Week 1-4

Optical Properties 1

Electronic structure of molecules

Born-Oppenheimer and the Franck-Condon Principle

LCAO – Calculating orbitals

Transitions and Fermi's Golden Rule

Chapter 3.1 – 3.5.2

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Objectives

- Optical properties are the *core to understanding* molecules both independently, in solutions, and in solids

- We will spend approximately 8 lectures on developing the physics and understanding optical phenomena

- Primarily, our understanding is based on quantum mechanics (but not always)

- Our discussion will take the following path:
  - Single molecules (and orbitals) ⇒pairs and small assemblies ⇒solids

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Electronic Orbitals
The Born-Oppenheimer Approximation and the Franck-Condon Principle

- To calculate the wavefunction, we write the **spinorbital** wavefunction:

$$\Psi\left(\{\mathbf{r}_i\};\{\mathbf{R}_j\};\{S_k\}\right) = \Phi\left(\{\mathbf{r}_i\};\{\mathbf{R}_j\}\right)\sigma\left(\{S_k\}\right)$$

Electronic   Nuclear   Spin

$\{\mathbf{r_i}\}=\mathbf{r}_1, \mathbf{r}_2,....\mathbf{r}_N$ = all electron position vectors.
$\{\mathbf{R_i}\}=\mathbf{R}_1, \mathbf{R}_2,....\mathbf{R}_M$ = all nuclear position vectors.

- To make the problem of excited and ground state calculations tractable, we invoke the **Born-Oppenheimer approximation**:
  - Electronic and nuclear motion are *independent*
  - Wavefunctions and variables are separable

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Singlet and triplet states

Spatially symm.   Spin antisymm.

$$\psi(\mathbf{r}_1,\mathbf{r}_2;0,0)=\frac{1}{\sqrt{2}}\big(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)+\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\big)(\alpha_1\beta_2-\alpha_2\beta_1)$$

Singlet
$S=0$
$m_s=0$

$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,1)=\frac{1}{\sqrt{2}}\big(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\big)\alpha_1\alpha_2$$
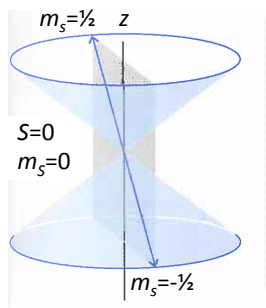
Triplet
$S=1$
$m_s=\pm1, 0$

$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,0)=\frac{1}{\sqrt{2}}\big(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\big)(\alpha_1\beta_2+\alpha_2\beta_1)$$

and

$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,-1)=\frac{1}{\sqrt{2}}\big(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\big)\beta_1\beta_2$$
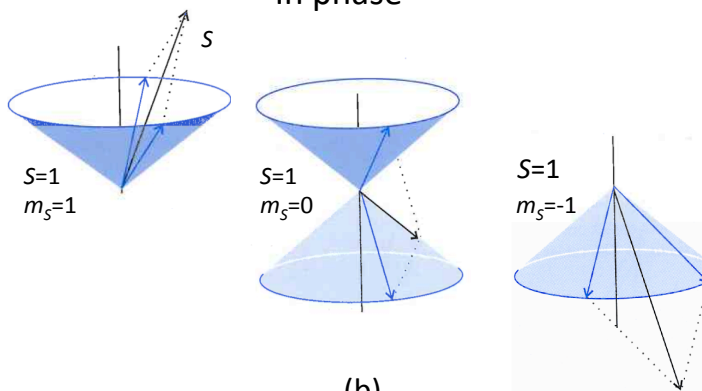
180° out of phase   In phase

$m_s=\tfrac{1}{2}$ z

$S=0$
$m_s=0$

$m_s=-\tfrac{1}{2}$

S

$S=1$
$m_s=1$

$S=1$
$m_s=0$
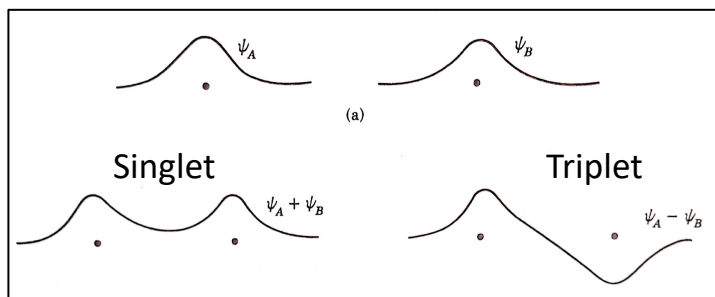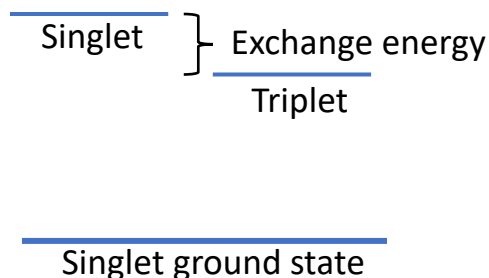
$S=1$
$m_s=-1$

(a)   (b)

Pauli Exclusion Principle: Total wavefunctions must be antisymmetric

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Answers to a couple of questions

- Why do triplet states have lower energy than singlets?

Symmetric **spatial states** have electrons in closer proximity than antisymmetric states
➜ larger Coulomb repulsive energy

- Why does the wavefunction have to be antisymmetric to agree with Pauli exclusion?
    - Take two particle wavefunctions, $|1\rangle, |2\rangle$
    - The total wavefunction is a linear combination of the two under exchange:

$$|tot\rangle = \text{constant} \times \left\{ |1\rangle|2\rangle \pm |2\rangle|1\rangle \right\}$$

    - If $|1\rangle = |2\rangle$ the antisymmetric wavefunction (-) vanishes but the symmetric one (+) does not.
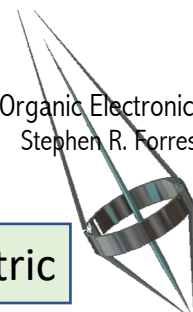
Pauli Exclusion demands no two electrons occupy the same state ⇒ antisymmetric

We can write anti-symmetric functions in terms of determinants

$$\psi\left(\mathbf{r}_1,\mathbf{r}_2\right)=\frac{1}{\sqrt{2}}\det\begin{vmatrix} \Phi^{\uparrow}\left(\mathbf{r}_1\right) & \Phi^{\downarrow}\left(\mathbf{r}_1\right) \\ \Phi^{\uparrow}\left(\mathbf{r}_2\right) & \Phi^{\downarrow}\left(\mathbf{r}_2\right) \end{vmatrix}$$

det=0 if any two rows or columns are identical

More generally, for N electrons, we write the **Slater determinant**:

$$\psi\left(\{\mathbf{r}_i\}\right)=\frac{1}{\sqrt{N!}}\det\begin{vmatrix} \Phi^a\left(\mathbf{r}_1\right) & \Phi^b\left(\mathbf{r}_1\right) & .. & .. & \Phi^z\left(\mathbf{r}_1\right) \\ \Phi^a\left(\mathbf{r}_2\right) & \Phi^b\left(\mathbf{r}_2\right) & .. & .. & \Phi^z\left(\mathbf{r}_2\right) \\ .. & .. & .. & .. & .. \\ .. & .. & .. & .. & .. \\ \Phi^a\left(\mathbf{r}_N\right) & \Phi^b\left(\mathbf{r}_N\right) & .. & .. & \Phi^z\left(\mathbf{r}_N\right) \end{vmatrix}$$

B-O implies that the nuclear and electronic parts of the wavefunction are separable:

$$\Phi\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right)=\phi_e\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right)\phi_N\left(\{\mathbf{R}_I\}\right)$$

Total Hamiltonian:

$$H_T=-\frac{\hbar^2}{2m_e}\sum_i^N\nabla_{\mathbf{r}_i}^2-\frac{\hbar^2}{2}\sum_I^M\frac{1}{m_{NI}}\nabla_{\mathbf{R}_I}^2+\frac{q^2}{4\pi\varepsilon_0}\left(\sum_{i>j}^N\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}-\sum_{i,I}^{N,M}\frac{Z_I}{\left|\mathbf{r}_i-\mathbf{R}_I\right|}+\sum_{I>J}^M\frac{Z_IZ_J}{\left|\mathbf{R}_I-\mathbf{R}_J\right|}\right)$$

