

## Week 8

# Electronic Structure of Atoms and Molecules

### 8.1 Hybridization and Time-Dependent Quantum Mechanics

11/15:

- Consider BeH<sub>2</sub>.
  - Then we can form the  $sp$  molecular orbital

$$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$

- Draws an orbital diagram of BeH<sub>2</sub>.
- BH<sub>3</sub>.
  - Lists  $sp^2$  hybrid orbital wave functions.
- CH<sub>4</sub>.
  - Lists  $sp^3$  hybrid orbital wave functions.
- The probability of finding a  $\psi_1$  electron in the  $2p_z$  orbital.
  - The absolute value of the coefficient of  $2p_z$  in the wave function, squared.
  - Alternatively,

$$\text{Prob} = \left| \int 2p_z^* \psi_1 d\tau \right|^2$$

- Time-dependent Schrödinger equation:

$$\hat{H}\psi = i\hbar \frac{d\psi}{dt}$$

- Let  $\psi_n(r, t) = \phi_n(r)e^{-iE_n t/\hbar}$ . Plugging this into the time-dependent Schrödinger equation yields

$$\begin{aligned}\hat{H}\psi &= i\hbar \frac{d}{dt} \left( \phi_n(r) e^{-iE_n t/\hbar} \right) \\ &= i\hbar \cdot -\frac{iE_n}{\hbar} \cdot \phi_n(r) e^{-iE_n t/\hbar} \\ &= E_n \psi_n\end{aligned}$$

- Thus, to this point, we've been solving the spatial part of the time-dependent Schrödinger equation.

- The probability density of the time-dependent solution is equal to the probability density of the time-independent solution.

$$\begin{aligned}
 |\psi(r, t)|^2 &= \left| \phi(r) e^{-iEt/\hbar} \right|^2 \\
 &= \psi^*(r) \psi(r) e^{iEt/\hbar} e^{-iEt/\hbar} \\
 &= \psi^*(r) \psi(r) \\
 &= |\psi(r)|^2
 \end{aligned}$$

- The time-dependent Schrödinger equation allows us to make predictions for how long it takes an electron to relax back to a lower energy state after excitation, for instance.
- Using the time-dependent Schrödinger equation to describe the interaction of the system with electromagnetic radiation.

1. Solution:  $\vec{E} = \vec{E}_0 \cos(\omega t)$ <sup>[1]</sup>.

2. Dipole moment of the molecule ( $\mu$ ).

- We let  $\hat{V} = -\vec{\mu} \cdot \vec{E}$ . This is how radiation interacts with matter.
- This leads to the overall Hamiltonian for the molecule interacting with the electric field as  $\hat{H} = \hat{H}_0 + \hat{V}$ , where  $\hat{H}_0$  is the Hamiltonian of the molecule and  $\hat{V}$  is the dipole-electric field perturbation defined above.
- If the electron is transitioning from the ground to the first-excited state, we let

$$\psi(t) = a_1(t)\phi_1 e^{-iE_1 t/\hbar} + a_2(t)\phi_2 e^{-iE_2 t/\hbar}$$

where the first part refers to the ground state, the second part refers to the excited state, and  $a_1, a_2$  are time-dependent expansion coefficients that we are solving for.

- Substitution into the time-dependent Schrödinger equation yields

$$\begin{aligned}
 i\hbar \left( \psi_1 \frac{da_1}{dt} + \psi_2 \frac{da_2}{dt} \right) &= a_1(t)\hat{V}\psi_1 + a_2(t)\hat{V}\psi_2 \\
 i\hbar e^{-iE_2 t/\hbar} \frac{da_2}{dt} &= a_1(t) \int \phi_2^* \hat{V} \psi_1 d\vec{r} + a_2(t) \int \phi_2^* \hat{V} \psi_2 d\vec{r}
 \end{aligned}$$

## 8.2 Time-Dependent Schrödinger Equation

11/17:

- The TD SE is an **initial value differential equation** since we know  $\psi_0$  and can propagate that over time.
- We will approximate the solutions to this with both an expansion (variational method) and perturbation theory.
- Now we continue from before (finding the time-dependence of the interaction of a EM radiation with a molecule).
  - Let

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where  $\hat{H}_0$  is the Hamiltonian of the molecule and  $\hat{V}$  describes the interaction of the photon and the molecule.

---

<sup>1</sup>This is the definition of a classical electric radiation field. In Advanced Quantum Mechanics, we can turn this into a photon field for quantum electrodynamics.

- Let

$$\psi(t) = a_1(t) \underbrace{\phi_1 e^{-iE_1 t/\hbar}}_{\psi_1} + a_2(t) \underbrace{\phi_2 e^{-iE_2 t/\hbar}}_{\psi_2}$$

- Substituting into the TD SE, multiplying through by  $\phi_2^*$ , and integrating and simplifying yields (continuing from before)

$$i\hbar \frac{da_2}{dt} = a_1(t) e^{-i(E_1-E_2)t/\hbar} \int \phi_2^* \hat{V} \phi_1 d\vec{r} + a_2(t) \int \phi_2^* \hat{V} \phi_2 d\vec{r}$$

- Computing  $a_2(t)$  as a function of time.
- Initial values:

$$a_1(0) = 1$$

$$a_2(0) = 0$$

i.e., all of the electron density is in the ground state, and none is in the excited state.

