Week 3

Optical Properties 1
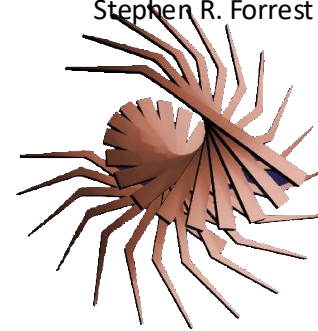
Born-Oppenheimer and Franck-Condon
Fermi's golden rule
Transitions and selection rules
Interpreting spectra and the energy gap law
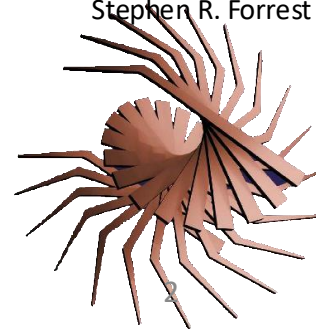
Concepts in Organic Electronics
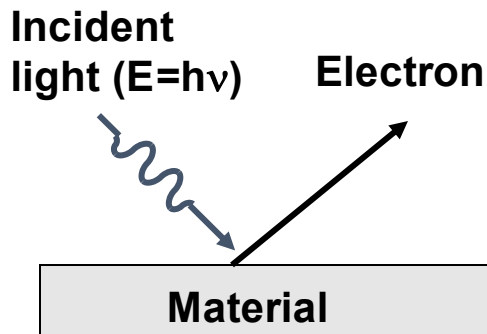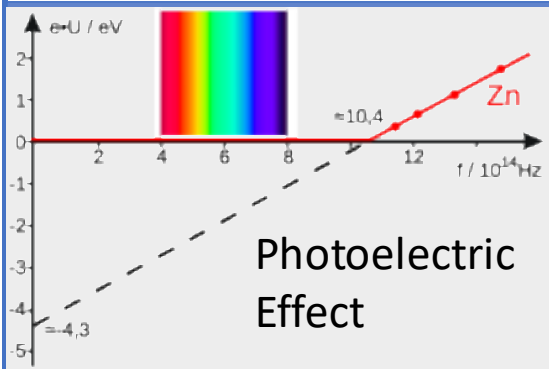Stephen R. Forrest

Chapter 3.1 - 3.6

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) $\Longrightarrow$ pairs and small assemblies $\Longrightarrow$ solids

Principles Of Quantum Mechanics

Energy Quanta

Photoelectric Effect

Incident light (E=hν) → **Electron**

Material

Electron current observed at photon energy hν>ϕ_m
ϕ_m = metal work function.

Einstein, 1905

Wave-Particle Duality

Waves show particle-like behavior (photons=light)

Particles show wave-like behavior (electron=wave)

de Broglie Wavelength

$$\lambda = \frac{h}{p}$$

h = 6.626 x 10^{-34} J-s

Electrons are a wave!
Electrons are a particle!

(Can't you make up your mind?!)

de Broglie, 1924

Uncertainty Principle

Uncertainty in position/momentum of particle and energy/momentum of wave

$$\Delta p \Delta x \geq \hbar$$

$$\Delta E \Delta t \geq \hbar$$

$$\hbar = h/2\pi$$
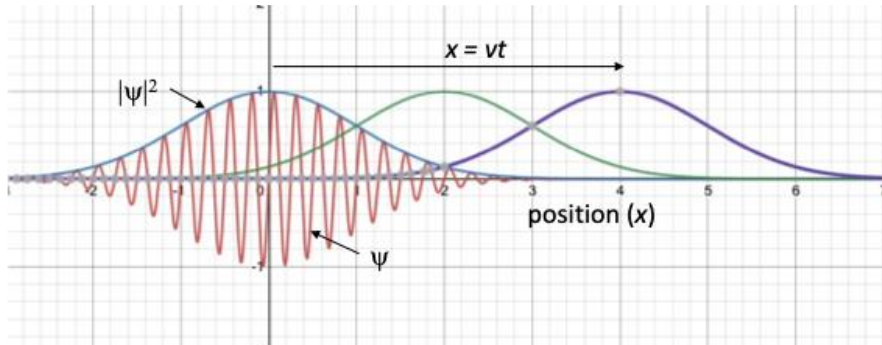
A particle, like a wave, is not at a single spot

Heisenberg, 1927
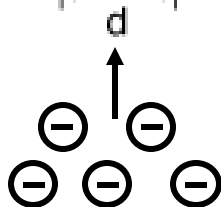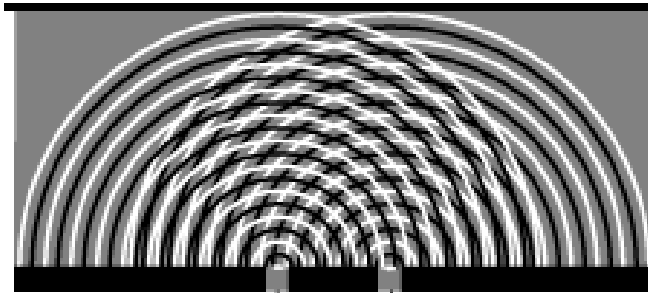
Wave-particle duality

Electron beam incident on "double-slit"

Detect electrons on other side

Electron described by a wave packet
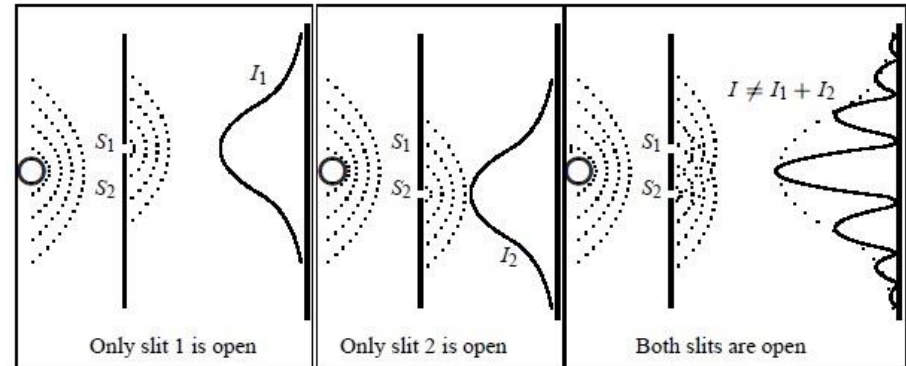

$x = vt$

$|\psi|^2$

position (x)

ψ

Result

I_1

I_2

$I \neq I_1 + I_2$

Only slit 1 is open

Only slit 2 is open

Both slits are open

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detect here

d

⊖ ⊖
⊖ ⊖ ⊖

Electrons have wave-like properties

Electron states in a Hydrogen Atom

Schrödinger's Equation is the Foundation of Quantum Mechanics

Schrödinger's Equation

ψ(x) is the *probability amplitude* that a particle will be at x.
$|\psi(x)|^2$ is its actual **probability**

KE   + PE   = Total E

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r) \right)\psi = E\psi$$

$$V(r) = -\frac{q^2}{4\pi\varepsilon_o r} \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Solution for Hydrogen atom

$$E = -\frac{m_0 q^4}{2(4\pi\varepsilon_0 \hbar n)^2} = -\frac{13.6eV}{n^2}$$

n = 1, 2, 3... (Principal quantum number)

ε_0 = 8.85 x 10^{-14} F/cm (Permittivity of free space)

Discrete Energy Levels

———————— E_{vac}

———————— E_4

———————— E_3

———————— E_2

———————— E_1

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"Accurately" predicts the spectrum of H, and every other atom and compound ever examined

Electronic Orbitals
The Born-Oppenheimer Approximation

- Understanding molecular energetics requires knowledge of the molecular orbital structure

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

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

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 motions are *independent*
  - $\Rightarrow$ Wavefunctions and variables are separable

Singlet and triplet states

Spatially symm.   Spin antisymm.

