

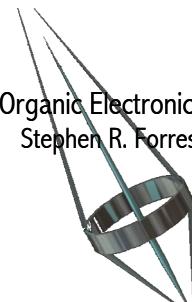
Week 3

Optical Properties 1

Born-Oppenheimer and Franck-Condon
Fermi's golden rule
Transitions and selection rules

Chapter 3.1, 3.2. 3.5

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Stephen R. Forrest



Objectives

- Optical properties are the *core to understanding* molecules both independently, in solutions, and in solids
- We will spend approximately 4 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) \Rightarrow pairs and small assemblies
 \Rightarrow solids

Electronic Orbitals

The Born-Oppenheimer Approximation

- Understanding molecular energetics requires knowledge of the molecular orbital structure
- To calculate the wavefunction, write the **spinorbital** wavefunction:

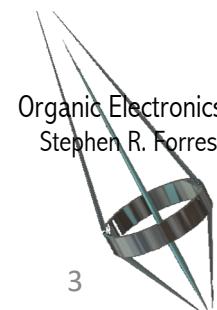
$$\Psi(\{\mathbf{r}_i\}; \{\mathbf{R}_j\}; \{S_k\}) = \Phi(\{\mathbf{r}_i\}; \{\mathbf{R}_j\}) \sigma(\{S_k\})$$

Electronic Nuclear Spin

$\{\mathbf{r}_i\} = \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ = all electron position vectors.

$\{\mathbf{R}_i\} = \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M$ = 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



Singlet and triplet states

Spatially symm. Spin antisymm.

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

S m_S

Singlet
 $S=0$
 $m_s=0$

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

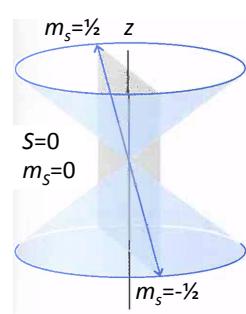
$$\psi(\mathbf{r}_1, \mathbf{r}_2; 1, 0) = \frac{1}{\sqrt{2}} (\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)) (\alpha_1\beta_2 + \alpha_2\beta_1)$$

Triplet
 $S=1$
 $m_s=\pm 1, 0$

and

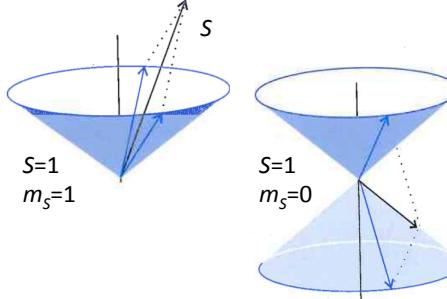
$$\psi(\mathbf{r}_1, \mathbf{r}_2; 1, -1) = \frac{1}{\sqrt{2}} (\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)) \beta_1\beta_2$$

180° out of phase

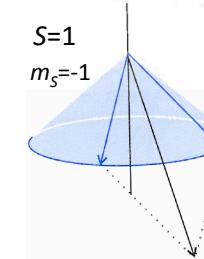


(a)

In phase



(b)

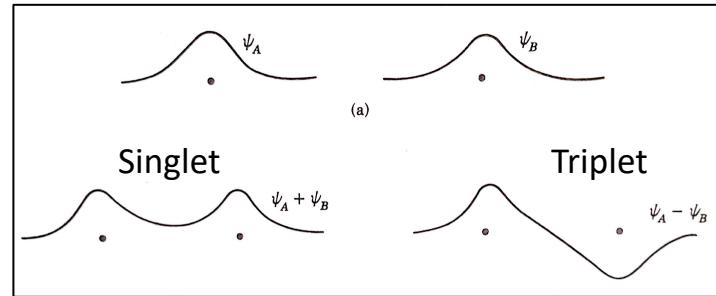
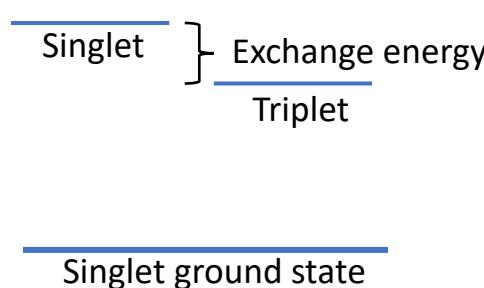


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Pauli Exclusion Principle: Total wavefunctions must be antisymmetric 4

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

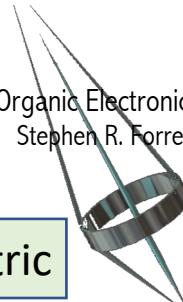
- Why does the wavefunction have to be antisymmetric to agree with Pauli exclusion?

- Take two particle wavefunctions, $|1\rangle, |2\rangle$
- The total wavefunction is a linear combination of the two under exchange:

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

- 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

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

$\det=0$ if any two rows or columns are identical

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

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

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

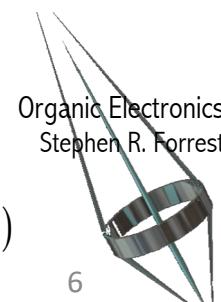
$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \phi_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \phi_N(\{\mathbf{R}_I\})$$

Total Hamiltonian:

$$H_T = -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_{\mathbf{r}_i}^2 - \frac{\hbar^2}{2} \sum_I^M \frac{1}{m_{NI}} \nabla_{\mathbf{R}_I}^2 + \frac{q^2}{4\pi\epsilon_0} \left(\sum_{i>j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}^{N,M} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I>J}^M \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \right)$$

Just the electronic part:

$$H_e \phi_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = \left[-\frac{\hbar^2}{2m_e} \sum_i^N \nabla_{\mathbf{r}_i}^2 + \frac{q^2}{4\pi\epsilon_0} \left(\sum_{i>j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}^{N,M} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) \right] \phi_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) = E_e \phi_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

