_2$ ,  $\text{Be}_2$ , and other diatomic molecules that violate the octet rule.
  - They also explain experimental phenomena that clash with VSEPR theory — for example, the Lewis structure of  $\text{O}_2$  predicts a diamagnetic molecule, but in reality,  $\text{O}_2$  is paramagnetic with two unpaired electrons.
- See Figure III.17 for the molecular orbitals in the homonuclear diatomic molecules formed by the first 10 elements, neglecting interactions between atomic orbitals of differing energy levels.
- Bond order:
$$\text{B.O.} = \frac{1}{2}(\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals})$$
  - Generally, we need only consider valence electrons to calculate the bond order: For example,  $\text{O}_2$  has  $\text{B.O.} = 2$  whether or not you factor valence electrons into the calculation.
- Core electrons are generally assumed to reside mostly on the original atom and negligibly participate in bonding and antibonding interactions.

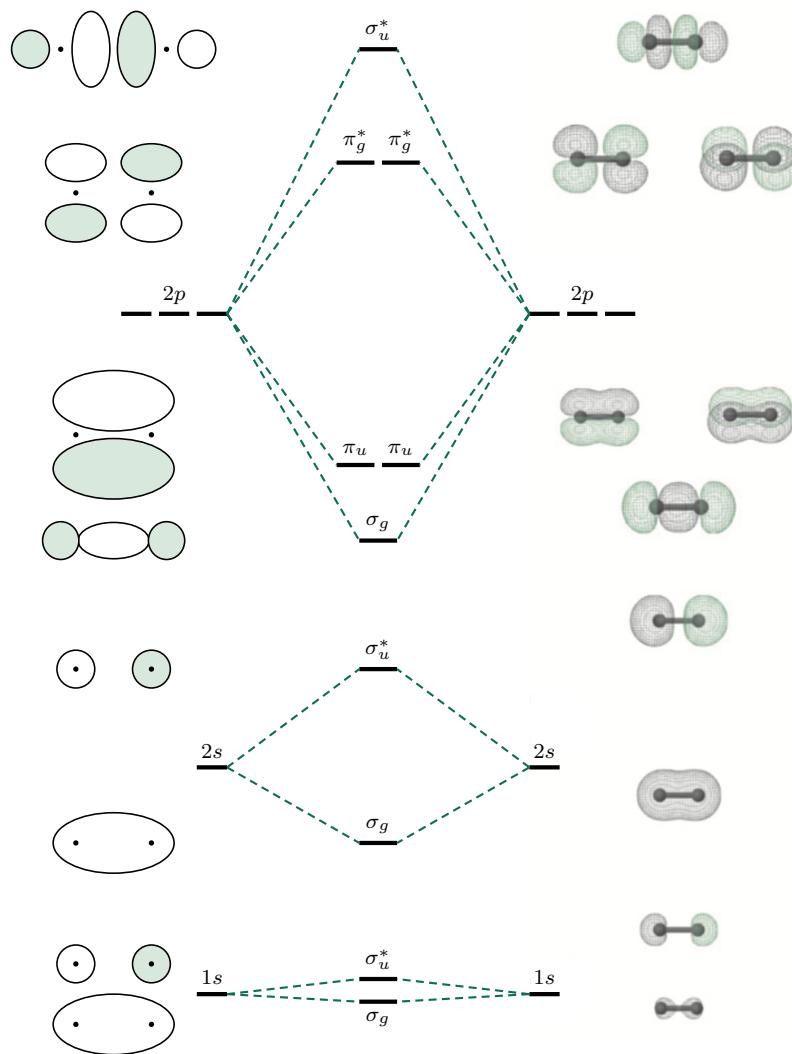


Figure III.17: Molecular orbitals for the first 10 elements.