S m_S

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

Singlet
S=0
m_s= 0

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

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

Triplet
S=1
m_s=±1, 0

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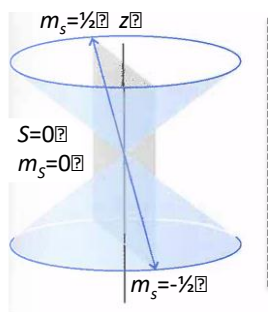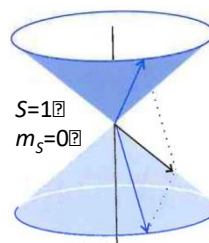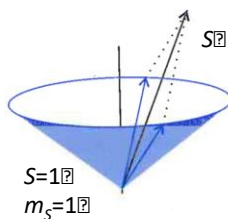
$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,-1)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\beta_1\beta_2$$

180° out of phase   In phase

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

S=0
m_s=0

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

S

S=1
m_s=1

S=1
m_s=0

S=1
m_s=-1
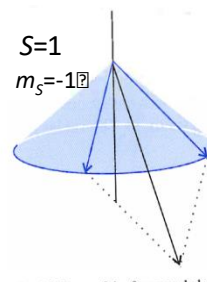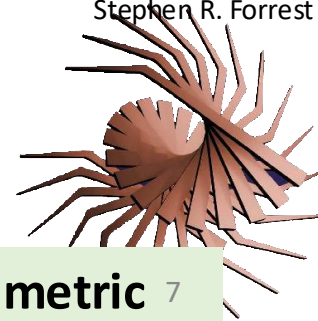
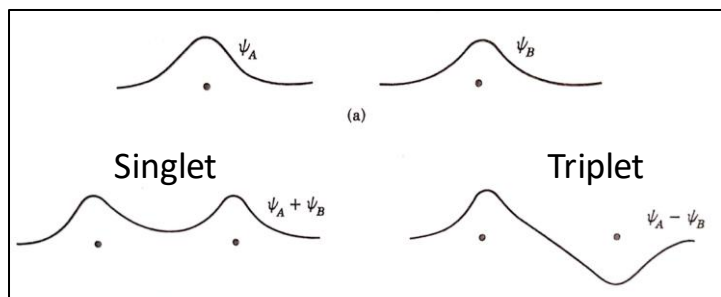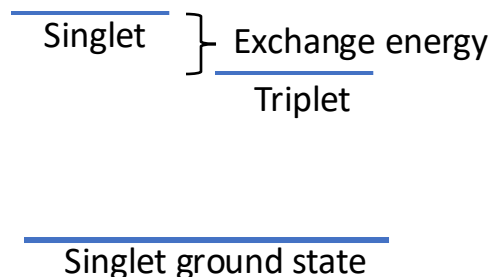(a)   (b)

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Pauli Exclusion Principle: Total wavefunctions must be antisymmetric 7

Answers to a couple of questions

- Why do triplet states have lower energy than singlets?

Singlet ⎱ Exchange energy
Triplet

Singlet ground state
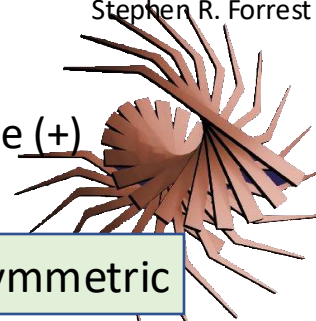

Singlet   Triplet

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: Concepts in Organic Electronics
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$$|tot\rangle = \text{constant} \times \{|1\rangle|2\rangle \pm |2\rangle|1\rangle\}$$

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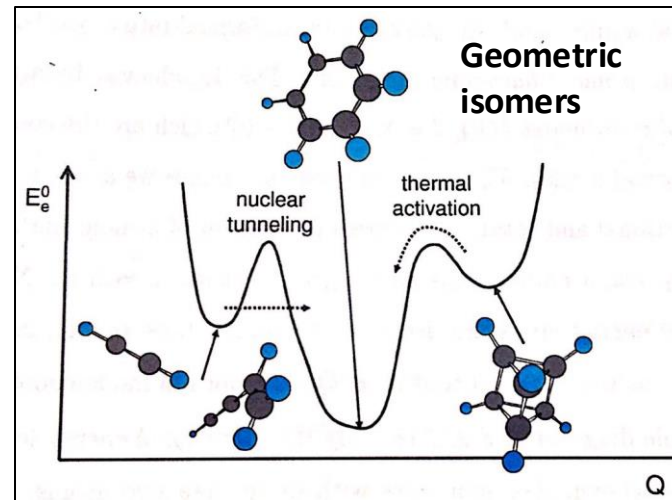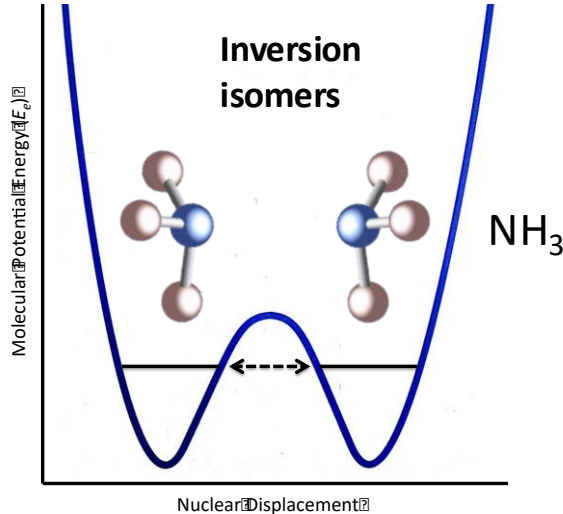
Pauli Exclusion demands no two electrons occupy the same state ⇒ antisymmetric

Solving for the orbitals

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

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

- 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. C_6H_6) but a different arrangement of atoms in the molecule, and with different properties.

Inversion isomers

Molecular Potential Energy (E_e)

NH_3

Nuclear Displacement

Geometric isomers

E_e^0

nuclear tunneling

thermal activation

Q

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Topological isomers: When the same molecule can have different topologies (i.e DNA can have both helices and knots).

H_2^+ molecular orbitals

- 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_{+}

Bonding

1σ

(a)

Energy/hcR

bonding orbital

anti-bonding orbital

2σ

1σ

R/a_0

(b)

electron density concentrated
between ionic cores

(c)

electron density repelled
between cores

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.