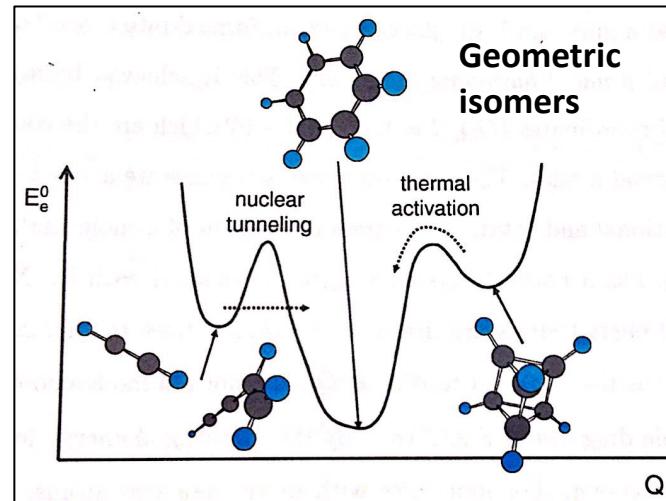
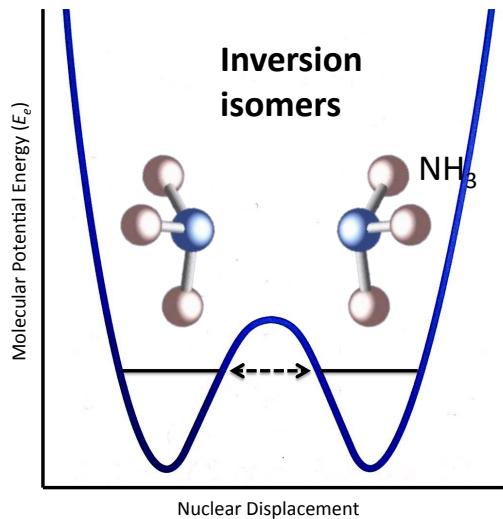


Solving for the orbitals

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

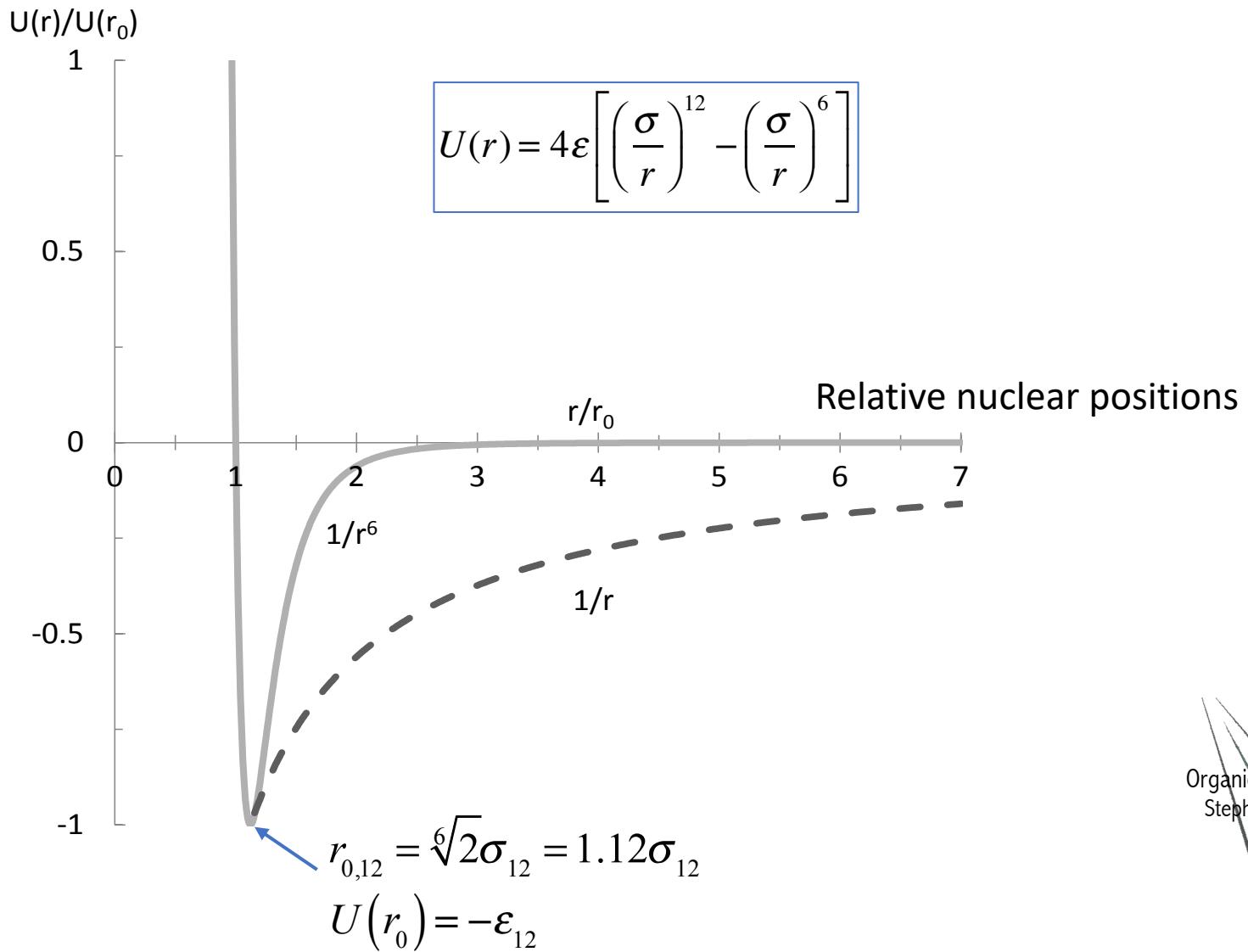
$$\phi_e^0(\{\mathbf{r}_i\}) = \prod_{i=1}^N \phi_{e,i}^0(\mathbf{r}_i)$$

- 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. C₆H₆) 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).