Just the electronic part:

$$H_e\phi_e\left(\{\mathbf{r}_i\};\{\mathbf{R}_I\}\right)=\left[-\frac{\hbar^2}{2m_e}\sum_i^N\nabla_{\mathbf{r}_i}^2+\frac{q^2}{4\pi\varepsilon_0}\left(\sum_{i>j}^N\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}-\sum_{i,I}^{N,M}\frac{Z_I}{\left|\mathbf{r}_i-\mathbf{R}_I\right|}\right)\right]\phi_e\left(\{\mathbf{r}_i\};\{\mathbf{R}_I\}\right)=E_e\phi_e\left(\{\mathbf{r}_i\};\{\mathbf{R}_I\}\right)$$

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Solving for the orbitals

- This is solved by taking the product of the N-electron wavefunctions for an M-atom system:

$$\phi_e^0\left(\{\mathbf{r}_i\}\right) = \prod_{i=1}^{N} \phi_{e,i}^0\left(\mathbf{r}_i\right)$$

- But we still don't know what the minimum energy nuclear configuration is—there can be one or many *isomers* at different energies!
  - **Isomer** = each of two or more compounds with the same formula (e.g. C_6H_6) but a different arrangement of atoms in the molecule, and with different properties.
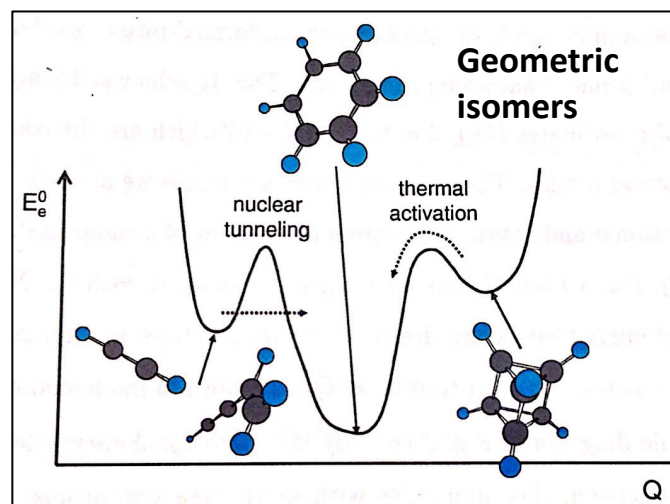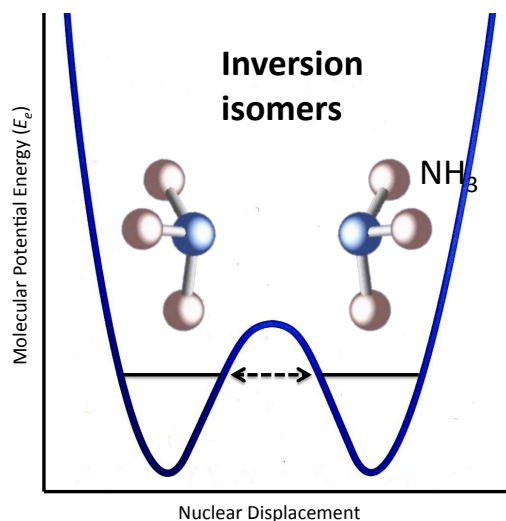
Topological isomers: When the same molecule can have different topologies (i.e DNA can have both helices and knots).

Solving Schrodinger's Equation

Convenient to introduce **normal coordinates**, Q_k
  - ➤ k^{th} configuration of all the nuclei in the molecule
  - ➤ Avoids having to consider the position of <u>each individual</u> nuclear position
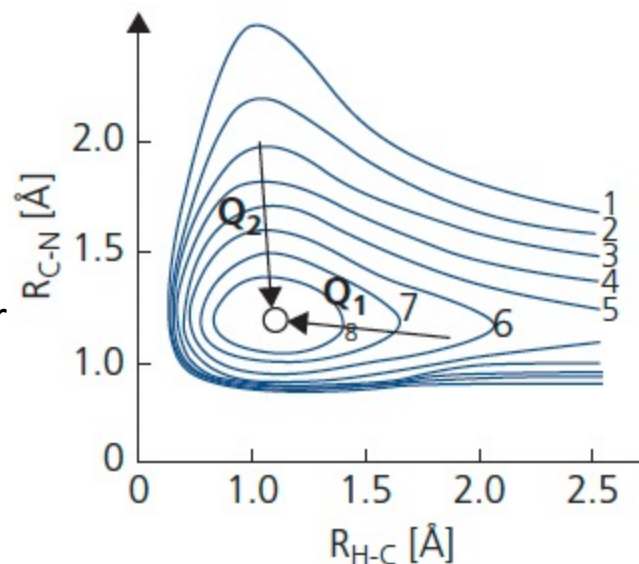
Now problem reduced to electronic coordinates, r_i, and *relative* nuclear coordinate, $\mathbf{Q_k}$.

Finding a solution to the isomer problem:
      Example, HCN (H-C≡N)

Choose two nuclear coordinates, for C-N and H-C.
Solve Schrodinger's equation along two trajectories until
      a minimum is found, defining equilibrium nuclear
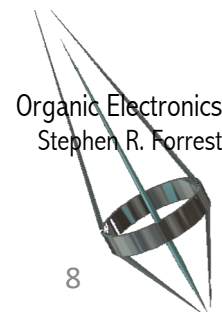   distances.

The total energy of the molecule is then:

Electron KE	Nuclear KE	interelec. repulsion	Elec-nuclear attraction	Nuclear repulsion

$$H_T = T_e(r) + T_N(Q) + V_e(r) + V_{eN}(r,Q) + V_N(Q)$$

Near equilibrium, the energy is:

$$E_T = E_e(0) + V_N(0) + \Delta E_e(Q) + \Delta V_N(Q)$$

Luckily, we only have to worry about things near equilibrium

- Recall, the molecule is held together by covalent, i.e. Coulomb forces. And near the bottom of the potential (in relative coordinates!) it "looks" like a parabola

  - SHO, with solutions for the jth electronic level,
  - l^{th} normal mode:

$$E_{N,j} = \hbar \sum_{l=1}^{3N-6} \omega_l \left(E_{e,j} \right) \left[n_l \left(E_{e,j} \right) + \frac{1}{2} \right]$$


- Things to notice:
  - A shift in nuclear coordinates between the ground and first excited state ($\Delta Q = \left| Q_1 - Q_0 \right|$)
  - Only relative coordinates (Q) important.
  - Equal spacing of levels near bottom of an electronic manifold
    - ➢ These "inner levels" called vibronics
    - ➢ They are phonon modes (e.g. C-H, C-C, C=C …. Vibrations)
  - Vibronics "compress" as we go to higher energies.

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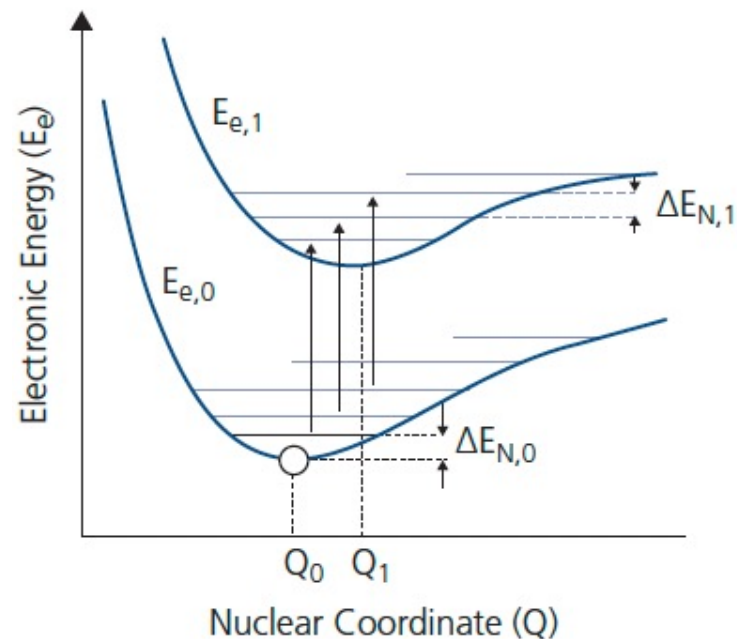
Intramolecular phonons