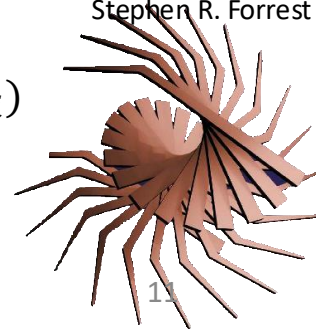$$\psi_i(\mathbf{r}_i) = \sum_{j=1}^{M} \sum_{k=1}^{L} c_{ijk}\phi_{jk}(\mathbf{r}_i - \mathbf{R}_J)$$

Molecular orbitals

Unperturbed atomic orbitals

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- But B-O says that nuclear positions are separable:

$$\psi_i(\mathbf{r}_i) = \sum_{k=1}^{M} c_{ik}\phi_k(\mathbf{r}_i)$$

New, electron-only atomic orbitals

11

Solving for Larger Molecules

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

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

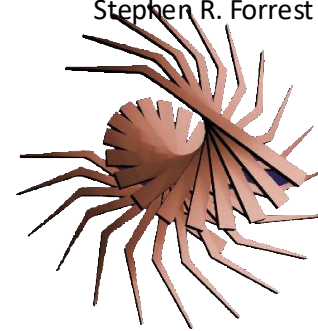$$H_{rs} = \left\langle \psi_r \left| \frac{1}{r} \right| \psi_s \right\rangle = \beta$$

ψ_r & ψ_s are orthonormal, i.e.

$$\int \psi_r \psi_s d^3 r = \delta_{rs}$$

Hückel rule:

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

We can write anti-symmetric functions in terms of determinants

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

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:

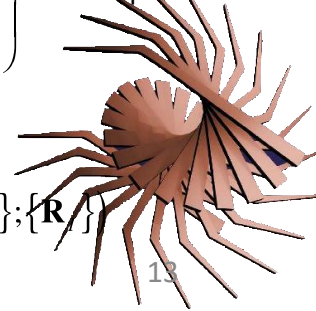$$\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) = \phi_e(\{\mathbf{r}_i\},\{\mathbf{R}_I\})\phi_N(\{\mathbf{R}_I\})$$

Total Hamiltonian:

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

Just the electronic part:

$$H_e\phi_e(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) = \left[-\frac{\hbar^2}{2m_e}\sum_i^N \nabla_{\mathbf{r}_i}^2 + \frac{q^2}{4\pi\varepsilon_0}\left(\sum_{i>j}^N \frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{i,I}^{N,M} \frac{Z_I}{|\mathbf{r}_i-\mathbf{R}_I|} \right) \right]\phi_e(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) = E_e\phi_e(\{\mathbf{r}_i\};\{\mathbf{R}_I\})$$
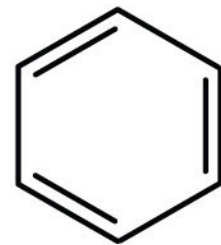
13

Benzene: Solving for a simple molecule

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

6x6 Secular determinant: $\det \begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$
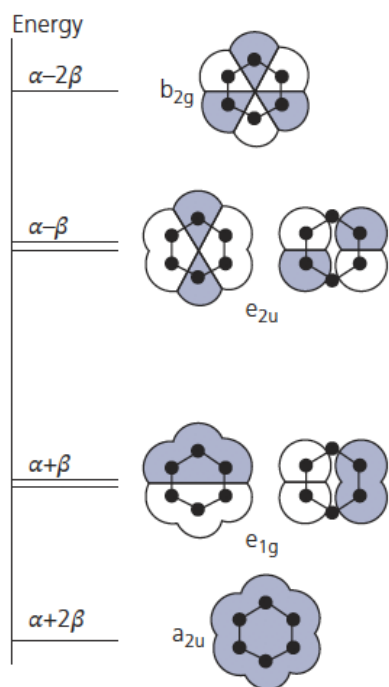
Yields valence solutions: $E(a_1) = \alpha + 2\beta; \; E(e_2) = \alpha + \beta; \; E(e_1) = \alpha - \beta; \; E(b_1) = \alpha - 2\beta$
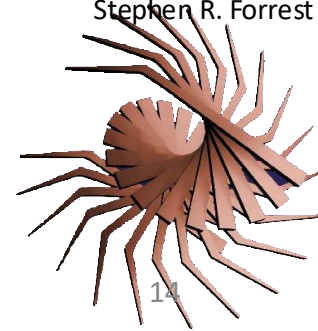
$$\alpha, \beta < 0$$

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

14

Density Functional Theory

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

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

    $$\rho(\mathbf{r}) = \sum_{k=1}^{n} |\phi_k(\mathbf{r}_i)|^2$$

    - Then energy is a function of local charge density

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

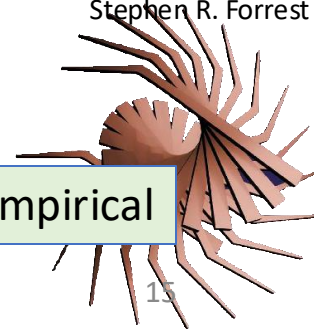   - With exchange-correlation energy (the outer electrons interact and their collective motion is cooperative) : local density approximation