- This is reflected by how much lower the 1s MOs are in Figure III.17 than the others, and by how slight the difference is between bonding and antibonding.
- “When two molecular orbitals of the same symmetry have similar energies, they interact to lower the energy of the lower orbital and raise the energy of the higher orbital” (Miessler et al., 2014, p. 124).
- **$\sigma_g$  symmetry:** Symmetry to infinite rotation and inversion.
  - Possessed by the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  orbitals in Figure III.17, for example.
- Molecular orbitals with the same symmetry and similar energies can **mix**, lowering the energy of the lower orbital and raising the energy of the higher orbital.
  - For example, the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  orbitals in Figure III.17 can mix, lowering the energy of the 2s one and raising the energy of the 2p one.
- 2/6: • Atomic orbital energies decrease across a row in the periodic table.
- Characterization of selected homonuclear diatomic molecules:

- He<sub>2</sub>’s bond order is 0, with two bonding and two antibonding electrons. Thus, it has no significant tendency to form (it’s bond energy is 0.01 J/mol, compared to H<sub>2</sub>’s 436 kJ/mol).
- B<sub>2</sub> is paramagnetic (because of its two unpaired  $\pi_u$  electrons). The 2p valence electrons do not occupy the  $\sigma_g$  MO because of orbital mixing and because the energy difference between  $\sigma_g(2p)$  and  $\pi_u(2p)$  is greater than  $\Pi_c$  (even if there were no mixing, the electrons would still occupy the  $\pi_u$  orbitals if it was more energetically favorable to do this than to occupy the same orbital).
- C<sub>2</sub> is a rarely encountered allotrope of carbon, but it has two  $\pi$  bonds and no  $\sigma$  bonds.
- In N<sub>2</sub>, some larger trends become apparent:
  - Since electrons in different orbitals vary in their shielding abilities and electron-electron interactions, the difference between the 2s and 2p energies increase as  $Z$  increases.
  - More specifically, 2s electrons have higher probabilities close to the nucleus than 2p electrons (Figure 0.8), so they are more affected by increasing nuclear charge (inverse square law).
  - As a result of this separation, the  $\sigma_g(2s)$  and  $\sigma_g(2p)$  orbitals mix less in N<sub>2</sub> than in C<sub>2</sub> or B<sub>2</sub>.
- The ions of O<sub>2</sub> (which include dioxygenyl O<sub>2</sub><sup>+</sup>, superoxide O<sub>2</sub><sup>-</sup>, and peroxide O<sub>2</sub><sup>2-</sup>) reveal that bond order and bond distance are inversely proportional. Here, mixing finally becomes small enough that the normal filling order (as in Figure III.17) returns.
- Notice how atomic radius consistently decreases across the second period, but bond length decreases until N<sub>2</sub> and then increases (because of the addition of antibonding electrons).
- At this point, we’ll assume (for PES purposes) the energy levels in the uncharged molecule to be essentially the same as those in the charged ions generated when we seek to examine core energy levels<sup>[3]</sup>.
- Comparing the PES spectra for N<sub>2</sub> and O<sub>2</sub>, it can be seen that the N<sub>2</sub> energy levels are closer together than the O<sub>2</sub> ones.
- PES also provides evidence for the existence of **vibrational energy levels**, energy levels that are much more closely spaced than electronic levels that cause the multiple peaks within one “peak.”
- Orbitals that are strongly involved in bonding have **vibrational fine structure** (multiple peaks), and vice versa for less involved orbitals.
  - Thus, the 10  $\pi_u$  vs. the 6  $\sigma_g$  vibrational peaks in O<sub>2</sub> indicate that the  $\pi_u$  orbitals are more strongly involved in bonding than the  $\sigma_g$  orbital.
- “The atomic orbitals of atoms that form homonuclear diatomic molecules have identical energies, and both atoms contribute equally to a given MO. Therefore, in the molecular orbital equations, the coefficients associated with the same atomic orbitals of each atom...are identical. In heteronuclear diatomic molecules...the atomic orbitals have different energies, and a given MO receives unequal contributions from these atomic orbitals; the MO equation has a different coefficient for each of the atomic orbitals that contribute to it” (Miessler et al., 2014, pp. 134, 136).
- Atomic orbitals closer in energy to an MO contribute more to that MO, and thus have larger coefficients in the wave equation.
- CO example:
  - The 1 $\pi$  orbitals are lower than the 3 $\sigma$  orbitals because of the strong mixing between the 2p<sub>z</sub> orbital of oxygen and the 2s and 2p<sub>z</sub> orbitals of carbon.
  - The 3 $\sigma$  orbital has a large lobe on the carbon end because two carbon orbitals (2s and 2p<sub>z</sub>) mix with one oxygen orbital (2p<sub>z</sub>).