- Assume a small perturbation and use the initial conditions on the right hand side of the above equation.
- This yields

$$i\hbar \frac{da_2}{dt} = e^{-i(E_1-E_2)t/\hbar} \int \phi_2^* \hat{V} \phi_1 d\vec{r}$$

- But since

$$\hat{V} = -\frac{\mu_z}{2} E_{0z} (e^{i2\pi\nu t} + e^{-i2\pi\nu t})$$

where we focus on the component of the electric field along the internuclear axis, we get

$$\frac{da_2}{dt} \propto \underbrace{\left( \int \phi_2 \mu_z \phi_1 d\vec{r} \right)}_{(\mu_z)_{12}} E_{0z} \left( e^{i(E_2-E_1+h\nu)t/\hbar} + e^{i(E_2-E_1-h\nu)t/\hbar} \right)$$

where  $(\mu_z)_{12}$  is the **transition dipole moment** between states 1 and 2.

■  $(\mu_z)_{12}$  must be nonzero to get a transition.

- Integrating from 0 to  $\tau$  gives

$$a_1(t) = (\mu_z)_{12} E_{0z} \left( \frac{1 - e^{i(E_2-E_1+h\nu)t/\hbar}}{E_2 - E_1 + h\nu} + \frac{1 - e^{i(E_2-E_1-h\nu)t/\hbar}}{E_2 - E_1 - h\nu} \right)$$

- The second term becomes large as  $E_2 - E_1 - h\nu \rightarrow 0$ .
- Thus, the probability in state 2 at  $\tau$  is

$$a_2^*(\tau) a_2(\tau) \propto \frac{\sin^2[(E_2 - E_1 - \hbar\omega)\tau/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2}$$

- The right term above is a function of the form  $\sin^2(xt/2\hbar)/x^2$ , which has a peak right at the resonance frequency.

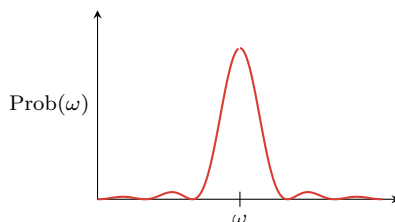


Figure 8.1: The sinc function.

■ This is the **sinc function**.

- Test 3:
  - Problem sets 6-7.
  - Helium from a perturbation theory/variational principle perspective.
  - Chemical bonding (MOs for  $\text{H}_2^+$ , bonding and antibonding orbitals).
  - MO diagrams for diatomics ( $\text{N}_2$ ,  $\text{O}_2$ , etc.)
  - Grassmann wedge notation.
  - Huckel theory (the MOs for conjugated molecules). There WILL be one of these on the test.
  - Hybridization.
  - Time-dependent perturbation theory and the TD SE (probably not a question on this, but if you have expansion coefficients evolving with time, how do you find the probability [modulus squared]).
  - 5 parts, formula page, calculator allowed.

## 8.3 Chapter 10: Bonding in Polyatomic Molecules

*From McQuarrie and Simon (1997).*

11/15:

- Consider  $\text{BeH}_2$ .
  - The two Be–H bonds are equivalent with an angle of  $180^\circ$  between them
  - MOs are formed from orbitals that are similar in energy, so in addition to the  $\text{H}(1s)$  and  $\text{Be}(2s)$ , throw in the energetically close  $\text{Be}(2p)$ .
  - We also add in a  $2p$  orbital because we need the resultant molecular orbitals to point in opposite directions so as to explain the linear structure of the molecule, and directionality is not something the spherically symmetric  $2s$  orbital can provide.
  - Thus, choose
 
$$\psi_{\text{Be-H}} = c_1\psi_{\text{Be}(2s)} + c_2\psi_{\text{Be}(2p)} + c_3\psi_{\text{H}(1s)}$$
  - The first two terms in the above linear combination can be thought of as representing a new **hybrid** “orbital” on beryllium.
  - The normalized  $sp$  hybrid orbitals are given by

$$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$

where the  $z$ -axis is defined to be the internuclear H–Be–H axis.

- Note that  $sp$  hybrid orbitals concentrate electron density in one specific direction since the sign of the  $2p$  wave function is different in the two direction ( $\pm z$ ) but the sign of the  $2s$  wave function is everywhere positive.
- **Hybrid orbital:** A linear combination of atomic orbitals on the same atom.
- The normalized  $sp^2$  hybrid orbitals are

$$\begin{aligned}\psi_1 &= \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z & \psi_2 &= \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x \\ \psi_3 &= \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x\end{aligned}$$

- The normalized  $sp^3$  hybrid orbitals are

$$\begin{aligned}\psi_1 &= \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) & \psi_2 &= \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z) \\ \psi_3 &= \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) & \psi_4 &= \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)\end{aligned}$$

- Bonding vs. lone pair electrons:  $H_2O$ .