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

    Single electron exchange energy
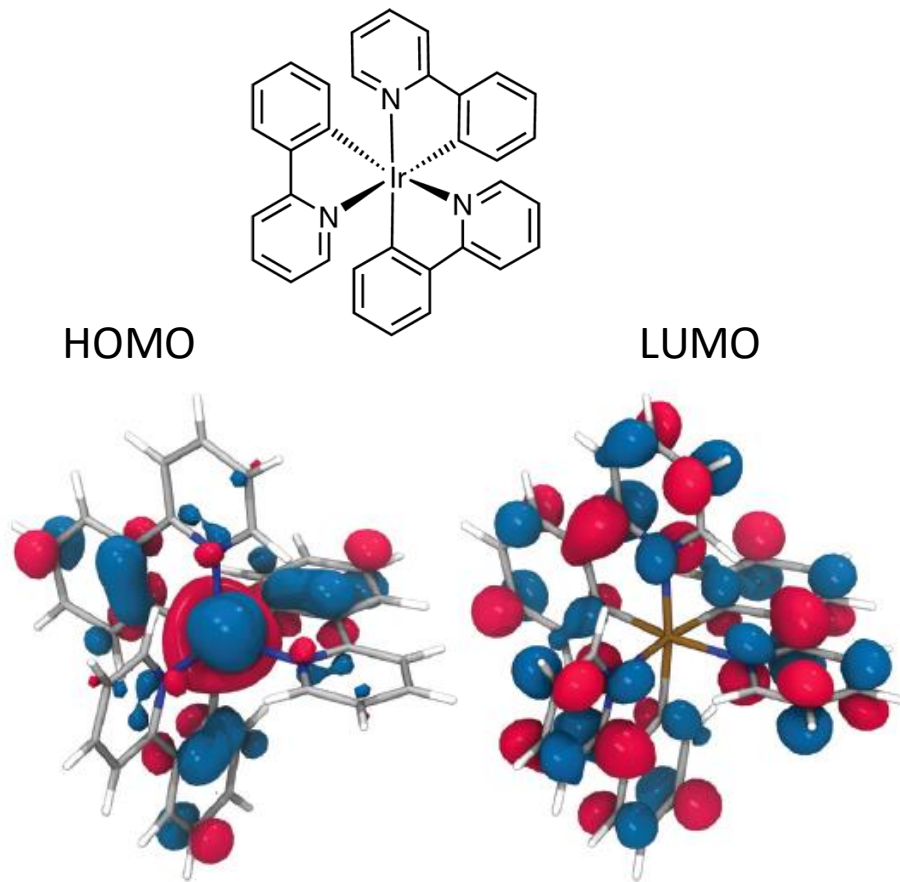
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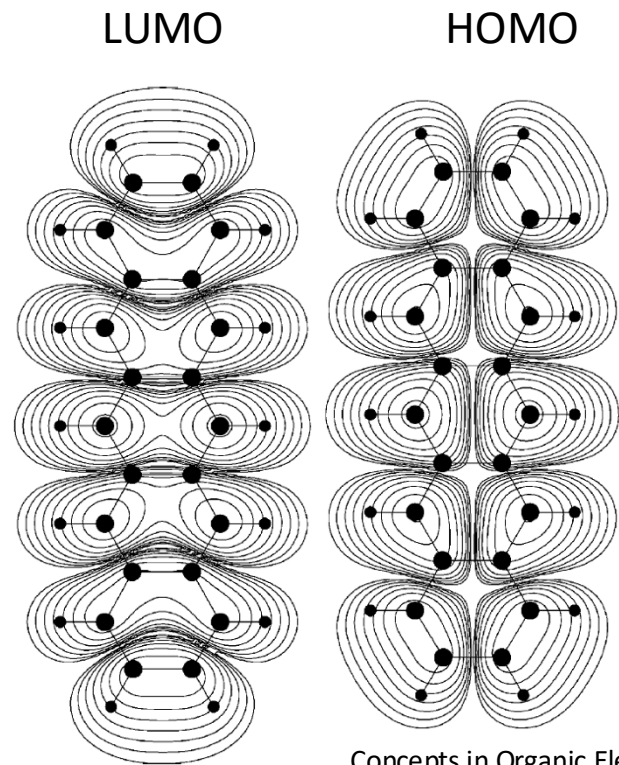
The trick is finding the correct basis set and density functional: Semi-empirical

15

DFT Examples: Ir(ppy)$_3$ and Pentacene

LUMO   HOMO

HOMO   LUMO

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J. Frey, J., et al. (2014). Dalton Transactions, **43**, 5667–5679   de Wijs et al. Synthetic Metals, **139**, 109 (2003).

vdW Potential is the basic intermolecular interaction

U(r)/U(r$_0$)

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

Relative nuclear positions

r/r$_0$

1/r^6

1/r

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$$r_{0,12} = \sqrt[6]{2}\,\sigma_{12} = 1.12\,\sigma_{12}$$

$$U(r_0) = -\varepsilon_{12}$$

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 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:

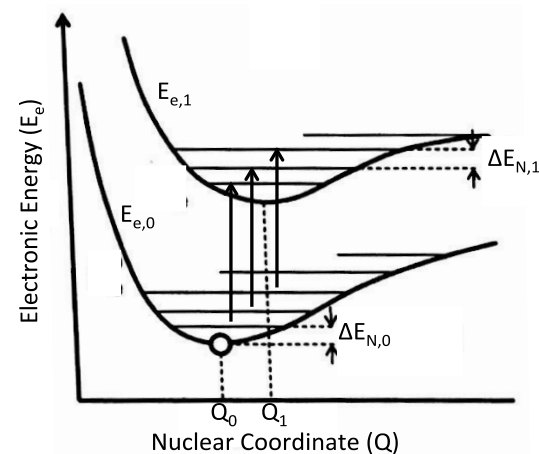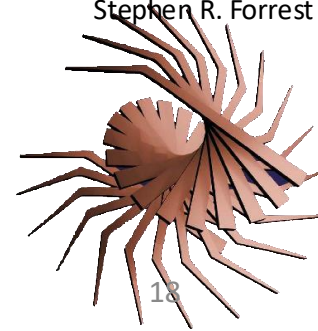 - A shift in **nuclear coordinates** between the ground and first excited state ($\Delta Q = \left| Q_1 - Q_0 \right|$)

  - Only relative <u>nuclear</u> 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)

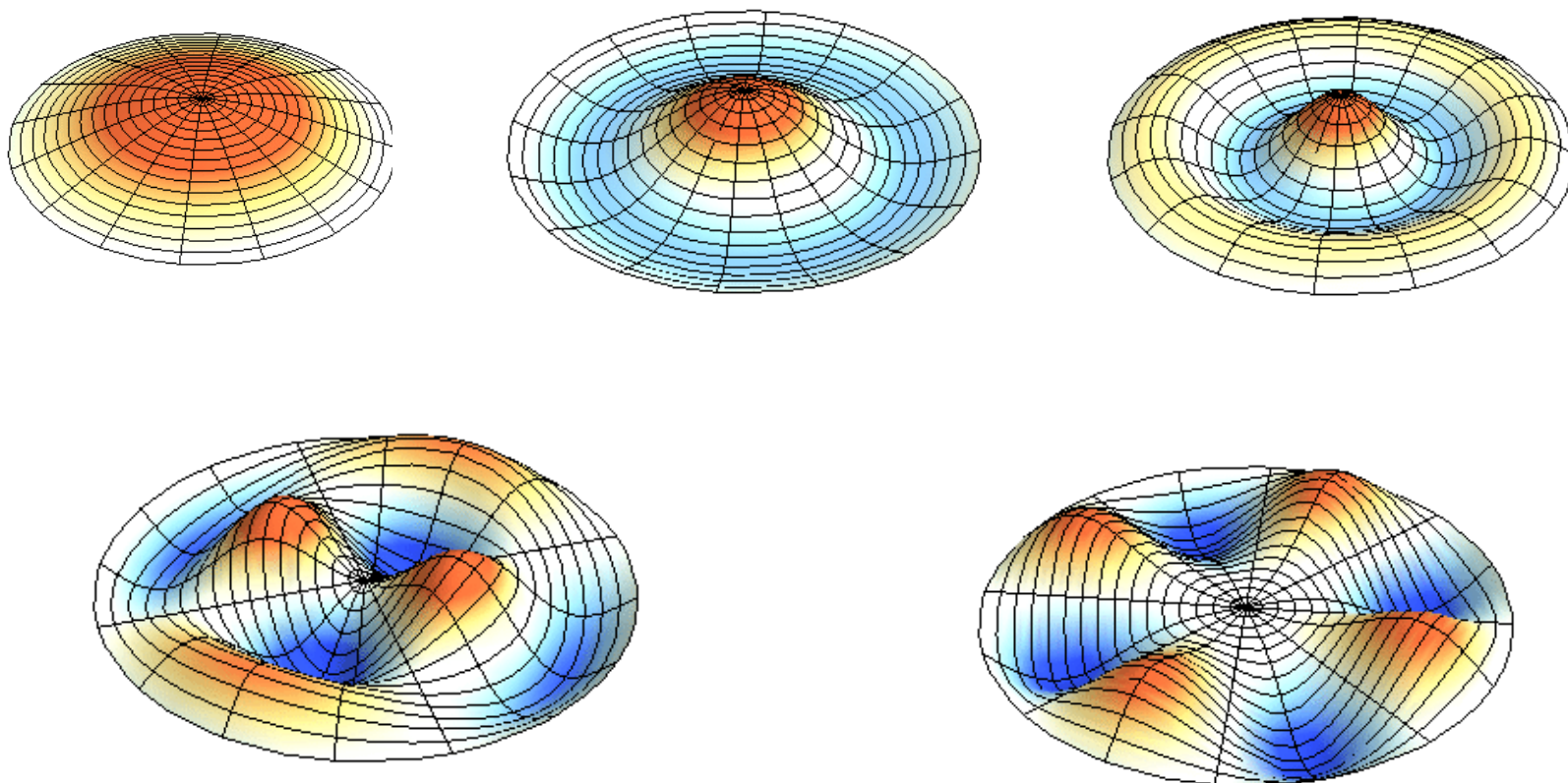 - Vibronics "compress" as we go to higher energies.

