

## 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  $\hat{H}$ :

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

- Shortcomings: Does not count 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  $s$ -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,  $E \times T_1 \times T_2 = (18, 0, 2, 0, 0)$ .
  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.

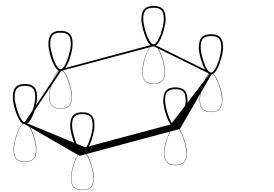
$$\begin{aligned} \Psi_3(E_1) &= \Psi'_3(E_{1a}) + \Psi'_4(E_{1b}) = 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6 \\ \Psi_4(E_1) &= \Psi'_3(E_{1a}) - \Psi'_4(E_{1b}) = \phi_2 + \phi_3 - \phi_5 - \phi_6 \\ \Psi_5(E_2) &= \Psi'_5(E_{2a}) + \Psi'_6(E_{2b}) = 2\phi_1 - \phi_2 - \phi_3 + 2\phi_4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

- We can now normalize: If  $\Psi_i = \sum_j c_j \phi_j$ , the normalizing constant is

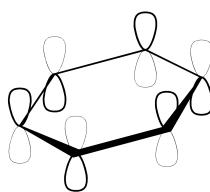
$$N = \frac{1}{\sqrt{\sum_j c_j^2}}$$

meaning that

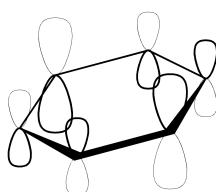
$$\begin{array}{ll} \Psi_1(A) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) & \Psi_2(B) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\ \Psi_3(E_1) = \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) & \Psi_4(E_1) =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



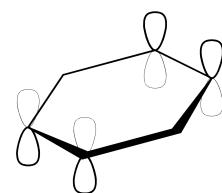
(a)  $\Psi_1(A) \sim \Psi(A_{2u})$ .



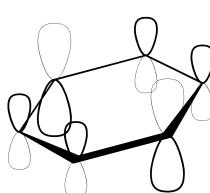
(b)  $\Psi_2(B) \sim \Psi(B_{2g})$ .



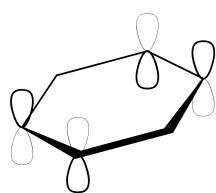
(c)  $\Psi_3(E_1) \sim \Psi(E_{1g}^a)$ .



(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).

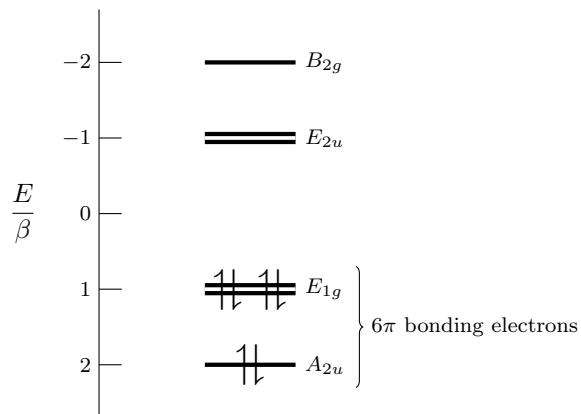


Figure III.2: Energy level diagram of benzene.

- 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.

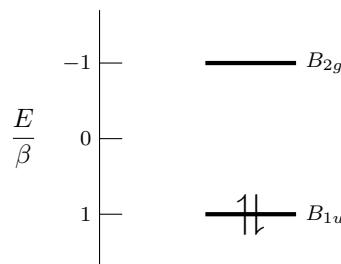


Figure III.3: Energy level diagram of ethene.

- 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 (photons in the 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.