Think of benzene as an approximately circular drumhead
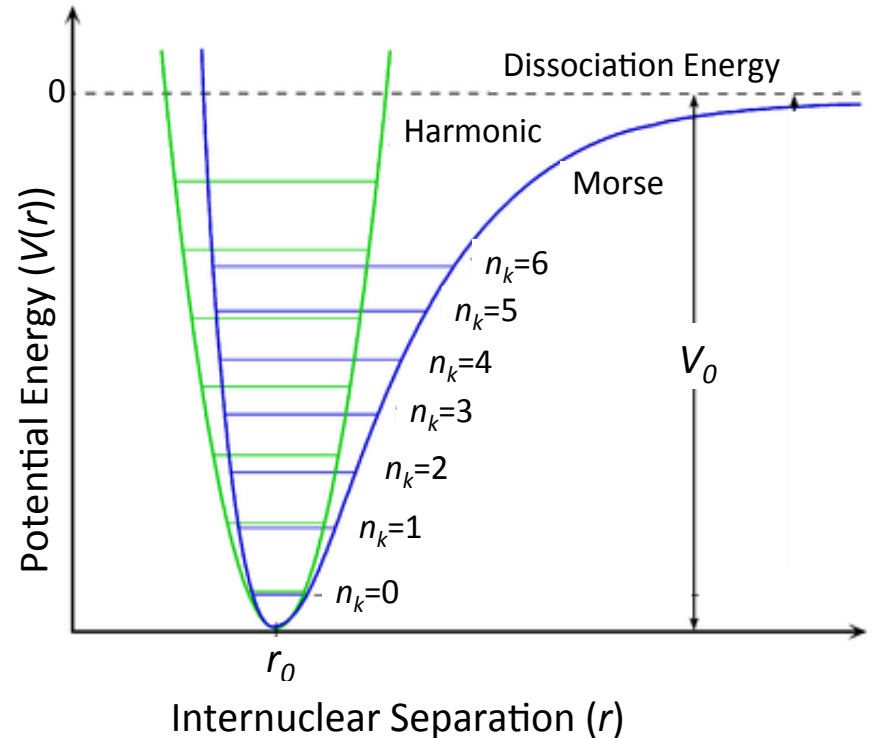These represent several of the lowest possible normal vibrational modes
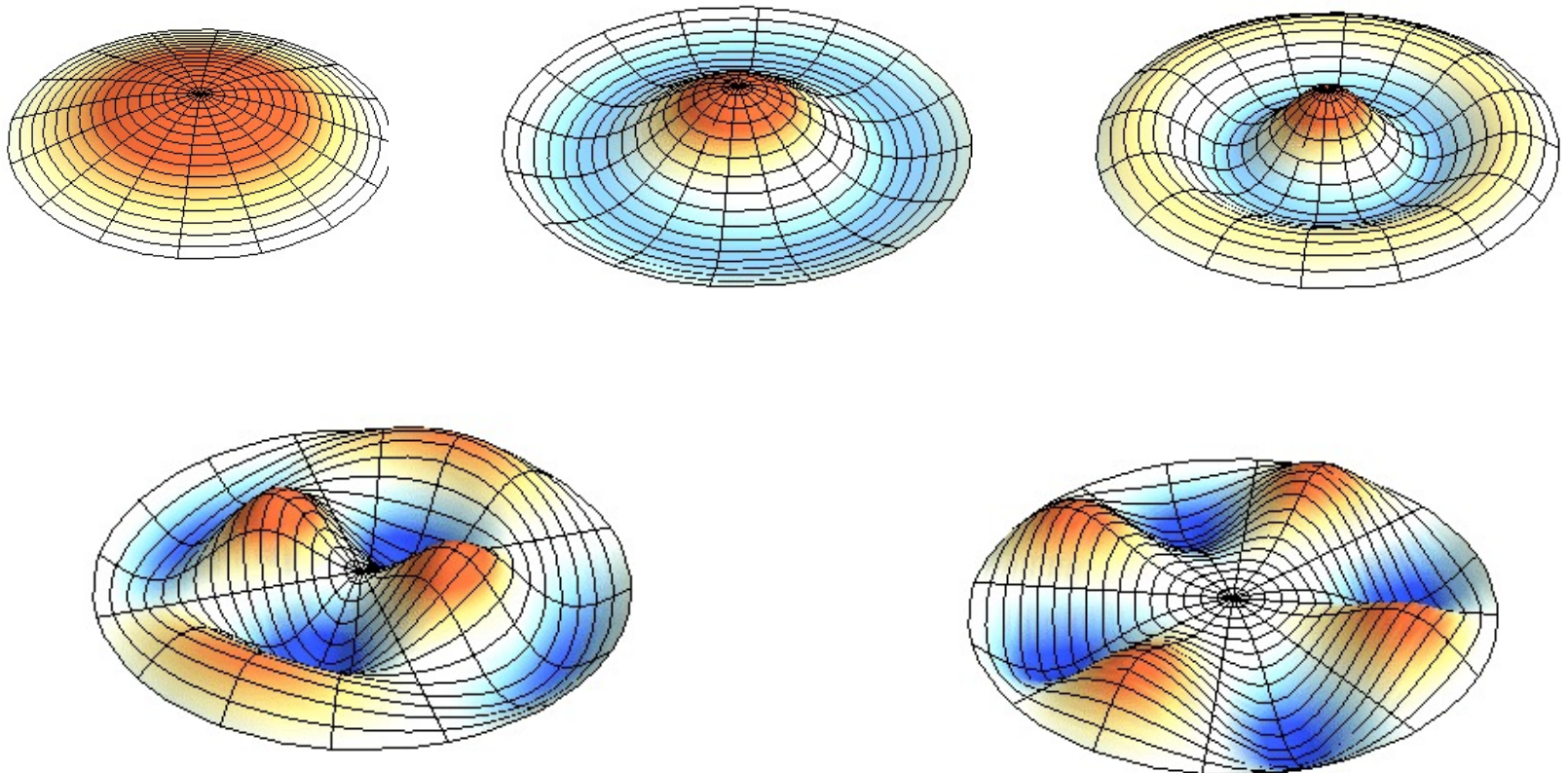
The Morse Potential

−The simple parabola is not particularly accurate ⇒Morse potential

$$V(r) = V_0 \left(1 - \exp\left[-\alpha(r - r_0) \right] \right)^2$$

$$\alpha = \sqrt{k_0 / 2V_0}$$

V_0=well depth

k_0=force constant

Dissociation Energy

Harmonic

Morse

$n_k=6$

$n_k=5$

$n_k=4$

V_0

$n_k=3$

$n_k=2$

$n_k=1$

$n_k=0$

Potential Energy ($V(r)$)

r_0

Internuclear Separation (r)

- Comparison to SHO
  - Energy levels at bottom of well almost the same
  - SHO is an infinite harmonic potential, Morse is a finite anharmonic potential
  - There is a maximum vibronic energy level (you can solve it!)
  - Both are still quite approximate, Morse is an improvement

What are the normal mode frequencies?

# Another important approximation

- **Franck-Condon Principle**
  - Molecules relax after excitation, <u>but</u> we assume that relaxation takes place on a time scale much slower than the excitation (i.e. absorption or emission of a photon).
  - That is, the electron distribution changes upon excitation much faster than the nuclear positions change (they are "static" during transitions) due to their larger mass.
    - Electronic time scales: femtoseconds
    - Nuclear time scales: picoseconds (phonon lifetime)
  - Implication: All transitions are <u>vertical</u>