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18

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, <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 ($\sim 1/\nu$)
        - Nuclear time scales: picoseconds (phonon lifetime)
    - Implication: All transitions are <u>vertical</u>

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Molecular reconfiguration leads to Stokes shifts

ΔH

$-\Delta H$

S*   P*

S_0

$! * \rightarrow !_\$$ $\%^* \rightarrow !_\$$

ΔQ_S^* ΔQ_{P^*}

$! * \leftarrow !_\$$

Two excited isomers

S*: saddle-like

P*: planar-like

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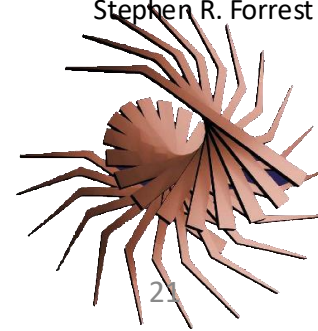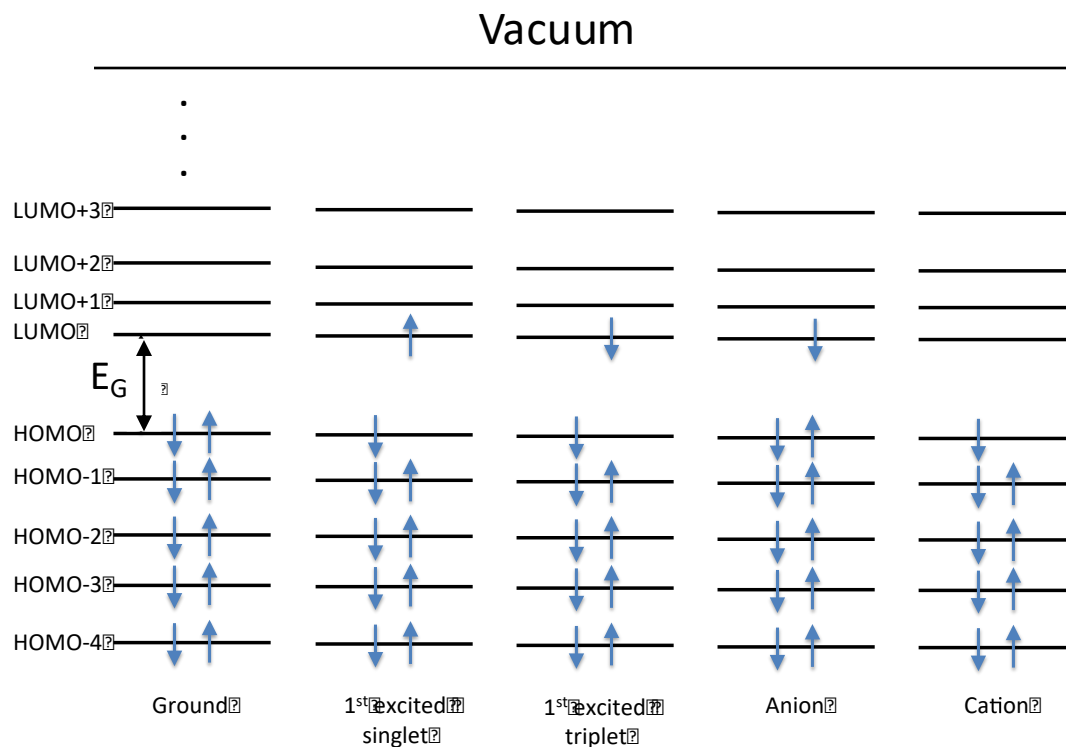Molecule: 9-(9,9-dimethyl-9Hfluoren-3yl)-14-phenyl-
9,14-dihydrodibenzo[a,c]phenazine (FIPAC) in MeTHF
(methyl tetrahyrofuran) solution

J. Chen, Phys. Chem. Chem. Phys., **17**, 27658 (2015)

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.

Vacuum

Excited state pictures **prior** to relaxation

LUMO+3
LUMO+2
LUMO+1
LUMO

E_G

HOMO
HOMO-1
HOMO-2
HOMO-3
HOMO-4

Ground | 1st excited singlet | 1st excited triplet | Anion | Cation

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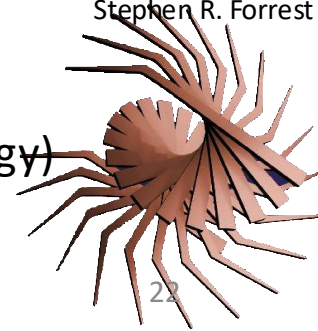
$E_G = E_{LUMO} - E_{HOMO}$ (unrelaxed)

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

HOMO and LUMO are "frontier orbitals"

22

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

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

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

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

23

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 dipole matrix element is: $\mu_{if} = \left\langle \phi_{e,f}(\mathbf{r},Q)\phi_{N,f}(Q) \middle| \mu_{\mathbf{r,R}} \middle| \phi_{e,i}(\mathbf{r},Q)\phi_{N,i}(Q) \right\rangle$

- 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.

  FC = Franck-Condon factor

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

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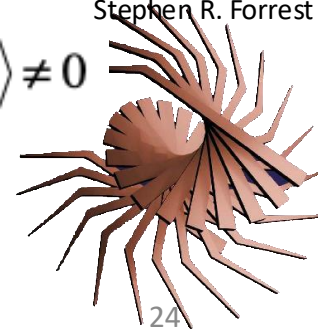
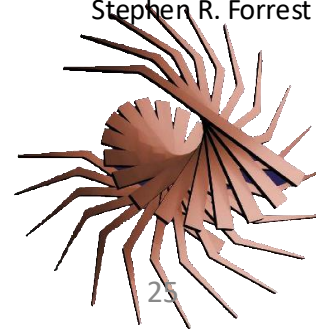Three rules: Spatial   Nuclear   Spin

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
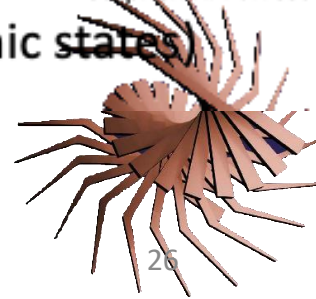
Transition Selection Rules-II