<sup>3</sup>However, we should note that this is an oversimplification; a rigorous treatment of PES considers how the energy levels and orbital shapes vary between the neutral and ionized species.

- The  $\pi$  orbital has electron density concentrated on oxygen because of the better energy match between the MO and the  $2p_{x,y}$  orbitals of oxygen; the  $\pi^*$  orbital has electron density concentrated on carbon because of the better energy match between the MO and the  $2p_{x,y}$  orbitals of carbon.
- Atomic orbitals with energy differences greater than 10-14 eV usually do not interact significantly.
- MOs in HF predict a polar bond since electron density is concentrated on F to such a greater extent in every occupied orbital.
- **Frontier orbitals:** The HOMO and LUMO, so-named because they lie at the occupied-unoccupied frontier.
- Frontier orbitals help explain reaction chemistry with transition metals.
  - In CO for example, we'd predict based on electronegativity that the O would be more reactive, and hence we'd get a preponderance of M–O–C structures.
  - However, carbonyl complexes are typically of the form M–C–O because the frontier orbitals both lie more on C. Indeed, the HOMO contains the least stabilized (most reactive) electrons in the molecule, and the LUMO is ready to accept whatever electrons are donated first.
- Ionic compounds can still be treated, MO theory-wise, like covalent compounds; we just get MOs that are almost identical to the more favored constituent atomic orbitals.
- Crystalline lattice salts are much more stable than diatomic ones.
  - Such crystal lattices are held together by a combination of electrostatics (ionic) attraction and covalent bonding.
  - Salts do not exhibit directional bonds; instead, the orbitals form energy bands (see Chapter 7).
- Considers lattice enthalpies and Born-Haber cycles<sup>[4]</sup>.
- **Group orbitals:** Collections of matching orbitals on outer atoms.
  - Sets of orbitals that potentially could interact with the central atom orbitals.
  - The same combinations that formed bonding and antibonding orbitals in diatomics.
- FHF<sup>-</sup> example:
  - The group orbitals are formed by adding and subtracting the F orbitals as we would in F<sub>2</sub>.