Recall: vdW Potential is the basic intermolecular interaction



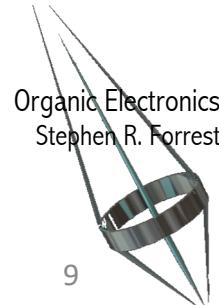
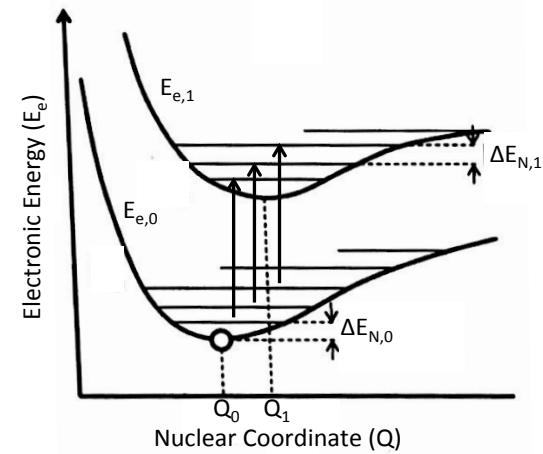
Luckily, we only have to worry about things near equilibrium

- 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

- Simple Harmonic Oscillator (SHO) with solutions for the j^{th} electronic level,
- j^{th} normal mode:

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

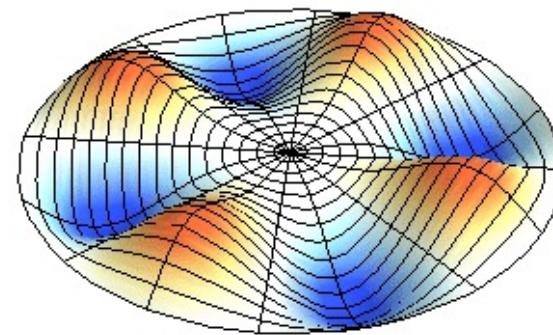
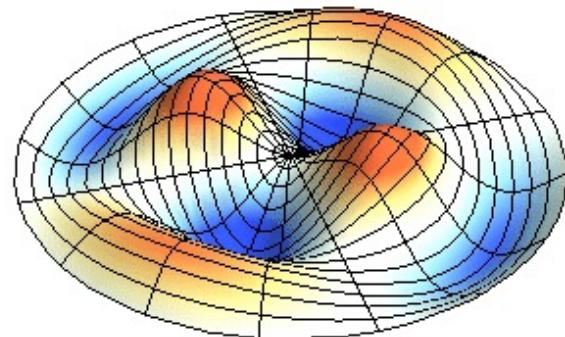
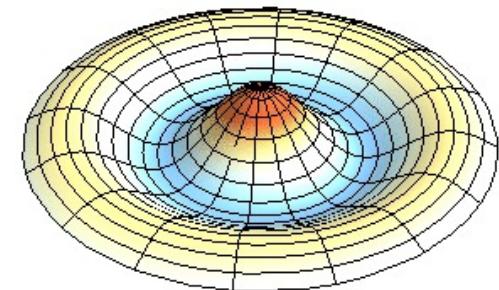
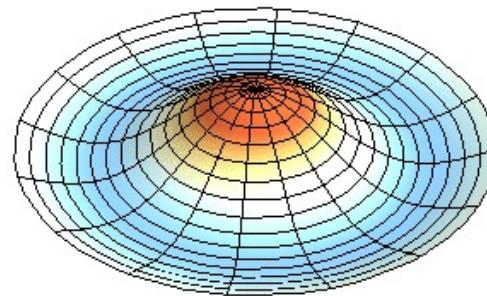
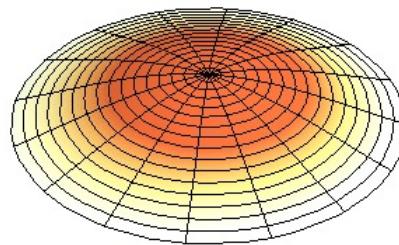
- Things to notice:
 - A shift in **nuclear coordinates** between the ground and first excited state ($\Delta Q = |Q_1 - Q_0|$)
 - Only relative nuclear coordinates (Q) are important.
 - Equal spacing of levels near bottom of an electronic manifold
 - These “inner levels” called vibronics
 - They are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