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

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

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

  - 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)

Transition Selection Rules-III

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

- 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 underlined highest energy state is always to the left.
  - Thus: the transitions above are from a high initial to a low final energy state $\Rightarrow$ emission
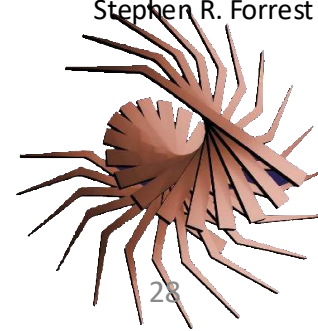 - Absorption is written: $S_1 \leftarrow S_0 \text{ or } T_2 \leftarrow T_1$

Summarizing the Transition Rules

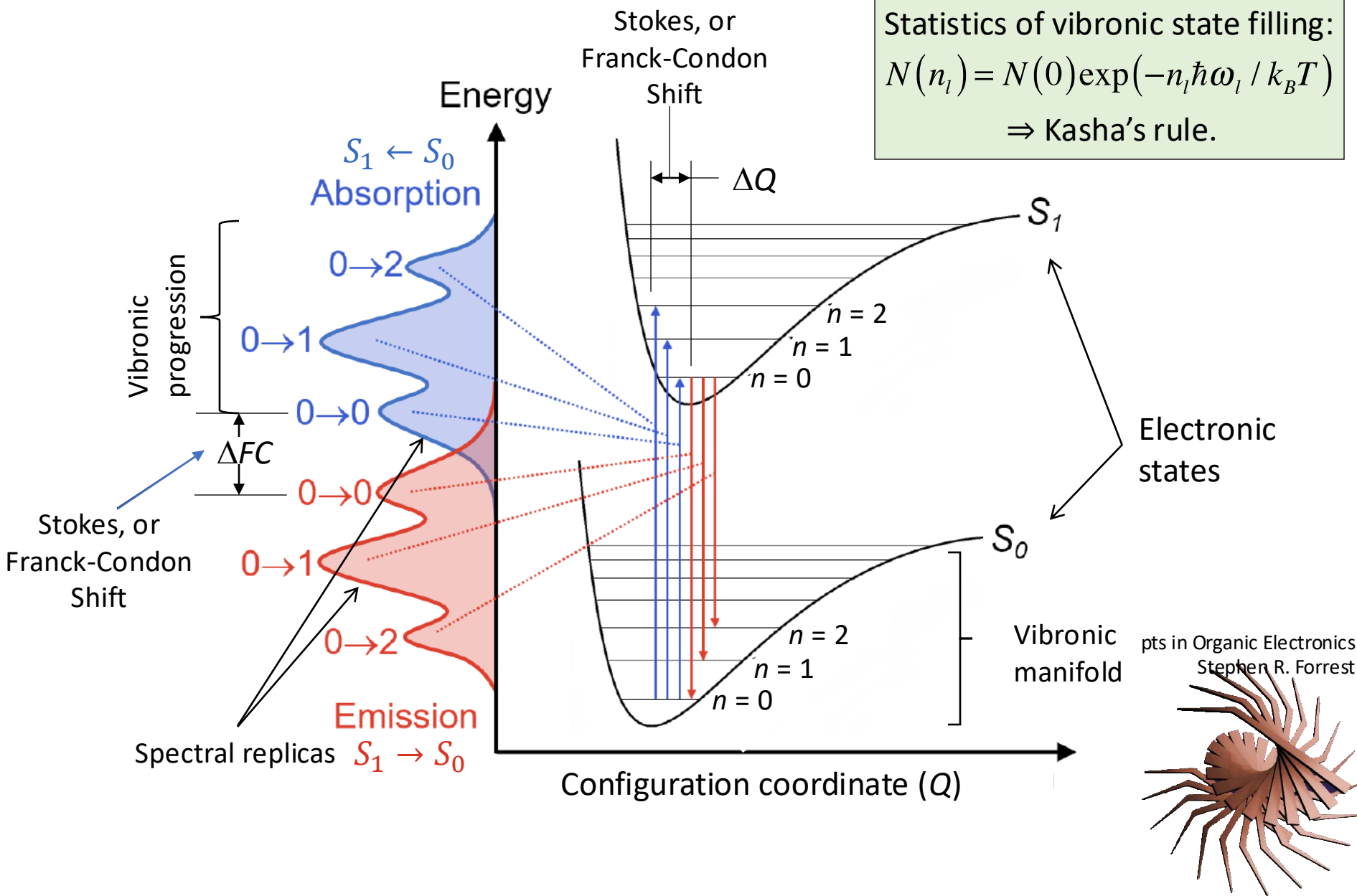| Transition	Selection rule	Matrix Element	Exception
Between electronic states	Parity of $\phi_{e,f}$ and $\phi_{e,i}$ must be different (e.g. even $\rightarrow$ odd)	$\left\langle \phi_{e,f}(r) \middle\| \mathbf{r} \middle\| \phi_{e,i}(\mathbf{r}) \right\rangle$	Low symmetry molecules, two photon transitions, 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'

Understanding molecular spectra

Stokes, or Franck-Condon Shift

Energy

$S_1 \leftarrow S_0$
Absorption

ΔQ

S_1

$0 \rightarrow 2$

$0 \rightarrow 1$

$0 \rightarrow 0$

$n = 2$
$n = 1$
$n = 0$

Vibronic progression

ΔFC

$0 \rightarrow 0$

Electronic states

Stokes, or Franck-Condon Shift

$0 \rightarrow 1$

S_0

$0 \rightarrow 2$

$n = 2$
$n = 1$
$n = 0$

Vibronic manifold

Emission

Spectral replicas $S_1 \rightarrow S_0$

Configuration coordinate (Q)

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A classic spectrum at low temperature

(a)

absorp' on)

0-o

Intensity)

emission)

1603 1403 1291 545 430 357 357 420 545 1298 1380 1573

Wavelength (nm)