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Electronic State Filling
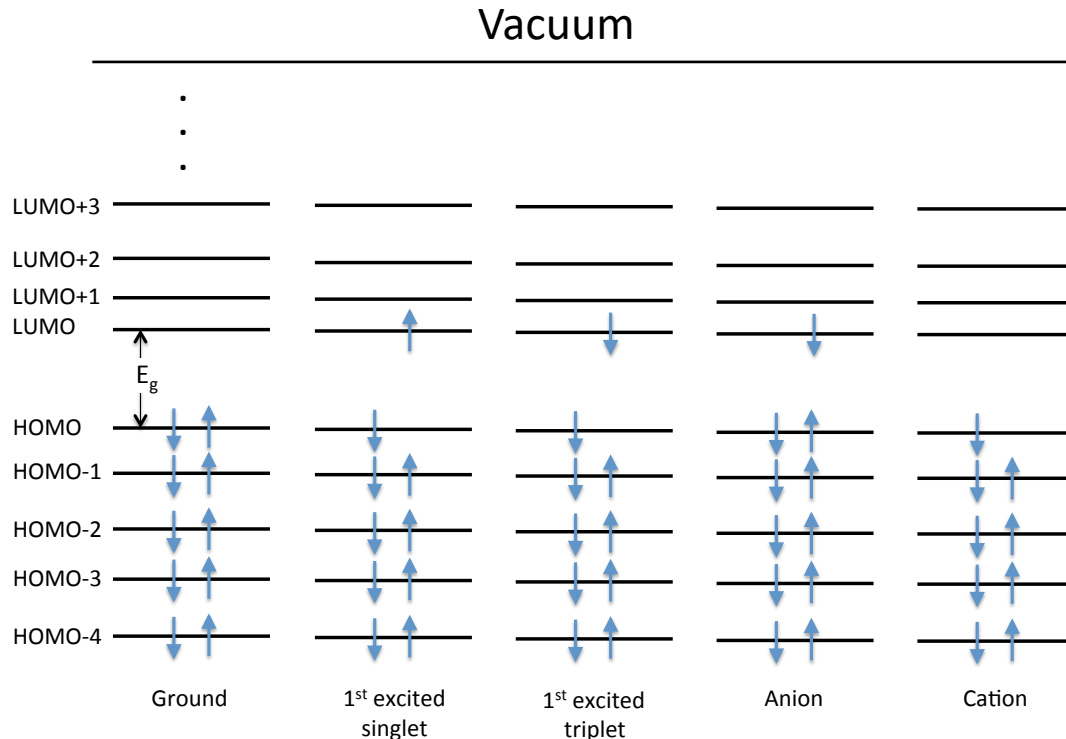
Energy Gap

$$E_G = E_{LUMO} - E_{HOMO}$$
(unrelaxed)

HOMO= highest occupied molecular orbital (e.g. valence energy)
LUMO= lowest unoccupied molecular orbital (e.g. conduction energy)

HOMO and LUMO are "frontier orbitals"

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# Linear Combination of Atomic Orbitals (LCAO)

- To determine the energies of all the orbitals, we start by assuming that they are simply <u>linear combinations </u>of electronic states of the comprising atoms

- Original atomic orbitals only <u>slightly perturbed</u> when placed within the molecule
    - First order perturbation theory applies
    - M atoms, L orbitals

- The most important electron is the <u>last electron </u>that completes the valence states of the molecule.

$$\psi_i(\mathbf{r}_i) = \sum_{j=1}^{M} \sum_{k=1}^{L} c_{ijk} \phi_{jk}(\mathbf{r}_i - \mathbf{R}_j)$$

Molecular
orbitals

Unperturbed
atomic orbitals

- But B-O says that nuclear positions are separable: $\psi_i(\mathbf{r}_i) = \sum_{r=1}^{M} c_{ir} \phi_r'(\mathbf{r}_i)$
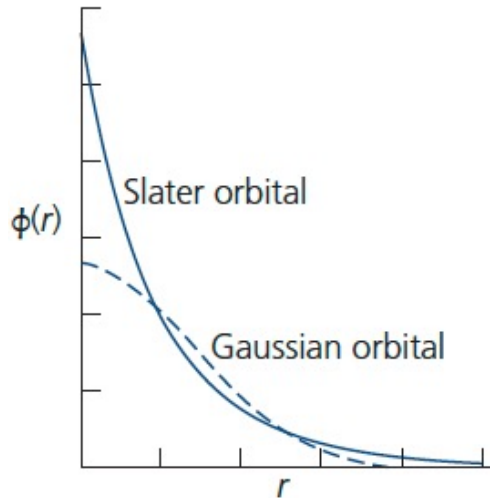
New, electron-only
atomic orbitals
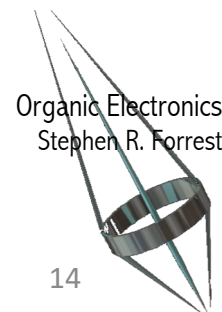
Calculating Orbitals

We need to find a basis set, $\phi_{jk}(\mathbf{r})$

Typically assume Gaussian orbitals, $\phi(r) = x^a y^b z^c \exp(-\alpha r^2)$; (a,b,c) contain wavefunction symmetry

Or Slater (hydrogenic) functions: $\phi(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) = (2\alpha)^{n+\frac{1}{2}}\left[(2n)!\right]^{-\frac{1}{2}} r^{n-1} \exp(-\alpha r)$

Gaussian is easy to use but inaccurate near origin and as $r \to$ large

Now we can solve for the orbitals using Schrodinger: $\displaystyle\sum_{r=1}^{M} c_r \left(\left\langle \phi'_s \middle| H_{\text{int}} \middle| \phi'_r \right\rangle - E \left\langle \phi'_s \middle| \phi'_r \right\rangle \right) = 0$

The *overlap* between the initial and final wavefunctions is: $S_{rs} = \left\langle \phi'_s \middle| \phi'_r \right\rangle$

H_{rr} = <u>Coulomb integral</u> (provides kinetic and Coulomb electronic potential energies

H_{rs} = <u>Resonance integral</u> (provides energy in the region of overlap between ϕ'_s and ϕ'_r

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Calculating Electronic Orbitals, cont'd.

- This amounts to solving the *secular equation*: $\det|\mathbf{H} - E_i\mathbf{S}| = 0$
  - **H**, **S** matrices

- Example: H_2^+ molecule

Diagonal
$$H_{rr} = \left\langle \phi_r' \middle| H \middle| \phi_r' \right\rangle = E_{1s} - \frac{q^2}{4\pi\varepsilon_0}\left\langle \phi_r' \middle| \frac{1}{|\mathbf{r}_r - \mathbf{R}_s|} \middle| \phi_r' \right\rangle + \frac{q^2}{4\pi\varepsilon_0|\mathbf{R}_r - \mathbf{R}_s|}$$

e- with own proton

e- with other proton ($\tilde{j}$): Coulomb

2 proton interactions

Off-diagonal
$$H_{rs} = H_{sr} = \left\langle \phi_r' \middle| H \middle| \phi_s' \right\rangle = \left[E_{1s} + \frac{q^2}{4\pi\varepsilon_0|\mathbf{R}_r - \mathbf{R}_s|} \right] S_{rs} - \frac{q^2}{4\pi\varepsilon_0}\left\langle \phi_r' \middle| \frac{1}{|\mathbf{r}_r - \mathbf{R}_s|} \middle| \phi_s' \right\rangle$$

Or, simply:
$$H_{rs} = H_{sr} = \left[E_{1s} + \frac{q^2}{4\pi\varepsilon_0|\mathbf{R}_r - \mathbf{R}_s|} \right] S_{rs} - \tilde{k}$$

overlap

Full solution from secular eq.: $E_{\mp} = \left[E_{1s} + \frac{q^2}{4\pi\varepsilon_0|\mathbf{R}_r - \mathbf{R}_s|} \right] \pm \frac{\tilde{j} \mp \tilde{k}}{1 \mp S_{rs}}$

Splitting term

Energies are split! One is for the *bonding orbital* (1σ) and the other for the *anti-bonding orbital* (2σ)

H$_2^+$ molecular orbitals

(2 degenerate levels, E$_{1s}$)

- Wavefunctions split by **Coulomb repulsion**

1σ: $\psi = \dfrac{1}{\sqrt{2}}\left(\phi_r' + \phi_s'\right)$

($c_r = c_s = 1$)

2σ: $\psi = \dfrac{1}{\sqrt{2}}\left(\phi_r' - \phi_s'\right)$

($c_r = -c_s = 1$)