Intramolecular phonons

Think of benzene as an approximately circular drumhead

These represent several of the lowest possible normal vibrational modes

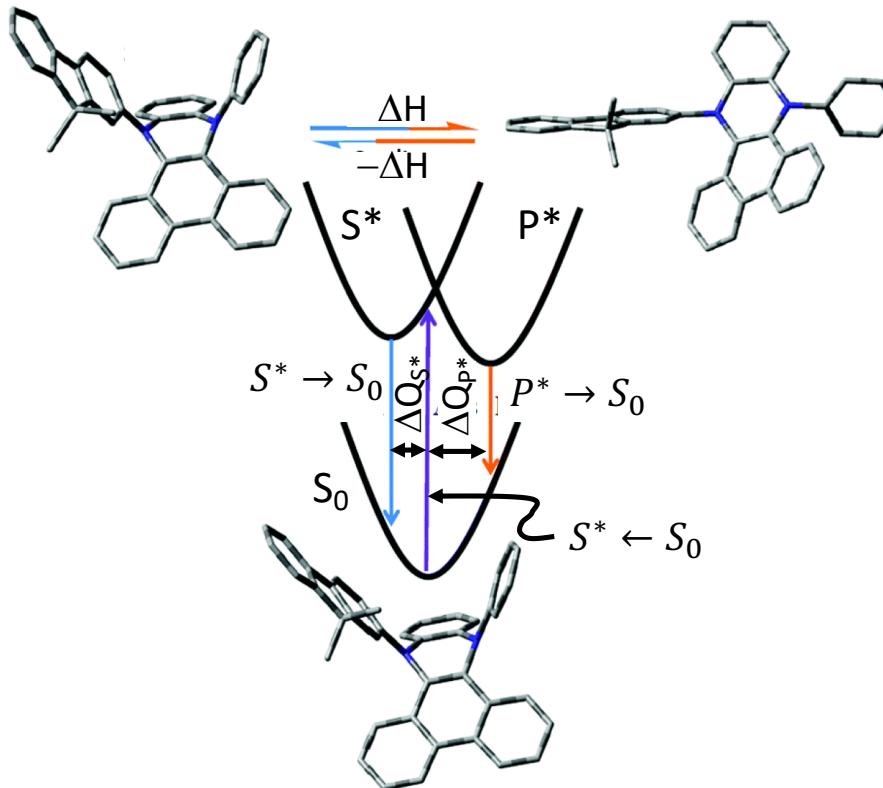


Another important approximation

- **Franck-Condon Principle**

- Molecules relax after excitation, but 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 vertical

Molecular reconfiguration leads to Stokes shifts



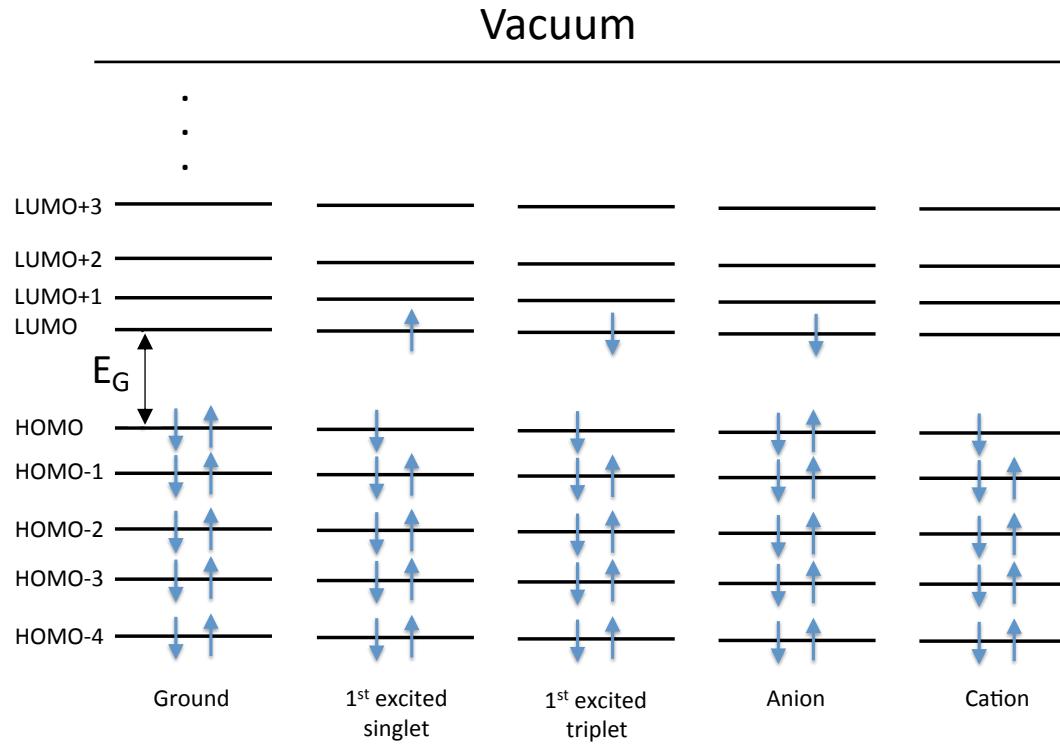
Two excited isomers

S^* : saddle-like
 P^* : planar-like

Molecule: 9-(9,9-dimethyl-9Hfluoren-3yl)-14-phenyl-9,14-dihydrodibenzo[a,c]phenazine (FIPAC) in MeTHF (methyl tetrahyfuran) solution

Possible electronic states

Aufbau principle: “Building up” principle – state filling begins at the lowest level (HOMO- n) and continues until it fills up the highest (HOMO) state.



Excited state pictures
prior to relaxation

Energy Gap

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

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 linear combinations of electronic states of the comprising atoms
- Original atomic orbitals only slightly perturbed when placed within the molecule
 - First order perturbation theory applies
 - M atoms, L orbitals
- The most important electron is the last electron 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 Unperturbed
orbitals 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