- We could form bond orbitals out of the singly occupied  $p_{y,z}$  orbitals of O, but this would predict a bond angle of  $90^\circ$ . Thus, we need hybrid orbitals.
- The bond angle in water is between that predicted using  $sp^2$  hybrid orbitals and  $2p$  orbitals.
- Since oxygen has two bonding and four lone pair electrons, we let

$$\psi = c_1 2s + c_2 2p_y + c_3 2p_z$$

- Determining the coefficients such that two orthogonal orbitals directed at an angle of  $104.5^\circ$  are generated yields

$$\psi_1 = 0.45 \cdot 2s + 0.71 \cdot 2p_y + 0.55 \cdot 2p_z \quad \psi_2 = 0.45 \cdot 2s - 0.71 \cdot 2p_y + 0.55 \cdot 2p_z$$

- Physical interpretation of the normalization constants:  $c_i^2$  is the fractional character of the  $i^{\text{th}}$  orbital<sup>[2]</sup>.
- $\psi_1, \psi_2$  accommodate the bonding electrons. Our unused hybrid orbital and unused  $2p_x$  orbital accommodate the lone pair electrons as a linear combination (since symmetry necessitates that the two lone pair orbitals be equivalent).

- Why  $BeH_2$  is linear but  $H_2O$  is bent.

- Using a more general LCAO-MO with all relevant orbitals and solving yields a set of molecular orbitals.
- Upon bending, the degeneracy of the  $\pi$  orbitals is lifted as the hydrogen orbitals move to intersect more with one specific side of the molecule.
- Such changes are summarized by a **Walsh correlation diagram** (see Labalme (2021, p. 65)).
- We want the minimal energy for however many electrons we have, and with the additional electrons of  $H_2O$ , it is more energetically favorable to bend than to remain linear.

- **Walsh correlation diagram:** A plot of the energy of a molecular orbital as a function of a systematic change in molecular geometry.

- **$\sigma$ -bond framework:** The collection of all  $\sigma$  bonds in a molecule.

## Problems

12/1:10-47. The dipole moment of a polyatomic molecule is defined by

$$\boldsymbol{\mu} = e \sum_j z_j \mathbf{r}_j$$

where  $z_j e$  is the magnitude of a charge located at the point given by  $\mathbf{r}_j$ . Show that the value of  $\boldsymbol{\mu}$  is independent of the origin chosen for  $\mathbf{r}_j$  if the net charge is zero. Show that  $\boldsymbol{\mu} = 0$  for  $SO_3$  (trigonal planar),  $CCl_4$  (tetrahedral),  $SF_6$  (octahedral),  $XeF_4$  (square planar), and  $PF_5$  (trigonal bipyramidal).

---

<sup>2</sup>Think  $s$ -character,  $p$ -character.

## 8.4 Chapter 12: Group Theory — The Exploitation of Symmetry

From McQuarrie and Simon (1997).

11/30:

- **Dihedral** (plane of symmetry): A plane of symmetry that bisects the angle between two-fold axes that are perpendicular to the principal axis.
- Deriving the two-dimensional irreducible representation  $E$  corresponding to the  $\mathbf{C}_{3v}$  point group.
  - Consider an arbitrary vector  $\mathbf{u}_1 = u_{1x}\mathbf{i} + u_{1y}\mathbf{j} = (\cos \alpha)\mathbf{i} + (\sin \alpha)\mathbf{j}$ .
  - Applying  $\hat{C}_3$  to  $\mathbf{u}_1$  yields

$$\begin{aligned}
 \mathbf{u}_2 &= \hat{C}_3 \mathbf{u}_1 \\
 &= \cos(120^\circ + \alpha)\mathbf{i} + \sin(120^\circ + \alpha)\mathbf{j} \\
 &= \left(-\frac{1}{2}\cos\alpha - \frac{\sqrt{3}}{2}\sin\alpha\right)\mathbf{i} + \left(\frac{\sqrt{3}}{2}\cos\alpha - \frac{1}{2}\sin\alpha\right)\mathbf{j} \\
 &= \left(-\frac{1}{2}u_{1x} - \frac{\sqrt{3}}{2}u_{1y}\right)\mathbf{i} + \left(\frac{\sqrt{3}}{2}u_{1x} - \frac{1}{2}u_{1y}\right)\mathbf{j} \\
 &= \underbrace{\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}}_{\hat{C}_3} \underbrace{\begin{pmatrix} u_{1x} \\ u_{1y} \end{pmatrix}}_{\mathbf{u}_1}
 \end{aligned}$$

- The other matrices can be derived similarly.
- This derivation also illustrates why  $(x, y)$  are coupled in this point group.
- **Basis** (of a representation): The components of the vectors used to generate the representation.
  - For example,  $u_x, u_y$  form a basis of  $E$ . Alternatively, we can say that they **belong** to  $E$ .
  - As another example, the basis vectors for  $R_z$  corresponding to the  $\mathbf{C}_{3v}$  are depicted in the following figure.

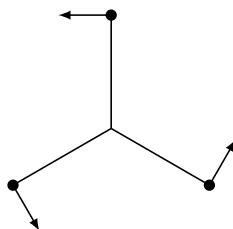


Figure 8.2: Rotational basis vectors.