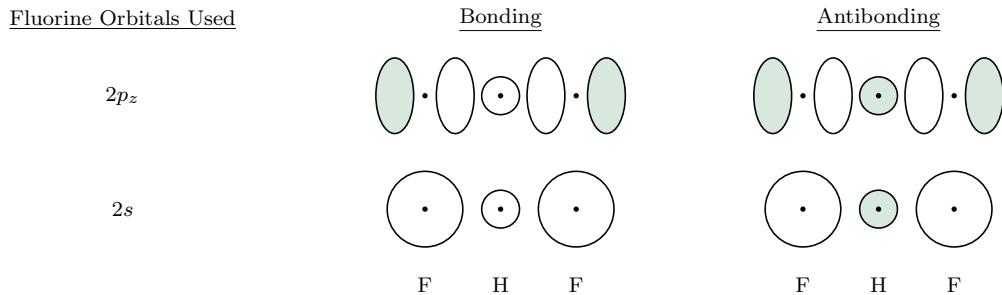
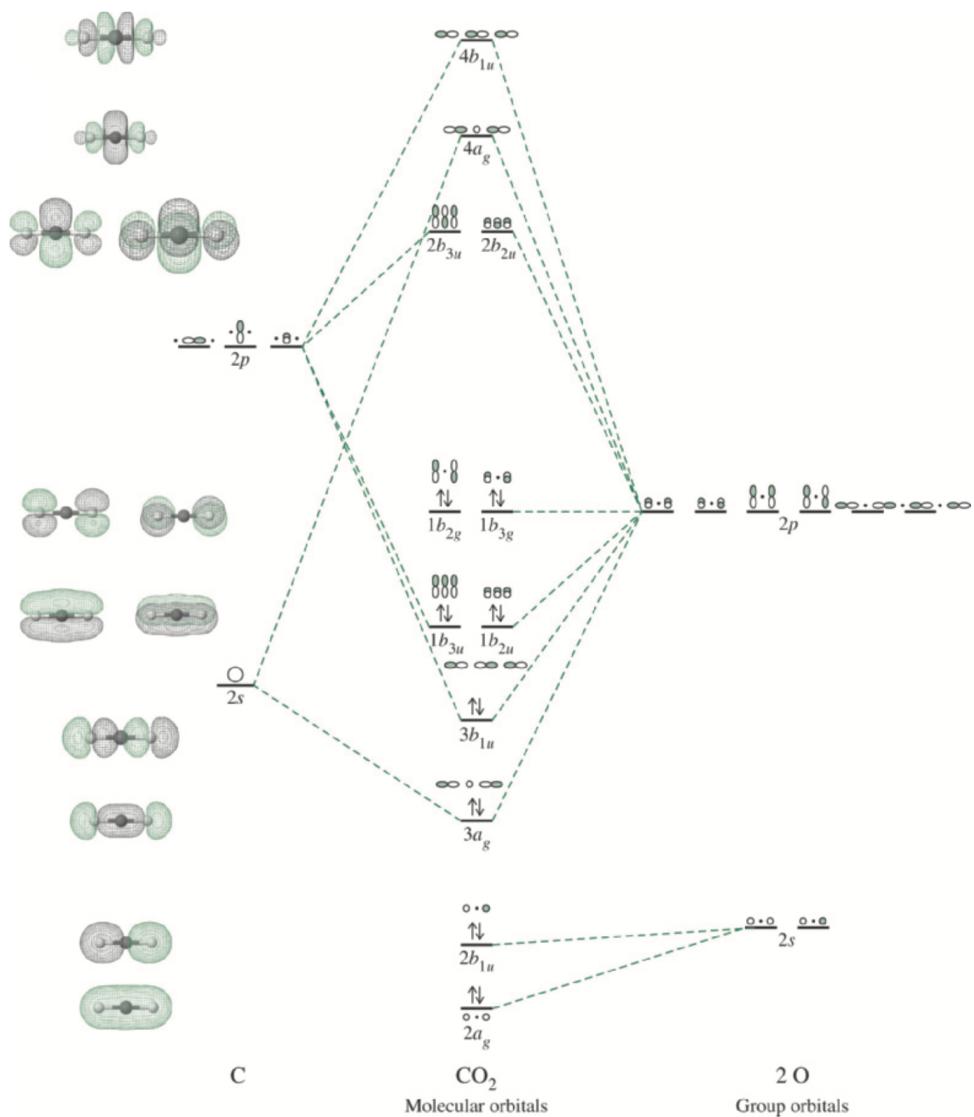


Figure III.18: Interaction of fluorine group orbitals with the hydrogen 1s orbital.

- The only two group orbitals eligible for bonding with the H(1s) orbital based on symmetry are  $2s + 2s$  and  $2p_{z_a} - 2p_{z_b}$ . Having the H orbital with the same sign as the surrounding lobes gives bonding orbitals, and the opposite sign generates antibonding orbitals.