Splitting increases
as distance decreases

Energy

E$_-$
2σ
Anti-bonding

E$_{1s}$ E$_{1s}$

E$_+$
1σ
Bonding

(a)

bonding orbital

(b)

electron density concentrated
between ionic cores

anti-bonding orbital

2σ

1σ

electron density concentrated
repelled
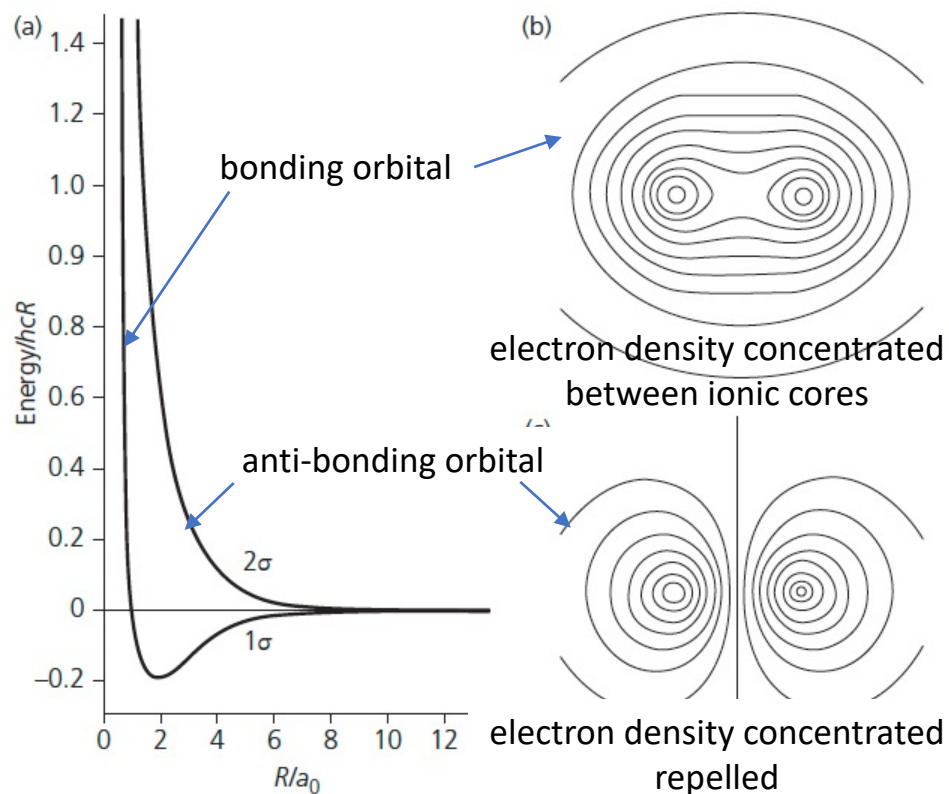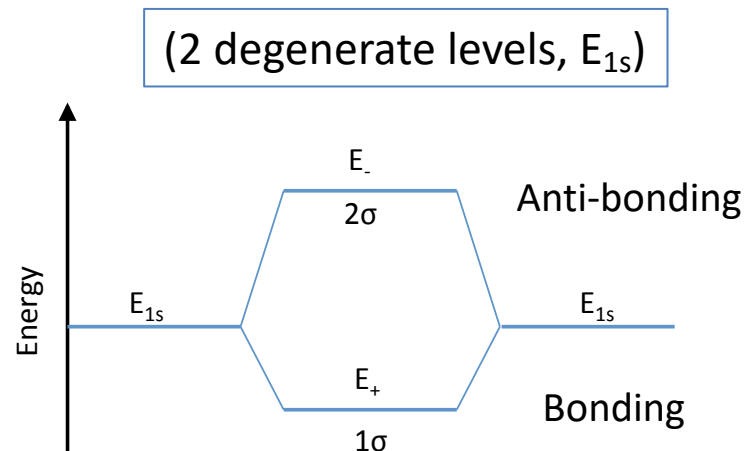
Hybridization of bonds

- When s and p bonds co-exist on the same molecule, they become mixed; or **hybridized**.

- The LCAO method is used to calculate these resulting *hybrid atomic orbitals* (HAOs).

- Simple example: Ethyne (sp^1 hybridization) $HC \equiv CH$
  - Each spherically symmetric H 1s state linearly combines with a C 2s and $2p_x$ orbital to form two hybrid *sp hybridized orbital*s.
  - The $2p_x$-orbital is not spherically symmetric. Thus, it is oriented along the x-axis, and contains electron density contributed from both the s- and p-orbitals.

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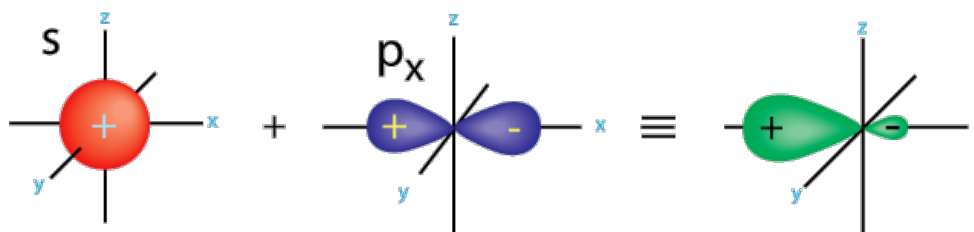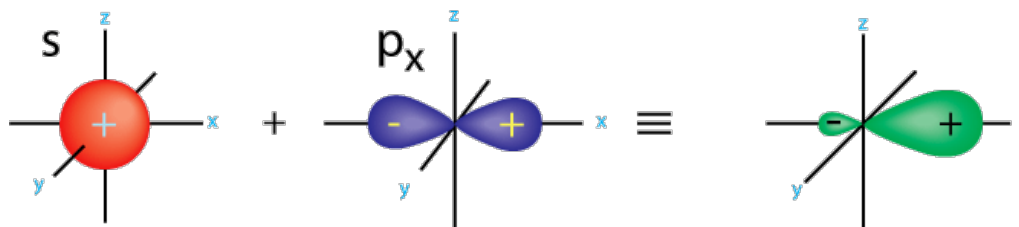
Hybridization of ethyne: Step by Step

- Ethyne comprises H ($1s^1$) and C ($1s^2 2s^2 2p_x^1 2p_y^1$).

- The C atom does not have enough unpaired electrons to form four bonds (1 to the H and 3 to the other C)

- $\Rightarrow$ It must promote one of the $2s^2$ pair into the empty $2p_z$ orbital.
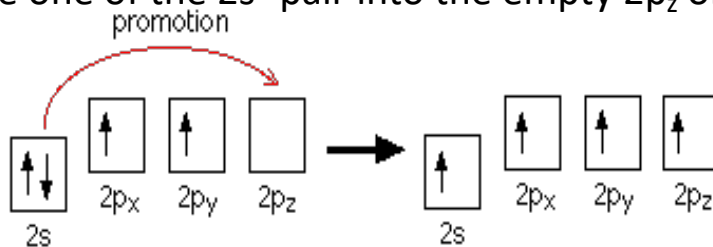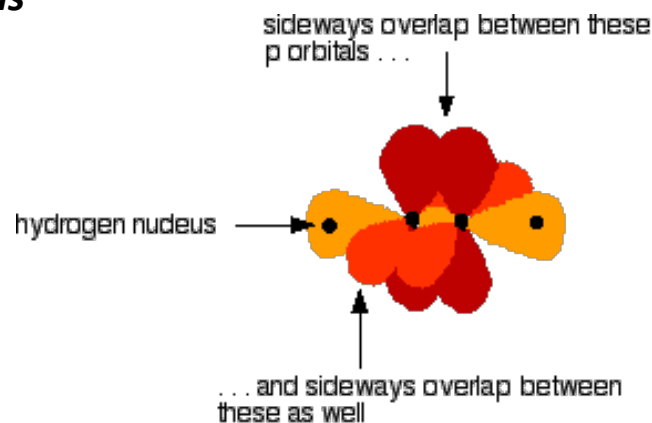

- Each carbon joins to 2 other atoms $\Rightarrow$ they only hybridize *2* of the orbitals.

- They use the 2s electron and one of the 2p electrons, leaving the other 2p electrons unchanged.

- The new hybrid orbitals formed are called ***sp¹ hybrids***.
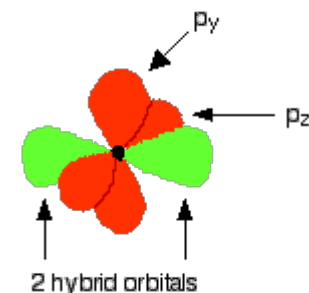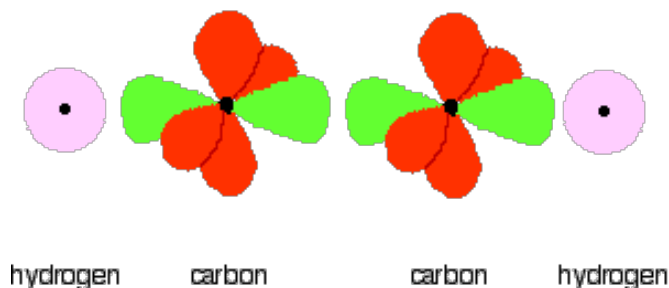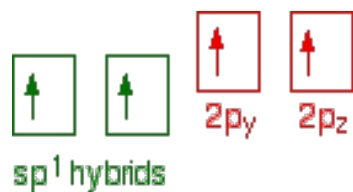
- The two green lobes are two *different* hybrid orbitals – Separated as far from each other as possible.