H_2^+ molecular orbitals

- Wavefunctions split by Coulomb repulsion

$$1\sigma: \psi = \frac{1}{\sqrt{2}}(\phi_r + \phi_s)$$

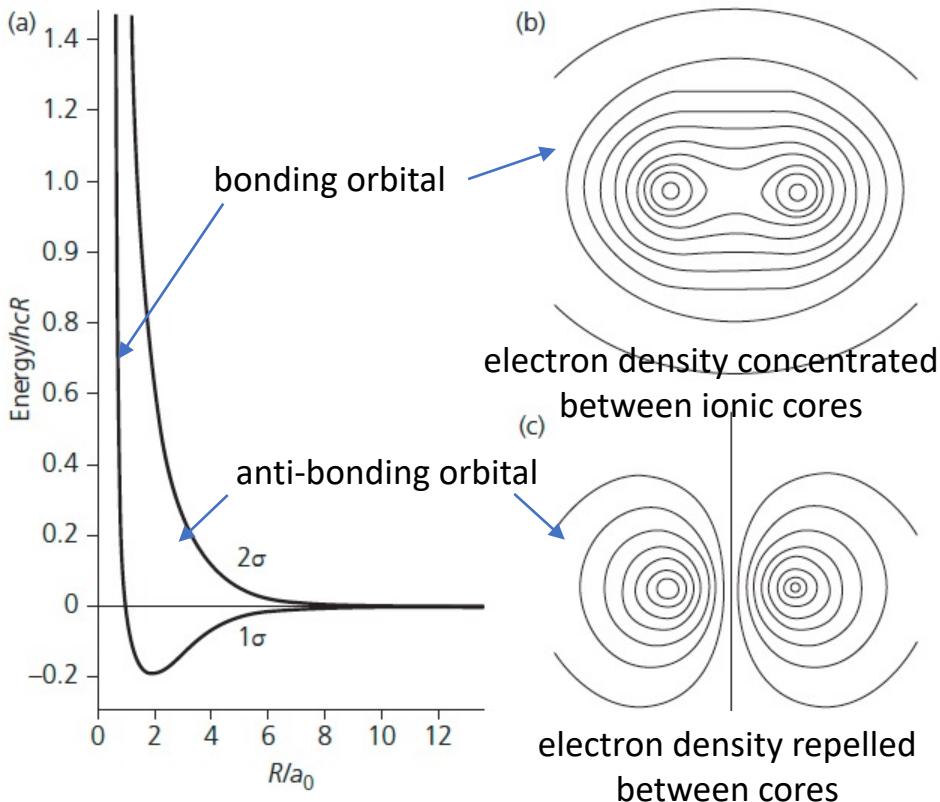
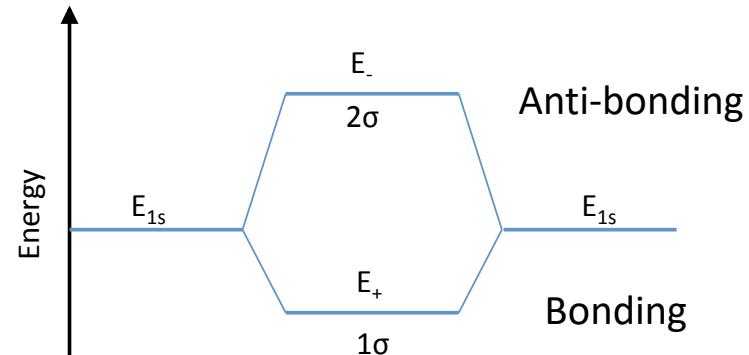
($c_r=c_s=1$)

$$2\sigma: \psi = \frac{1}{\sqrt{2}}(\phi_r - \phi_s)$$

($c_r=-c_s=1$)

Splitting increases
as distance decreases

(2 degenerate levels, E_{1s})



Solving for Larger Molecules

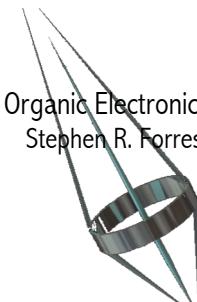
$$(H - E)\psi = 0$$

$$H_{rr} = \left\langle \psi_r \left| \frac{1}{r} \right| \psi_r \right\rangle = \alpha$$

$$H_{rs} = \left\langle \psi_r \left| \frac{1}{r} \right| \psi_s \right\rangle = \beta$$

Hückel rule:

Only nearest neighbors considered: $H_{rs} = 0$ unless $|r-s| = 1$



Benzene (again!)

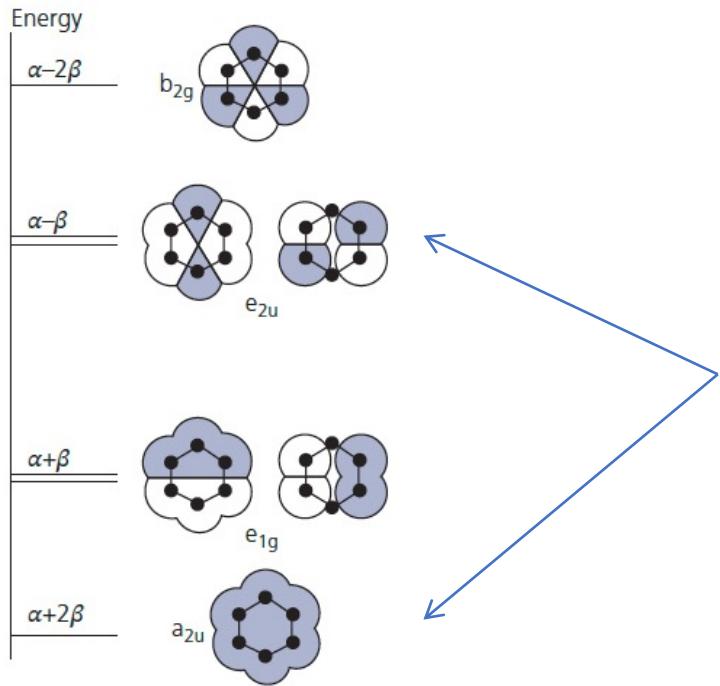
$$(H - E)\psi = 0$$

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: $E(a_1) = \alpha + 2\beta$; $E(e_2) = \alpha + \beta$; $E(e_1) = \alpha - \beta$; $E(b_1) = \alpha - 2\beta$
 $\alpha, \beta < 0$