<sup>4</sup>See Labalme (2020), specifically Figure 8.2 and the associated discussion

- Since the H(2s) orbitals match better energetically with the F(2p<sub>z</sub>) orbitals than the F(2s) orbitals, the 2p<sub>z</sub> interactions will be stronger.
  - Notice that the lone pairs are delocalized over both fluorine atoms, not confined to one as the Lewis dot model predicts.
  - Additionally, the Lewis approach predicts two, 2-electron bonds, resulting in 4 electrons around the central H atom. However, the MO model suggests 2 electrons (in a  $\sigma$  bond [ $a_g$ ]) decentralized over all three atoms.
- A stepwise approach to building MOs for more complex molecules (Miessler et al., 2014, p. 143):
    1. Determine the point group of the molecule. If it is linear, substituting a simpler point group that retains the symmetry of the orbitals (ignoring the wave function signs) makes the process easier. It is useful to substitute  $D_{2h}$  for  $D_{\infty h}$  and  $C_{2v}$  for  $C_{\infty v}$ . This substitution (known as a **Descent in Symmetry**) retains the symmetry of the orbitals without the need to use infinite-fold rotation axes.
    2. Assign  $x, y, z$  coordinates to the atoms, chosen for convenience. Experience is the best guide here. A general rule is that the highest order rotation axis of the molecule is assigned as the  $z$ -axis of the central atom. In nonlinear molecules, the  $y$ -axes of the outer atoms are chosen to point toward the central atom.
    3. Construct a (reducible) representation for the combination of the valence  $s$  orbitals on the outer atoms. If the outer atom is not hydrogen, repeat the process, finding the representations for each of the other sets of outer atom orbitals (for example,  $p_x$ ,  $p_y$ , and  $p_z$ ). As in the case of the vectors described in Chapter 4, any orbital that changes position during a symmetry operation contributes 0 to the character of the resulting representation; any orbital that remains in its original position — such as a  $p$  orbital that maintains its position and direction (signs of its orbital lobes) — contributes 1; and any orbital that remains in the original position, with the signs of its lobes reversed, contributes -1.
    4. Reduce each representation from Step 3 to the sum of its irreducible representations. This is equivalent to finding the symmetry of the group orbitals or the **symmetry-adapted linear combinations** (SALCs) of the orbitals. The group orbitals are then the combinations of atomic orbitals that match the symmetry of the irreducible representations.
    5. Identify the atomic orbitals of the central atom with the same symmetries (irreducible representations) as those found in Step 4.
    6. Combine the atomic orbitals of the central atom and those of the group orbitals with matching symmetry and similar energy to form molecular orbitals. The total number of molecular orbitals formed must equal the number of atomic orbitals used from all the atoms. Note that the MOs are assigned lowercase Mulliken symbols (e.g.,  $a_1$ ), whereas atomic orbitals and representations in general are assigned uppercase Mulliken symbols (e.g.,  $A_1$ ).
  - CO<sub>2</sub> example:
    - We find the same group orbitals as in FHF<sup>-</sup> but by using the stepwise procedure.
      - Note that saying  $\Gamma_{2s} = A_g + B_{1u}$ , for example, expresses the fact that there are two 2s orbitals (the sum and difference of the O(2s) orbitals) and that one has  $A_g$  symmetry while the other has  $B_{1u}$  symmetry.
      - The orbitals on the central atom are 2s, 2p<sub>z</sub>, 2p<sub>x</sub>, 2p<sub>y</sub>.
      - The  $A_g$  O(2s) orbital can be added to and subtracted from the C(2s) orbital, and the  $B_{1u}$  O(2s) orbital can be added to and subtracted from the C(2p<sub>z</sub>) orbital.
        - However, due to the large energy difference between the O and C orbitals, these do not generally form and are not included in Figure III.19.
        - Instead, the two O(2s) orbitals are included as  $\sigma$  2a<sub>g</sub> and 2b<sub>1u</sub>, respectively, nonbonding orbitals.

Figure III.19: Molecular orbitals for  $\text{CO}_2$ .