Hybridization of ethyne, cont'd

- The atomic orbitals that point towards each other merge to give molecular orbitals, each containing a **bonding pair** of electrons.

- These are *sigma bonds*

sideways overlap between these p orbitals . . .

hydrogen nucleus

. . . and sideways overlap between these as well

- The various p orbitals are now close enough that they overlap sideways.

- Sideways overlap between the two sets of p orbitals produces two π-bonds.

- π-bonds are at 90° to each other - one above and below the molecule, and the other in front of and behind the molecule.

one pi bond above and below the molecule

another pi bond in front of and behind the molecule
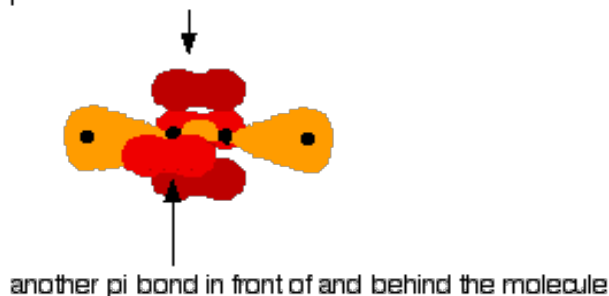
sp hybridized wavefunctions

- LCAO combines to form the following hybrid wavefunctions

$$\left|\psi_1^H\right\rangle = c_{1s}\left|\phi_s\right\rangle + c_{1p}\left|\phi_{pz}\right\rangle$$

[Recall $\quad \psi_i(\mathbf{r}_i) = \sum_{r=1}^{M} c_{ir}\phi_r'(\mathbf{r}_i)\quad$]

$$\left|\psi_2^H\right\rangle = c_{2s}\left|\phi_s\right\rangle + c_{2p}\left|\phi_{pz}\right\rangle$$

- Subject to the boundary conditions:

$$\left\langle\psi_1^H\middle|\psi_2^H\right\rangle = c_{1s}c_{2s} + c_{1p}c_{2p} = 0$$

$$\left\langle\psi_{1,2}^H\middle|\psi_{1,2}^H\right\rangle = c_{1s}^2 + c_{1p}^2 = c_{2s}^2 + c_{2p}^2 = 1$$

orthonormality

$$\left|\phi_s(z)\right\rangle = \left|\phi_s(-z)\right\rangle \text{ and } \left|\phi_{pz}(z)\right\rangle = -\left|\phi_{pz}(-z)\right\rangle, \text{ Symmetry} \Rightarrow c_{1s} = c_{2s} \text{ and } c_{1p} = -c_{2p}$$

- Giving the final <u>two</u> hybrid wavefunctions:

$$\left|\psi_1^H\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\phi_s\right\rangle + \left|\phi_{pz}\right\rangle\right)$$

$$\left|\psi_2^H\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\phi_s\right\rangle - \left|\phi_{pz}\right\rangle\right)$$

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These are located on the x-axis along the $C \equiv C$ axis
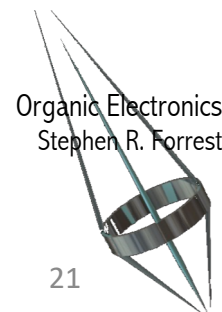
Application to large molecules
The Hückel Approximations

- The different s and p-orbital symmetries allow for separation of wavefunctions, Ψ_σ & Ψ_π, such that the total wavefunction is $\Psi_T = \Psi_\sigma \Psi_\pi$

- Nearest neighbor interactions are set equal to a constant. That is $H_{rr} = \alpha$, and $H_{rs} = \beta$ for $|r\text{-}s| = 1$, otherwise $H_{rs} = 0$.

  - α and β are negative (bonding) energies.

  - α is simply an energy offset

  - β is the energy due to the hybridization of the orbitals themselves.

- The overlap integrals $S_{rs} = \langle \phi'_s | \phi'_r \rangle = \delta_{rs}$, where $\delta_{rs} = 1$ when $r=s$; and $\delta_{rs} = 0$ otherwise.

  - This is the most problematic of the assumptions since the overlap from adjacent orbitals can be substantial; ≈0.2 or larger.
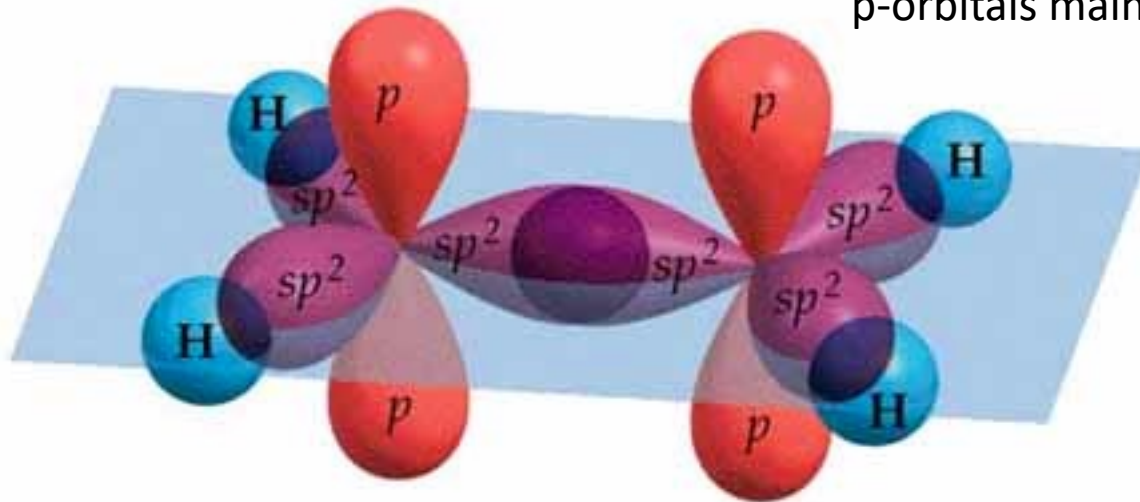
- Now the secular equation becomes simply:

$$\det\left|(\alpha - E)\mathbf{I} + \beta\mathbf{B}\right| = 0$$ where $\mathbf{I} = \delta_{rs}$, and $\mathbf{B} = \delta_{r,r\pm 1}$.

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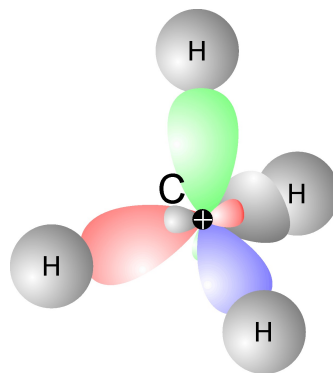# LCAO applied to solve for sp^2 and sp^3 hybridized orbitals

- sp^2: ethene $H_2C=CH_2$

3 solutions
p-orbitals maintain planarity
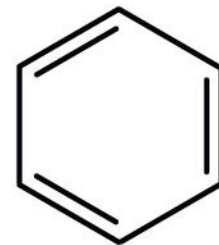

- sp^3: methane CH_4

4 solutions

Benzene (again!)

$$(H - E)\psi = 0$$

6x6 Secular determinant: $\det \begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$

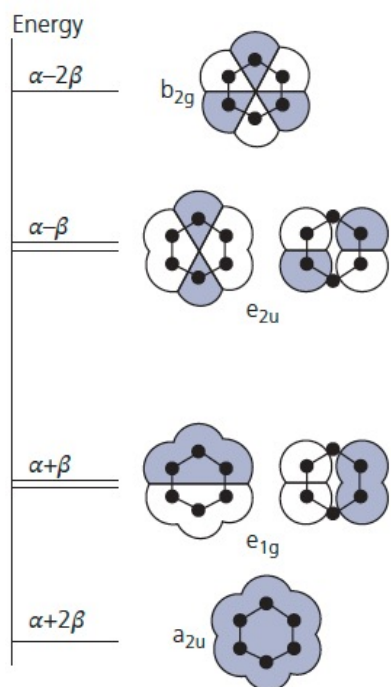Yields valence solutions: $E(a_1) = \alpha + 2\beta; \; E(e_2) = \alpha + \beta; \; E(e_1) = \alpha - \beta; \; E(b_1) = \alpha - 2\beta$

$$\alpha, \beta < 0$$

Constant offset

Energy

$\alpha - 2\beta$ b_{2g}

$\alpha - \beta$ e_{2u}

$\alpha + \beta$ e_{1g}

$\alpha + 2\beta$ a_{2u}

u=ungerade; spatially odd
g=gerade; spatially even

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This is getting complicated
(There must be an easier way)

- Not really.