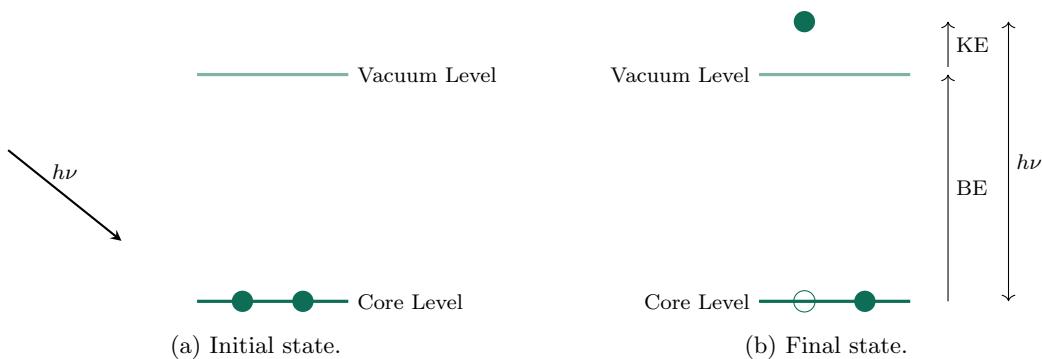


Figure III.4: Photoelectron spectroscopy at an atomic level.

- 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.

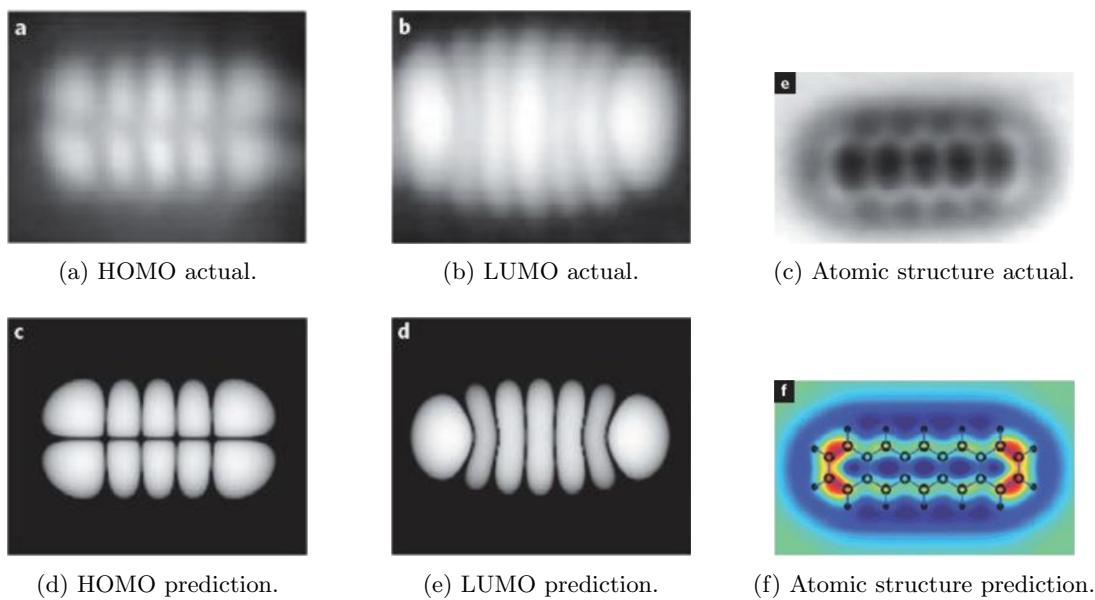


Figure III.5: Correspondence between MO predictions and scanning tunnelling microscopy.

- 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:

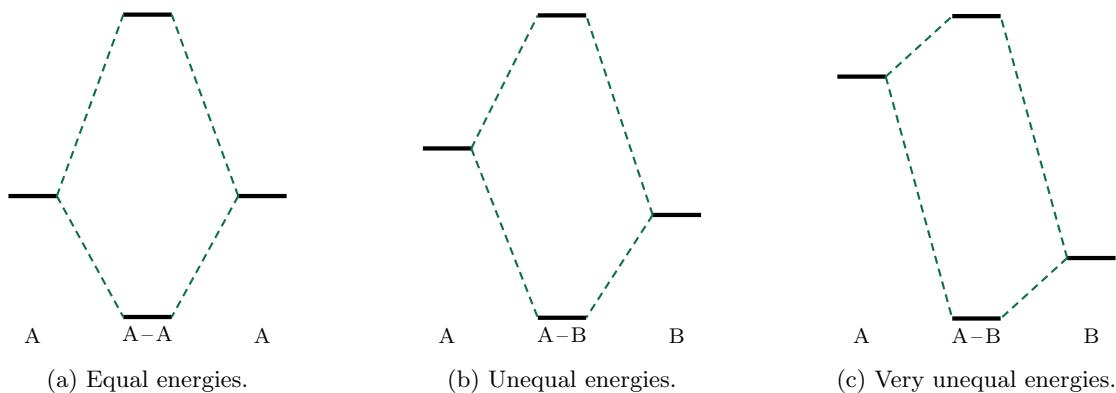


Figure III.6: Combining orbitals of varying energies.

- 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.
- Symmetry and orbital diagrams (suggested reading Cass and Hollingsworth (2004)):
  - **State conservation principle:** The number of molecular orbitals is equal to the number of incipient (atomic) orbitals.

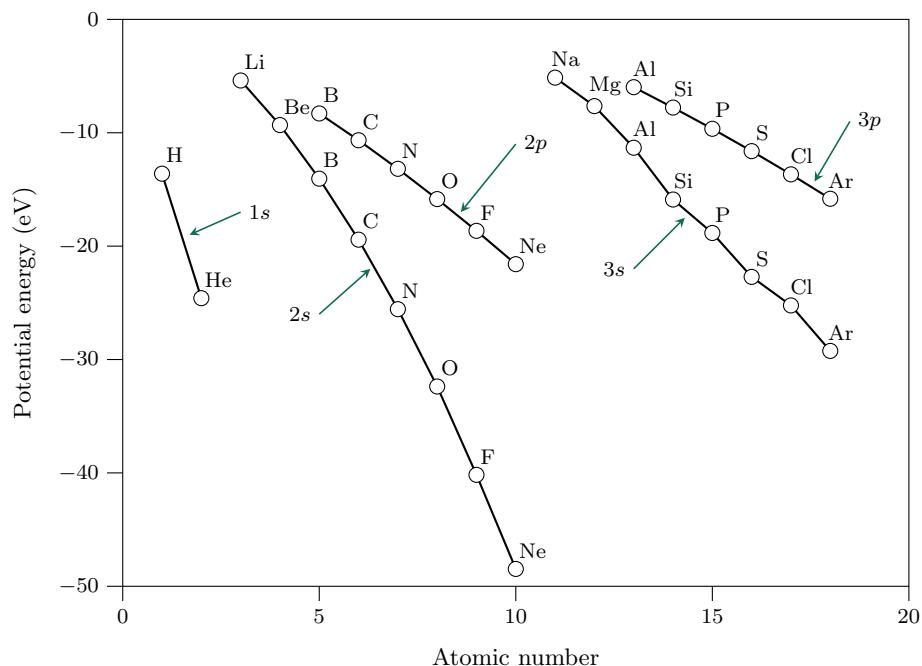
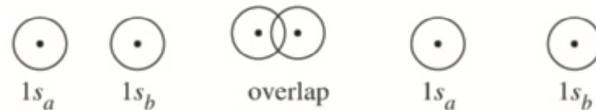
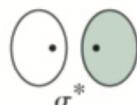


Figure III.7: Orbital potential energies.