- The  $A_g$  O( $2p_z$ ) orbital can be added to and subtracted from the C( $2s$ ) orbital, and the  $B_{1u}$  O( $2p_z$ ) orbital can be added to and subtracted from the C( $2p_z$ ) orbital.
  - From the first interaction: The  $\sigma$   $3a_g$  bonding orbital formed is the most stable, with only two nodes and an uninterrupted probability region between the three nuclei. The  $\sigma^*$   $4a_g$  antibonding orbital is the second least stable with four nodes.
  - From the second interaction: The  $\sigma$   $3b_{1u}$  bonding orbital formed is the second most stable, with only three nodes. The  $\sigma^*$   $4b_{1u}$  antibonding orbital is the least stable with a whopping five nodes.
- The  $B_{2u}$  O( $2p_y$ ) orbital can be added to and subtracted from the C( $2p_y$ ) orbital, yet the  $B_{3g}$  O( $2p_y$ ) orbital does not have matching symmetry with any C orbital.
  - From the first interaction: The  $\pi$   $1b_{2u}$  bonding orbital formed is less stable than the  $\sigma$   $3b_{1u}$  orbital since it lacks such direct probability between the nuclei but also has few nodes. The  $\pi^*$   $2b_{2u}$  antibonding orbital is more stable than the  $\sigma^*$   $4a_g$  antibonding orbital since it has fewer nodes.

- From the second interaction: The  $\pi 1b_{3g}$  nonbonding orbital formed resides in the middle of the energy diagram.
- The  $B_{3u}$  O( $2p_x$ ) orbital can be added to and subtracted from the C( $2p_x$ ) orbital, yet the  $B_{2g}$  O( $2p_x$ ) orbital does not have matching symmetry with any C orbital.
- The cases are symmetric to the previous two.
- This process may be used to obtain numerical values for the coefficients of the atomic orbitals, but the computational methods are beyond the scope of Miessler et al. (2014).
- H<sub>2</sub>O example:
  - We canonically select that  $xz$ -plane as the plane of the molecule when we have a choice.
  - Because the H( $1s$ ) orbitals have no directionality, it is not necessary to assign coordinate axes to the hydrogen atoms.

Symmetry	Molecular Orbitals	=	Oxygen Atomic Orbitals	Group Orbitals from Hydrogen Atoms	Description
$B_1$	$\Psi_6$	=	$c_9\psi(p_x)$	$+ c_{10}[\psi(H_a) - \psi(H_b)]$	Antibonding ( $c_{10}$ is negative)
$A_1$	$\Psi_5$	=	$c_7\psi(s)$	$+ c_8[\psi(H_a) + \psi(H_b)]$	Antibonding ( $c_8$ is negative)
$B_2$	$\Psi_4$	=	$\psi(p_y)$		Nonbonding
$A_1$	$\Psi_3$	=	$c_5\psi(p_z)$	$+ c_6[\psi(H_a) + \psi(H_b)]$	Slightly bonding ( $c_6$ is small)
$B_1$	$\Psi_2$	=	$c_3\psi(p_x)$	$+ c_4[\psi(H_a) - \psi(H_b)]$	Bonding ( $c_4$ is positive)
$A_1$	$\Psi_1$	=	$c_1\psi(s)$	$+ c_2[\psi(H_a) + \psi(H_b)]$	Bonding ( $c_2$ is positive)

Table III.2: Molecular orbital equations for H<sub>2</sub>O.

- Note that the nonbonding pairs afforded by the MO model are not equivalent as in the Lewis model.
- NH<sub>3</sub> example:
  - Is it not a bit circular to assign the point group  $C_{3v}$  and then later use Walsh diagrams to determine that it has a  $C_{3v}$  structure?
  - Here, we can no longer just add and subtract atomic orbitals. Instead, we must apply “the projection operator method, a systematic approach for deduction of group orbitals” (Miessler et al., 2014, p. 152).
  - This method illustrates how atomic orbitals should be combined to afford the SALCs that define the group orbitals.
  - First, determine the impact of each point group symmetry operation (individually, not within classes) on one atomic orbital.
  - Linear combinations of these atomic orbitals that match the symmetries of the group’s irreducible representations can be obtained via (1) multiplication of each outcome by the characters associated with each operation for these irreducible representations, followed by (2) addition of the results.
  - Finding SALC( $A_1$ ) =  $\frac{1}{\sqrt{3}}[\Psi(H_a) + \Psi(H_b) + \Psi(H_c)]$  and SALC( $E$ ) =  $\frac{1}{\sqrt{6}}[2\Psi(H_a) - \Psi(H_b) - \Psi(H_c)]$  is easy.
  - Now SALC( $E$ ) has  $y$  symmetry (note that this means that choosing the  $H_a$  that we did in Figure III.13 [i.e., the one lying along a coordinate axis] has simplified calculations). Thus, the other SALC should have  $x$  symmetry.