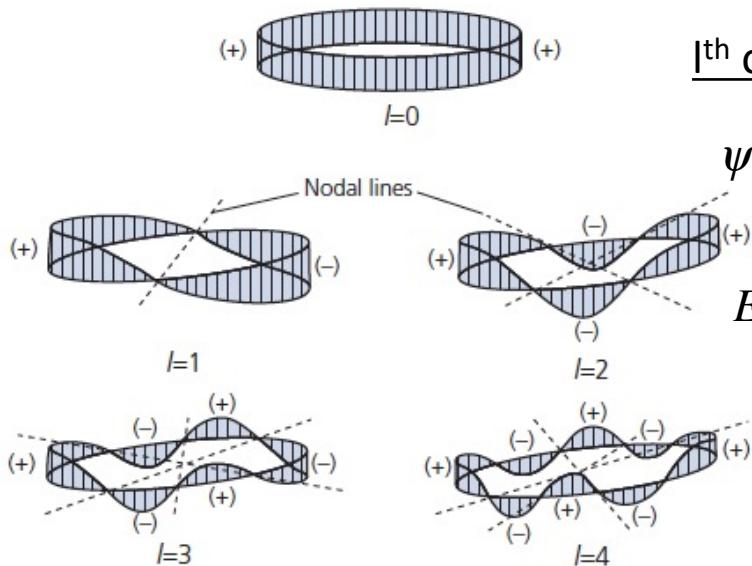


Constant offset

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

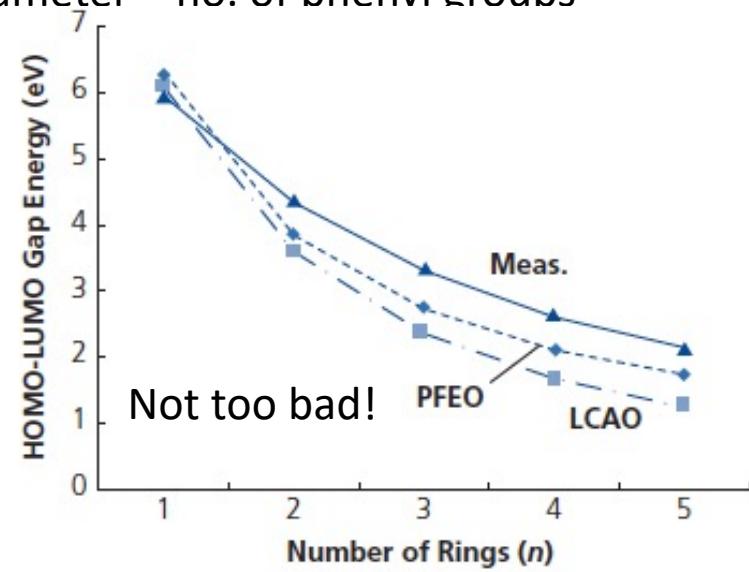
This is getting complicated (There must be an easier way)

- Not really.
- But for some molecules (e.g. **catacondensed** ring aromatics= molecules where no more than 2 rings have a C atom in common) we can use perimeter-free electron orbital model. More intuitive than accurate.
- Approximate the molecule by a ring of effective diameter \sim no. of phenyl groups



l 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*

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

$$E(\rho) = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \int \phi_e^*(\mathbf{r}) \nabla^2 \phi_e^*(\mathbf{r}) d^3r - \sum_{I=1}^M \int \frac{Z_I q^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{R}_I|} \rho(\mathbf{r}) d^3r + \frac{1}{2} \sum_{i=1} \sum_{j \neq i} \int \int \frac{\rho(\mathbf{r}_i)\rho(\mathbf{r}_j)}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} d^3r_i d^3r_j + E_{xc}(\rho)$$

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

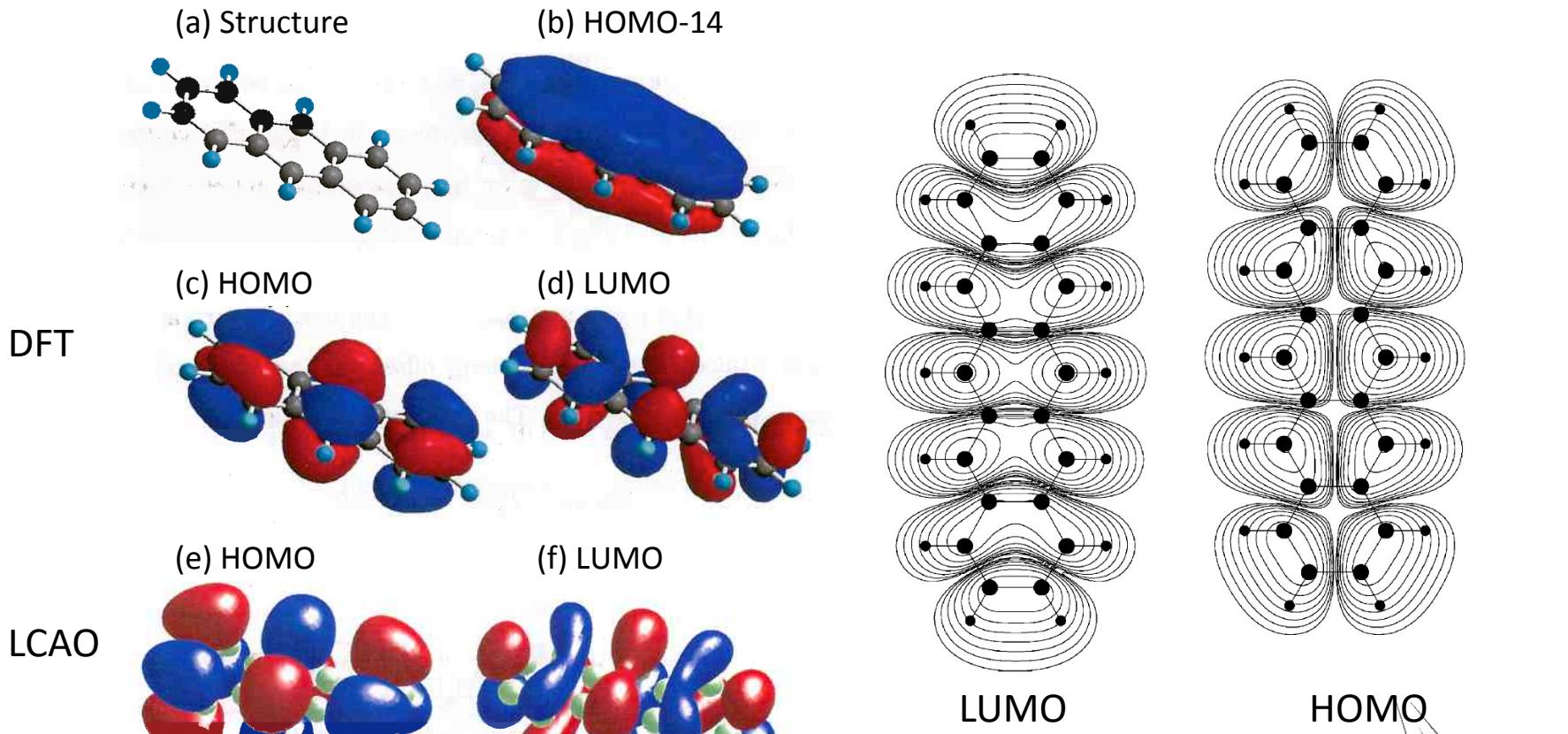
$$E_{xc} = \int \rho(\mathbf{r}) \varepsilon(\rho(\mathbf{r})) d^3r$$