(b)
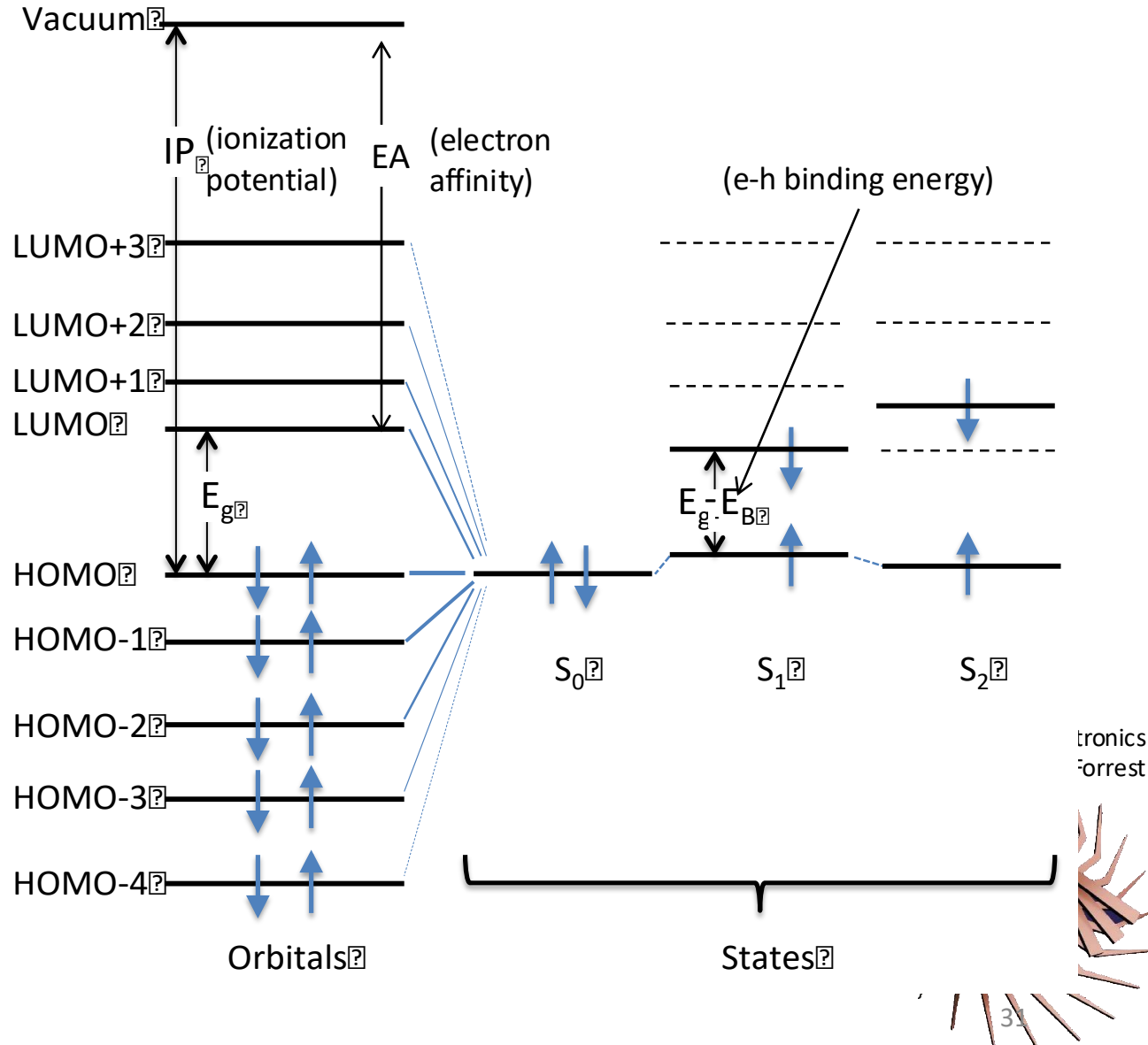
absorption

emission

Wavelength (nm)

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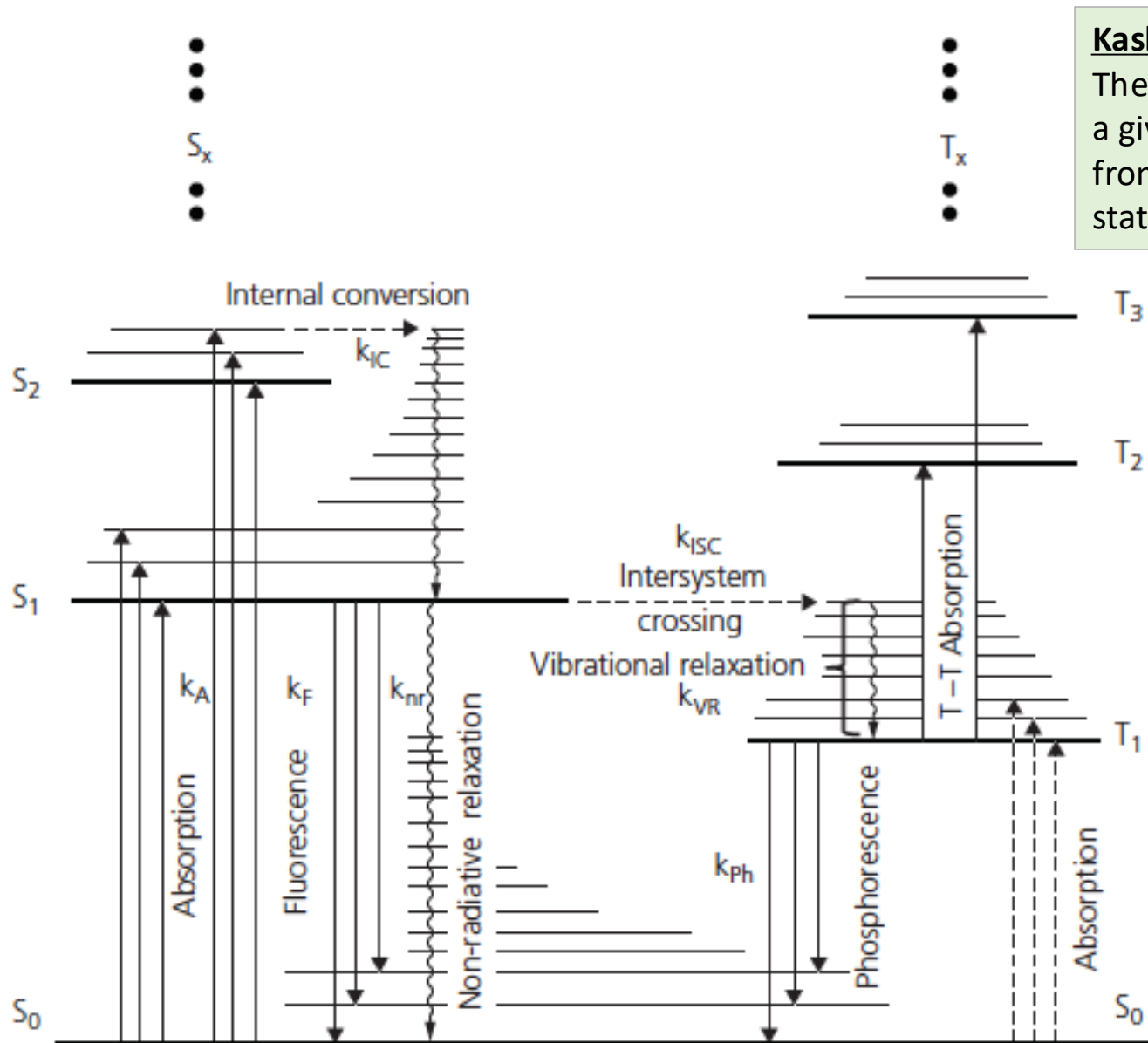- Numerous vibronics apparent in this progression: rotons, librons, etc…

30

Important distinctions between electronic *orbitals* and electronic *states*

1. **Orbital energies refer to single electrons**
2. Orbital energies are referenced to the vacuum level: All HOMO and LUMO energies < 0
3. **State energies refer to collections of electrons:** they are calculated from a linear combination of orbitals
4. State energies are referenced to each other (not vacuum)
5. States are formed after <u>relaxation</u> and include the electron-hole binding energy
6. States comprised of two or more electrons, and hence their spin multiplicity determines their character.
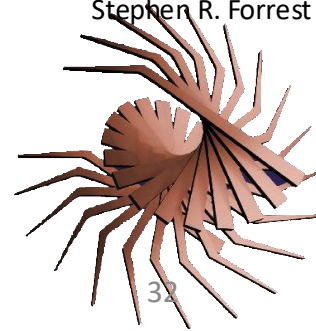7. *States and orbitals cannot co-exist meaningfully on the same diagram*