–  $H_a$  should not contribute to the new SALC because of the orthogonal node defined by the  $yz$ -plane (if it contributed, there would be no  $yz$  node). Thus, only  $H_b$  and  $H_c$  can contribute, and we can deduce that their coefficients are  $\frac{1}{\sqrt{2}}$  and  $-\frac{1}{\sqrt{2}}$ , respectively, to satisfy the normalization requirement while also leading to identical total contributions from all three  $1s$  wave functions across the three group orbitals.

- In the projection operator method, orbitals can become the inverses of other orbitals.
- $\text{BF}_3$  example:

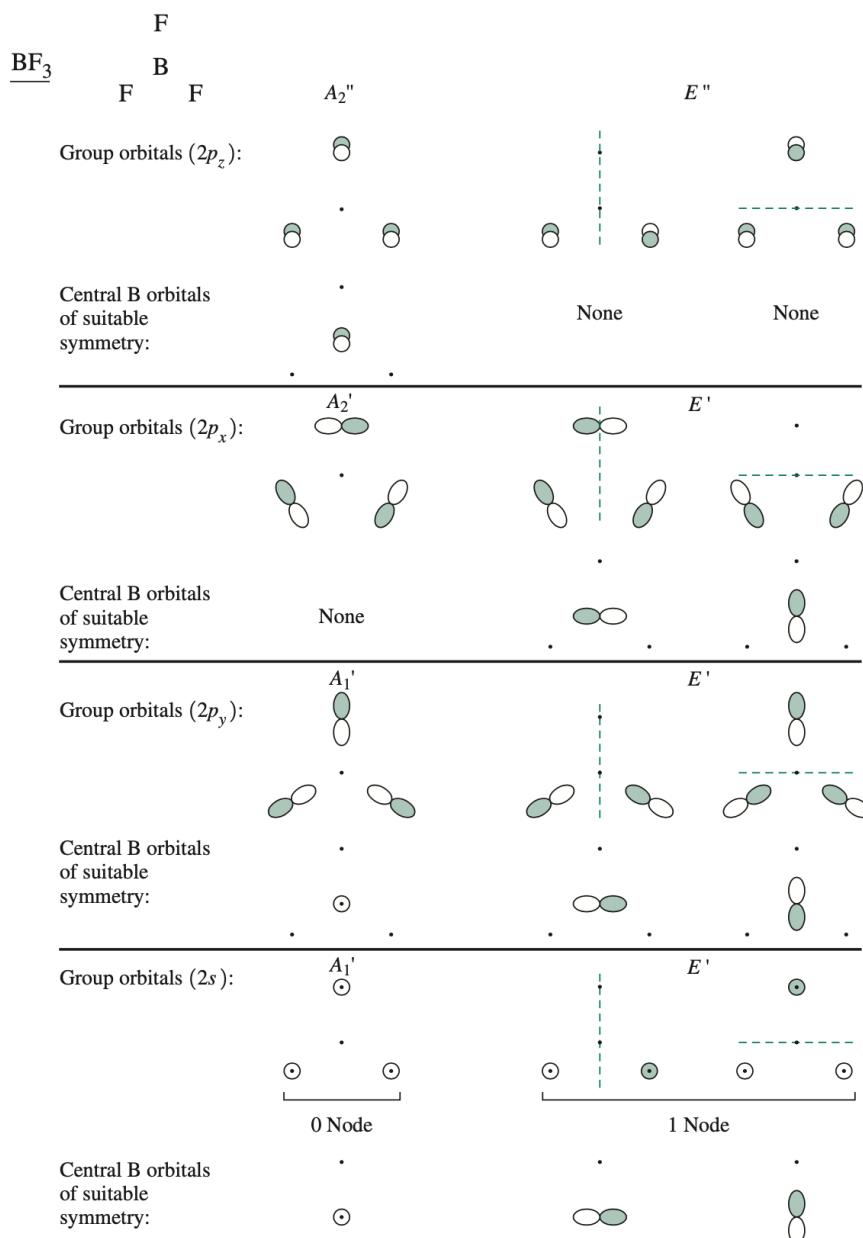


Figure III.20: Group orbitals for  $\text{BF}_3$ .

- The fluorine ligands have  $2p$  electrons, too, now. As such, let the  $C_3$  axis be the  $z$ -axis, the  $p_y$  axes point towards the central boron atom, and the  $p_x$  axes lie in the molecular plane.

- The partial double bonding character of the B–F bonds discussed in Chapter 3 can now be explained.
- The LUMO of  $\text{BF}_3$  is an empty antibonding  $\pi$  orbital with large lobes on boron that can act as electron pair acceptors; this is why  $\text{BF}_3$  is a Lewis acid.
- This approach is also applicable to other isoelectronic trigonal planar species such as  $\text{SO}_3$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^{2-}$ .
- “Because the extent of orbital overlap in  $\pi$  interactions is generally less than that in most  $\sigma$  interactions, a double bond composed of one filled  $\sigma$  orbital and one filled  $\pi$  orbital is not twice as strong as a single bond” (Miessler et al., 2014, p. 161).
- Note that single bond energies between the same atoms can vary widely based on steric crowding and adjacent bonding.