Single electron exchange energy

The trick is finding the correct basis set and density functional: Semi-empirical

Examples: Anthracene & Pentacene



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

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

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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

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

Transition matrix element:

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

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

Electric dipole transitions are dominant

- Dipole interaction: $H_\mu = -\mu_{\mathbf{r},\mathbf{R}} \cdot \mathbf{F}$
 - But the dipole moment is: $\mu_{\mathbf{r},\mathbf{R}} = \mu_e + \mu_N = -q \left[\sum_k \mathbf{r}_k - \sum_K Z_K \mathbf{R}_K(Q) \right]$
 - And then the matrix element is: $\mu_{if} = \langle \phi_{e,f}(\mathbf{r},Q) \phi_{N,f}(Q) | \mu_{\mathbf{r},\mathbf{R}} | \phi_{e,i}(\mathbf{r},Q) \phi_{N,i}(Q) \rangle$
 - 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.

FC = Franck-Condon factor

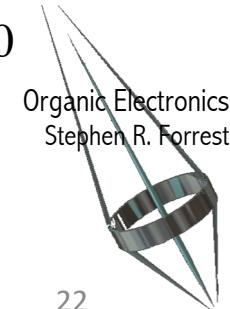
- A transition is allowed as long as the transition matrix element is non-zero:

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

Three rules:

A diagram illustrating the relationship between spatial and nuclear dimensions. It features two blue upward-pointing arrows. The left arrow is labeled "Spatial" and the right arrow is labeled "Nuclear". A horizontal blue line connects the bases of the two arrows, with a small blue bracket positioned below the line, indicating a connection or comparison between the two concepts.

See integral above



Transition Selection Rules-I

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

- Spatial transition requires a parity inversion:

- Since the dipole moment has odd parity: $\mu_r(\mathbf{r}) = -\mu_r(-\mathbf{r})$
- Then for the integral: $\langle \phi_{e,f}(\mathbf{r}_f) | \mathbf{r} \cdot \mathbf{F} | \phi_{e,i}(\mathbf{r}_i) \rangle \neq 0$
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

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

- Vibronic initial and final states must overlap:
 - The degree of overlap is expressed by the Franck-Condon Factor:

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

- 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)

Transition Selection Rules-III

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

- Spin must remain unchanged during the transition
- Otherwise: $\langle \sigma_f(S_f) | \sigma_i(S_i) \rangle = 0$
- Spectroscopically, we say that these transitions are allowed:

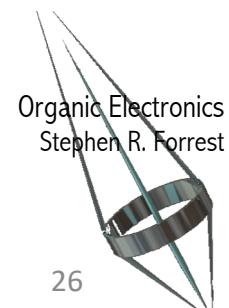


- Note on spectroscopic notation: the highest energy state is always to the left.
- Thus: the transitions above are from a high initial to a low final energy state
⇒ emission
- Absorption is written: $S_1 \leftarrow S_0$ or $T_2 \leftarrow T_1$