Vacuum

IP (ionization potential)   EA (electron affinity)

LUMO+3
LUMO+2
LUMO+1
LUMO

E_g

HOMO
HOMO-1
HOMO-2
HOMO-3
HOMO-4

Orbitals

(e-h binding energy)

$E_g - E_B$

S_0 S_1 S_2

States

tronics
Forrest

31

Jablonski Diagrams:
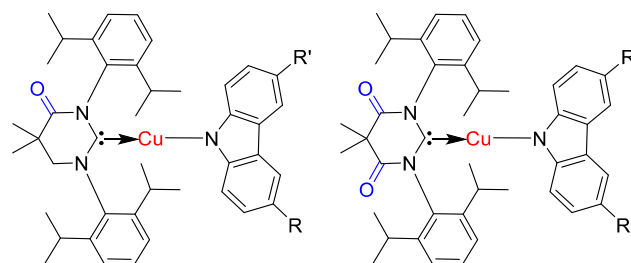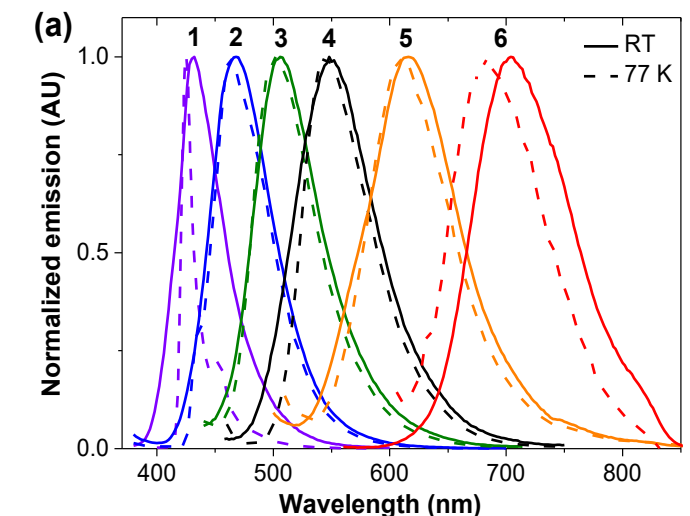## Life Histories of Excitons

Kasha's rule
The radiative transition from a given spin manifold occurs from the lowest excited state.

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Energy Gap Law

- The larger the energy gap, the lower the probability for non-radiative recombination.
- ⇒ As the energy gap of a molecular species decreases, radiative transitions have a higher probability for non-radiative decay.
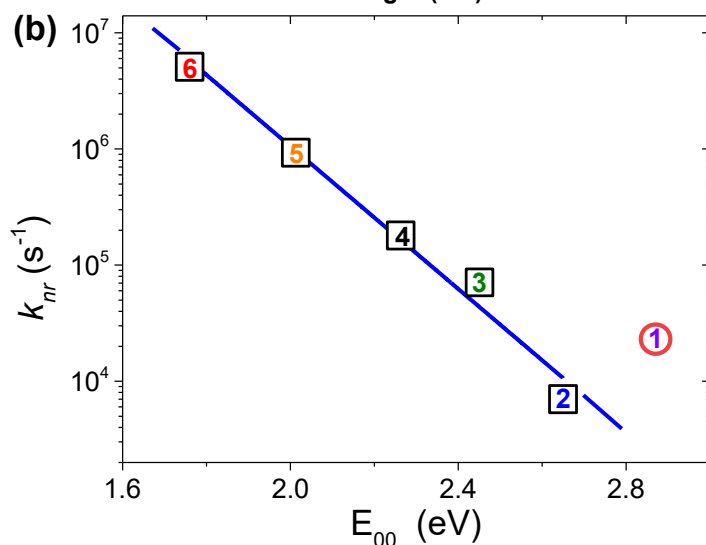
(a)

(b)

Carbene = MAC*
R, R' = CN (**1**)
R = CN, R' = H (**2**)
R, R' = H (**3**)

Carbene = DAC*
R, R' = CN (**4**)
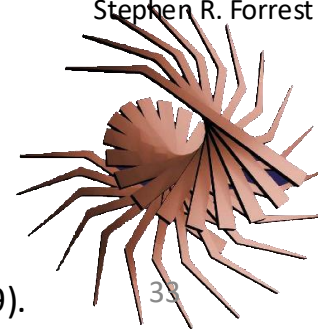R = CN, R' = H (**5**)
R, R' = H (**6**)

$$k_{if} = A \exp\left(-\gamma E_g / \hbar \omega_p\right) \quad \text{: non-rad. rate}$$
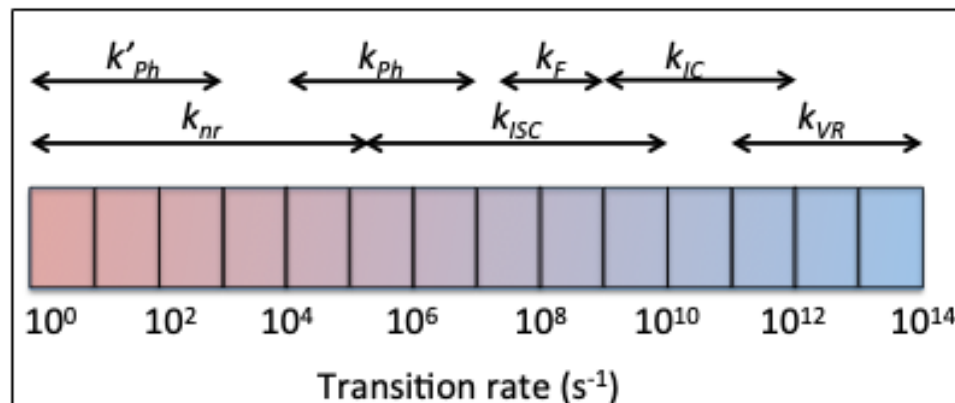
$$\gamma = \log\left(\frac{E_g}{\Omega E_p}\right) - 1$$

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Ω = number of modes contributing to the maximum phonon energy,
= ½ the Stokes shift.

Shi, S., et al. *J. Am. Chem. Soc.*, **141**, 3576 (2019).

33

Characteristic Transition Rates

k_{ph}' = phosphorescent transition rate in the absence of S-O coupling
k_{ph} = phosphorescent transition rate in the presence of S-O coupling

Quantum yields: (Ratio of photons emitted into 4π solid angle to photons absorbed)

Fluorescence: $\Phi_F = \dfrac{k_F}{k_F + k_{nrS} + k_{ISC}}$

Phosphorescence: $\Phi_P = \dfrac{\Phi_{ISC} k_{Ph}}{k_{Ph} + k_{nrT}}$; $\Phi_{ISC} = \dfrac{k_{ISC}}{k_{ISC} + k_F + k_{nrS}}$

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34