- A qualitative group orbital approach (what we’re doing) does not allow for the determination of the precise MO energies, but it generally allows for the placement of the MOs in the approximate order based on their shapes and expected orbital overlaps.
- “In the hybrid concept, the orbitals of the central atom are combined into sets of equivalent hybrids. These hybrid orbitals form bonds with orbitals of other atoms” (Miessler et al., 2014, p. 161).
- Hybrid orbitals correctly describe methane’s PES spectrum.
- “Like all bonding models, hybrids are useful so long as their limits are recognized” (Miessler et al., 2014, p. 161).
- $\text{CH}_4$  example:
  - Point group:  $T_d$ .
  - Basis functions:  $\sigma$  bond vectors.
  - $\Gamma = (4, 1, 0, 0, 2)$ .
  - $\Gamma = A_1 + T_2$ .
  - “The atomic orbitals of carbon used in the hybrids must have symmetry matching  $A_1 + T_2$ ; more specifically, one orbital must match  $A_1$ , and a set of three (degenerate) orbitals must match  $T_2$ ” (Miessler et al., 2014, p. 162).
  - For  $A_1$ , we choose the  $2s$  orbital. For  $T_2$ , we could choose  $d_{xy}, d_{xz}, d_{yz}$ , but since they’re much higher energy (and thus won’t mix well with the  $\text{H}(1s)$  orbitals), we’ll go for  $p_x, p_y, p_z$ .
  - Therefore, the hybridization is  $sp^3$ , combining four atomic orbitals into four equivalent hybrid orbitals, one directed toward each hydrogen atom.
- In addition to the  $sp^3$  explanation of  $\text{H}_2\text{O}$ , it is sometimes explained through a slightly more MO theory lens as  $sp^2$  since the oxygen orbitals used in MO bonding are  $2s, 2p_x, 2p_z$  where the  $\text{H}_2\text{O}$  molecule lies in the  $xz$ -plane.
- Only  $\sigma$  bonding is considered when determining the orbitals used in hybridization.