- But for some molecules (e.g.**catacondensed** ring aromatics) we can use perimeter-free electron orbital model. More intuitive than accurate.

- Approximate the molecule by a ring of effective diameter ~ no. of phenyl groups

I^{th} orbital wavefunction

$$\psi_l(\theta) = \frac{1}{\sqrt{2\pi}} \exp(il\theta)$$

$$E_l = \alpha + \frac{\hbar^2}{2mr^2}l^2$$
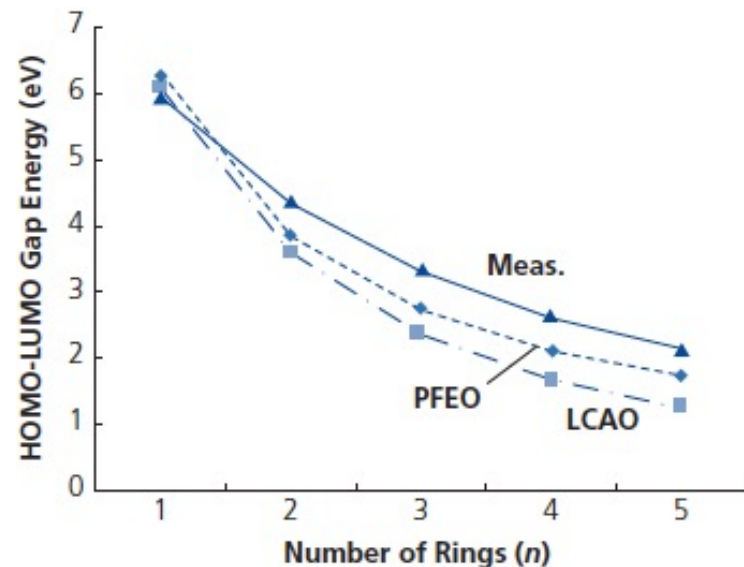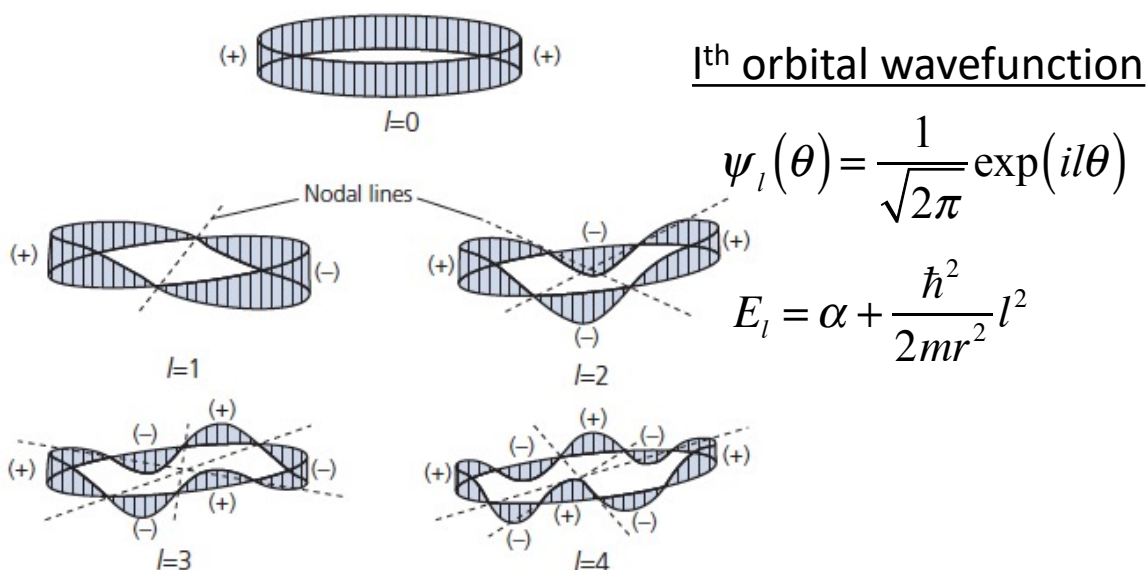
- l = 0 has 2 electrons (2 spins)
- l > 0 each has 4, (2 degenerate counter-propagating waves+ 2 spins) etc.
- Fill molecule to get to the highest l via aufbau principle
- e.g. benzene has 6 π-electrons (l = 1) called f-state

Not too bad!

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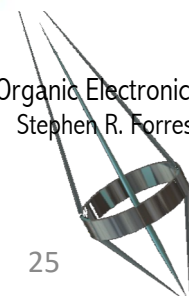
Density Functional Theory

- The primary approach to calculate molecular levels is density functional theory

  - Replaces electron distribution by an **electron density functional**

$$\rho(\mathbf{r}) = \sum_{i=1}^{n} |\phi_e(\mathbf{r})|^2$$

  - Then energy is a function of local charge density

$$E(\rho) = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \int \phi_e^*(\mathbf{r}) \nabla^2 \phi_e^*(\mathbf{r}) d^3r - \sum_{I=1}^{M} \int \frac{Z_I q^2}{4\pi\varepsilon_0 |\mathbf{r} - \mathbf{R}_I|} \rho(\mathbf{r}) d^3r + \frac{1}{2} \sum_{i=1}^{i \neq j} \int\int \frac{\rho(\mathbf{r}_i)\rho(\mathbf{r}_j)}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} d^3r_i d^3r_j + E_{XC}(\rho)$$

  - With exchange-correlation energy (the outer electrons interact and their collective motion is cooperative) : local density approximation

$$E_{XC} = \int \rho(\mathbf{r}) \varepsilon(\rho(\mathbf{r})) d^3r$$

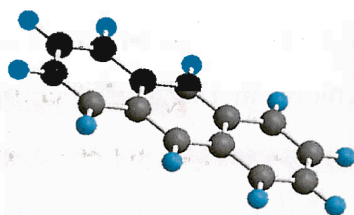Single electron exchange energy

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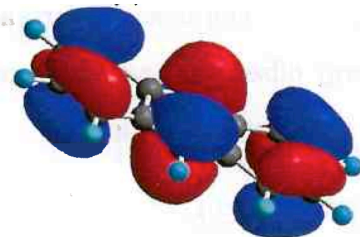The trick is finding the correct basis set and density functional: Semi-empirical
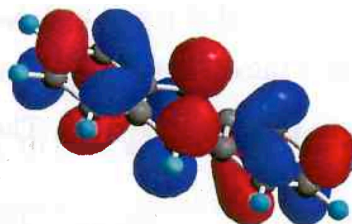
Examples: Anthracene & Pentacene
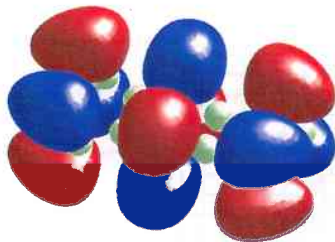
(a) Structure

(b) HOMO-14

(c) HOMO

(d) LUMO

DFT

(e) HOMO

(f) LUMO

LCAO

LUMO

HOMO

Peumans, P. 2004. Organic thin-film photodiodes.
Ph.D., Princeton U.

de Wijs et al. (2003)Synthetic Metals, 139, 109.
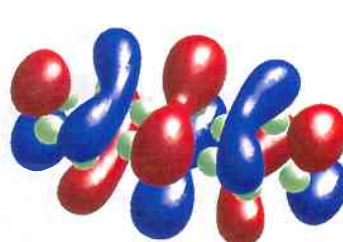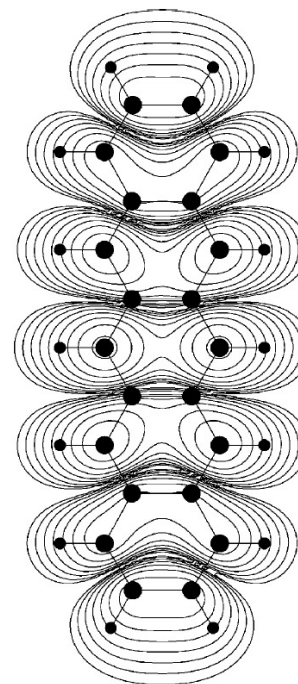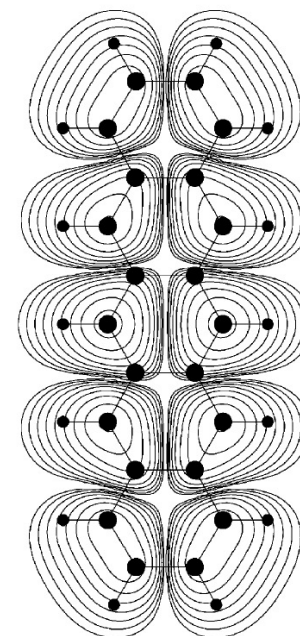
Transitions between levels