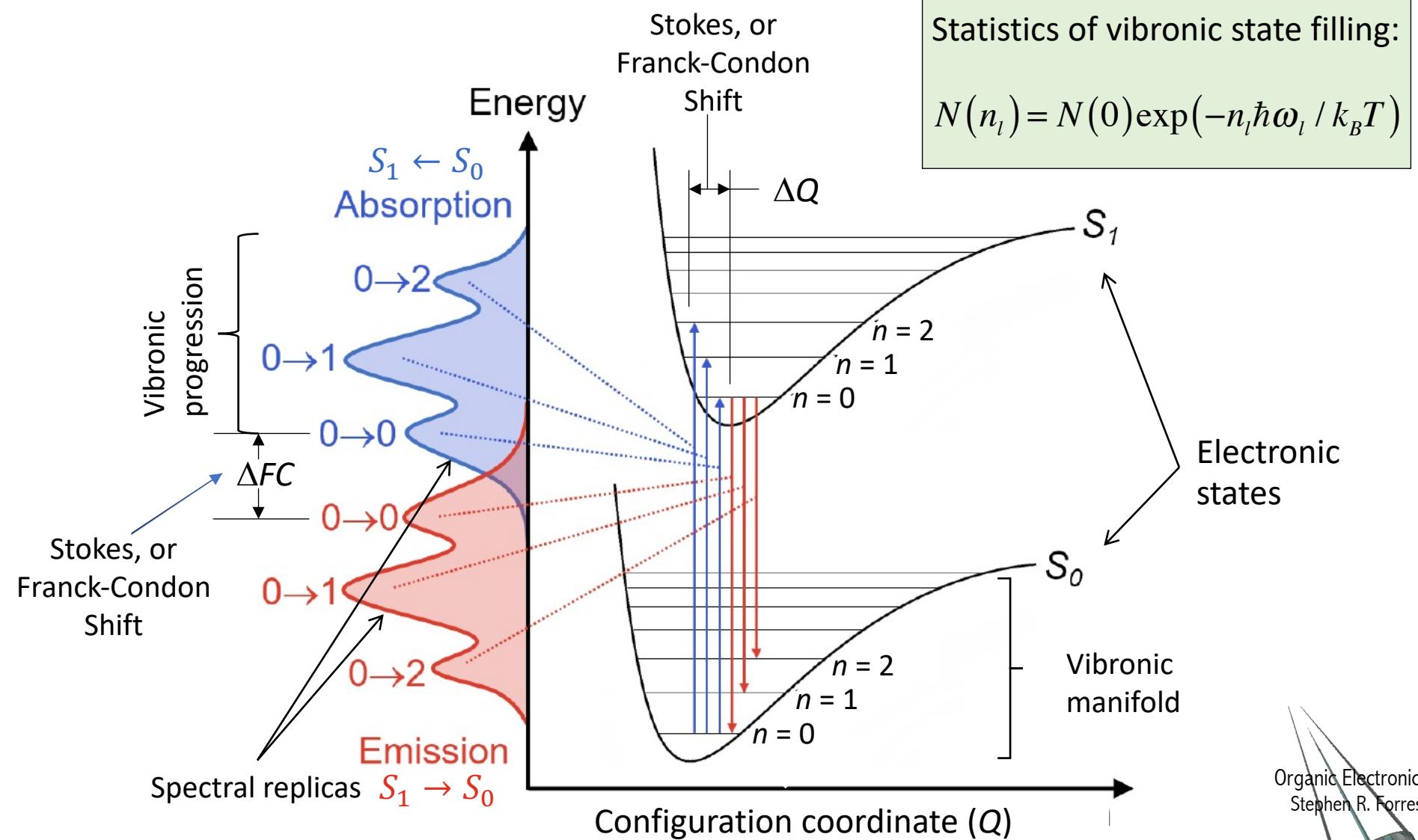
Summarizing the Transition Rules

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

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

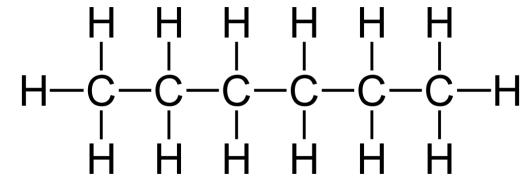
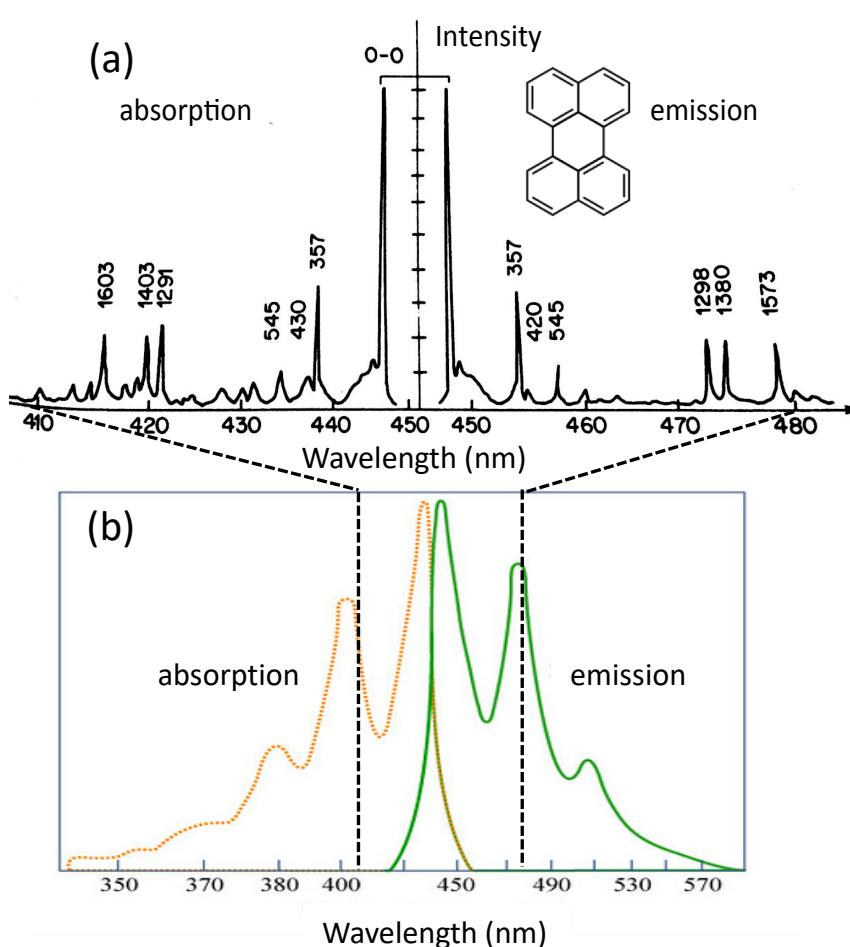


Understanding molecular spectra



Organic Electronics
Stephen R. Forrest

A classic spectrum at low temperature



- **Perylene in *n*-hexane solution**
- Perfect replica of absorption and emission
- Homogeneously broadened phonon lines narrow as the random disorder is “frozen” out
- Numerous vibronics apparent in this progression: rotons, librons, etc...