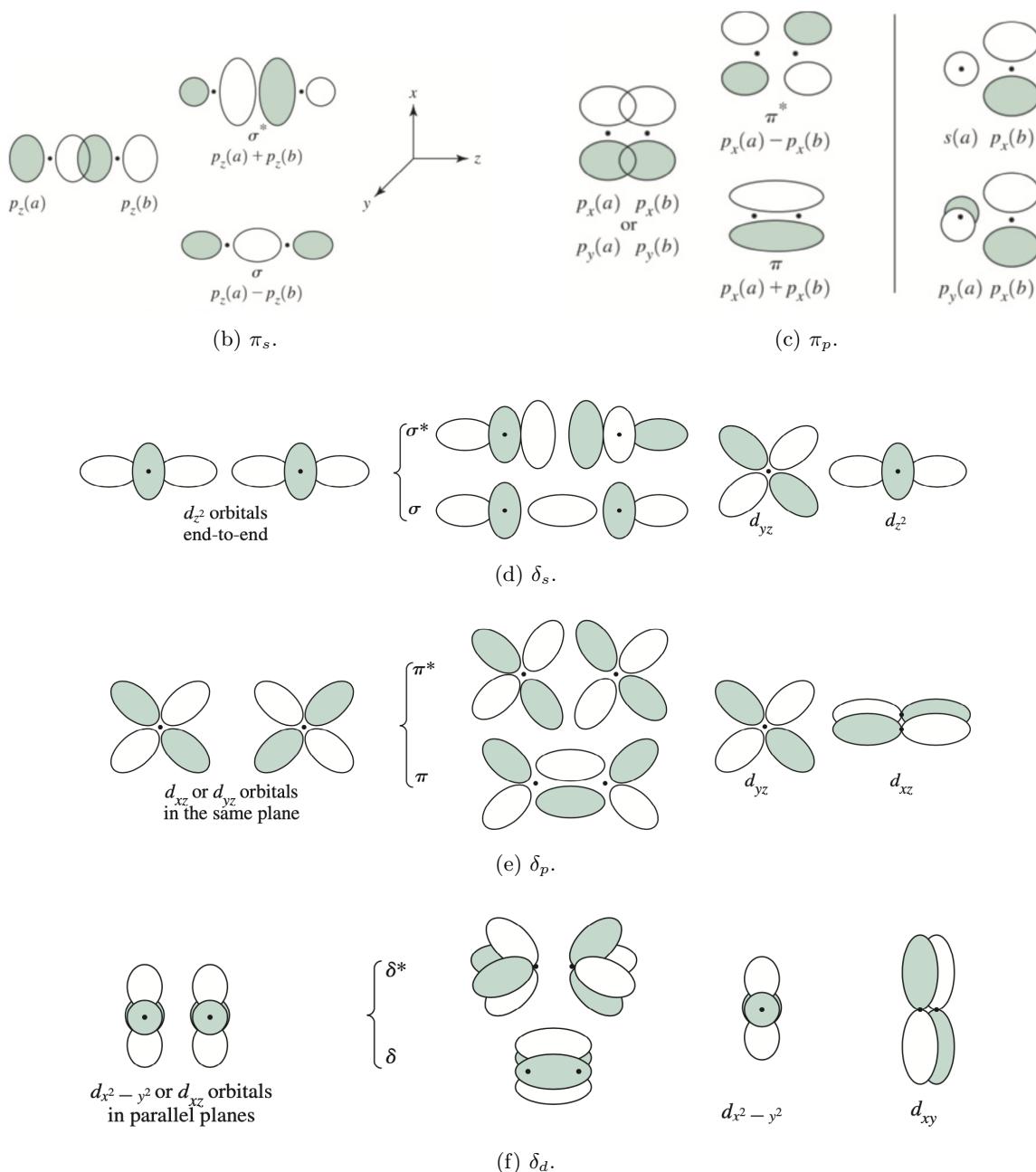
- Orbitals of the same symmetry mix.
- Orbital interactions can be bonding, nonbonding, or antibonding.
- There are three basic types of orbital overlap:  $\sigma$  (end-on interaction),  $\pi$  (side-by-side approach) and  $\delta$  (off-axis approach).
  - $\sigma$  orbitals are symmetric to rotation 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 Chapter 5: Molecular Orbitals

*From Miessler et al. (2014).*

- 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.