- Once we have the electronic structure, we can predict the most important optical property: the rate (i.e. the probability, strength) of a transition between states
  - Predicts emission and absorption spectra
  - Can predict exciton states and properties

- The cornerstone of our analysis: **Fermi's Golden Rule**
  - From time dependent perturbation theory
  - Easy to use and understand

$$k_{if} = \frac{2\pi}{\hbar}\left|\left\langle \psi_f \middle| H_{\text{int}} \middle| \psi_i \right\rangle\right|^2 \rho\left(E_{if}\right)$$

Transition matrix element:

$$M_{if}^2 = \left|\left\langle \psi_f \middle| H_{\text{int}} \middle| \psi_i \right\rangle\right|^2$$

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$\rho(E_{if})$ is the joint density of initial and final states of the wavefunctions, ψ_i and ψ_f
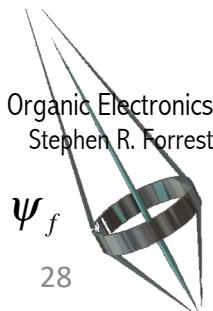
Electric dipole transitions are dominant

- Dipole interaction: $H_\mu = -\boldsymbol{\mu}_{\mathbf{r,R}} \cdot \mathbf{F}$

- But the dipole moment is: $\boldsymbol{\mu}_{\mathbf{r,R}} = \boldsymbol{\mu}_e + \boldsymbol{\mu}_N = -q\left[\sum_k \mathbf{r}_k - \sum_K Z_K \mathbf{R}_K(Q)\right]$

- And then the matrix element is: $\mu_{if} = \left\langle \phi_{e,f}(\mathbf{r},Q)\phi_{N,f}(Q)\middle|\boldsymbol{\mu}_{\mathbf{r,R}}\middle|\phi_{e,i}(\mathbf{r},Q)\phi_{N,i}(Q)\right\rangle$

- But B-O says that the electronic and nuclear coordinates are separable:

$$\mu_{if} = -q\left[\int \phi^*_{N,f}(Q)\phi_{N,i}(Q)dQ \sum_k \phi^*_{e,f}(\mathbf{r},Q)\mathbf{r}_k\phi_{e,i}(\mathbf{r},Q)d^3r\right] = \mu_{if,e}\sqrt{FC_{if}}$$

- This leads us to transition selection rules.

  - A transition is allowed as long as the transition matrix element is non-zero:

$$M_{if} = \left\langle \phi_{e,f}(\mathbf{r}_f)\middle|\mathbf{r}\cdot\mathbf{F}\middle|\phi_{e,i}(\mathbf{r}_i)\right\rangle\left\langle \phi_{N,f}(Q_f)\middle|\phi_{N,i}(Q_i)\right\rangle\left\langle \sigma_f(S_f)\middle|\sigma_i(S_i)\right\rangle \neq 0$$

Three rules: Spatial   Nuclear   Spin

See integral above

Transition Selection Rules-I

$$M_{if} = \boxed{\left\langle \phi_{e,f}\left(\mathbf{r}_f\right) \middle| \mathbf{r}\cdot\mathbf{F} \middle| \phi_{e,i}\left(\mathbf{r}_i\right) \right\rangle} \left\langle \phi_{N,f}\left(Q_f\right) \middle| \phi_{N,i}\left(Q_i\right) \right\rangle \left\langle \sigma_f\left(S_f\right) \middle| \sigma_i\left(S_i\right) \right\rangle \neq 0$$

- Spatial transition requires a parity inversion:
  - Since the dipole moment has odd parity: $\mu_{\mathbf{r}}\left(\mathbf{r}\right) = -\mu_{\mathbf{r}}\left(-\mathbf{r}\right)$
  - Then for the integral: $\left\langle \phi_{e,f}\left(\mathbf{r}_f\right) \middle| \mathbf{r}\cdot\mathbf{F} \middle| \phi_{e,i}\left(\mathbf{r}_i\right) \right\rangle \neq 0$

    we require transitions between states ($\phi_f(\mathbf{r})$ and $\phi_i(\mathbf{r})$) of opposite spatial parity!

  - E.g. one is a *gerade*, and the other an *ungerade* state under spatial inversion
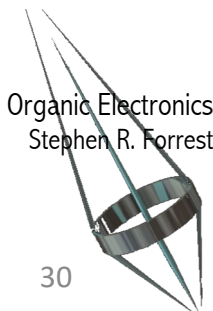
Transition Selection Rules-II

$$M_{if} = \left\langle \phi_{e,f}\left(\mathbf{r}_f\right) \middle| \mathbf{r} \cdot \mathbf{F} \middle| \phi_{e,i}\left(\mathbf{r}_i\right) \right\rangle \boxed{\left\langle \phi_{N,f}\left(Q_f\right) \middle| \phi_{N,i}\left(Q_i\right) \right\rangle} \left\langle \sigma_f\left(S_f\right) \middle| \sigma_i\left(S_i\right) \right\rangle \neq 0$$

- Vibronic initial and final states must overlap:

  - The degree of overlap is expressed by the <u>Franck-Condon Factor</u>:

$$FC_{if} = \left| \left\langle \phi_{N,f}\left(Q_f\right) \middle| \phi_{N,i}\left(Q_i\right) \right\rangle \right|^2$$

  - Note: orthogonality suggests that this integral always vanishes

  - But: the nuclear wavefunctions are in separate electronic manifolds

  - And: there is usually a "reconfiguration" of the molecule between ground and excited states (i.e. $\Delta Q = Q_f - Q_i \neq 0$)

  - So: $\phi_f(Q)$ and $\phi_i(Q)$ are no longer orthogonal and hence inter-vibronic transitions are possible. (i.e. vibronics are mixed with electronic states)

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Transition Selection Rules-III

$$M_{if} = \left\langle \phi_{e,f}\left(\mathbf{r}_f\right) \middle| \mathbf{r} \cdot \mathbf{F} \middle| \phi_{e,i}\left(\mathbf{r}_i\right) \right\rangle \left\langle \phi_{N,f}\left(Q_f\right) \middle| \phi_{N,i}\left(Q_i\right) \right\rangle \boxed{\left\langle \sigma_f\left(S_f\right) \middle| \sigma_i\left(S_i\right) \right\rangle} \neq 0$$

- Spin must remain unchanged during the transition

- Otherwise: $\left\langle \sigma_f\left(S_f\right) \middle| \sigma_i\left(S_i\right) \right\rangle = 0$

- Spectroscopically, we say that these transitions are allowed:

$$S_i \rightarrow S_f \ \text{ or } \ T_i \rightarrow T_f$$

  - Note on spectroscopic notation: the <u>highest energy state is always to the left</u>.
  - Thus: the transitions above are from a high initial to a low final energy state $\Rightarrow$ emission
  - Absorption is written: $\quad S_1 \leftarrow S_0 \ \text{ or } \ T_2 \leftarrow T_1$

Summarizing the Transition Rules

Transition	Selection rule	Matrix Element	Exception
Between electronic states	Parity of $\phi_{e,f}$ and $\phi_{e,i}$ must be different (e.g. even $\rightarrow$ odd)	$\left\langle \phi_{e,f}(r) \middle| \mathbf{r} \middle| \phi_{e,i}(\mathbf{r}) \right\rangle$	Low symmetry molecules, two photon transitions, higher order multipoles
Between vibronic states in different electronic manifolds	Vibronic quantum number n_i-n_f=0	$\left\langle \phi_{N,f}(Q) \middle| \phi_{N,i}(Q) \right\rangle$	$\Delta Q_{if} \neq 0$: nuclear reconfiguration between $\phi_{e,f}(\mathbf{r},Q)$ and $\phi_{e,i}(\mathbf{r},Q)$
Between spin states	$S_i \rightarrow S_f ; T_i \rightarrow T_f$	$\left\langle \sigma_f(S_f) \middle| \sigma_i(S_i) \right\rangle$	Spin-orbit coupling Spin-spin coupling

'to every rule there is an exception, including this one'

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