

# Excited Electronic States

Configuration Interaction

Video VII.iv

# Excited Electronic States

- We usually write the Schrödinger equation as

$$H\Psi = E\Psi$$

- However, that obscures the reality that there are infinitely many solutions to the Schrödinger equation, so it is better to write

$$H\Psi_n = E_n\Psi_n$$

- Hartree-Fock theory provides us a prescription to construct an approximate ground-state wave function (as a single Slater determinant)
- How do we build from there to construct an excited-state wave function?

# Correlated Methods. I. Configuration Interaction

A Hartree-Fock one-electron orbital (wave function) is expressed as a linear combination of basis functions with expansion coefficients optimized according to a variational principle (where **S** is the overlap matrix)

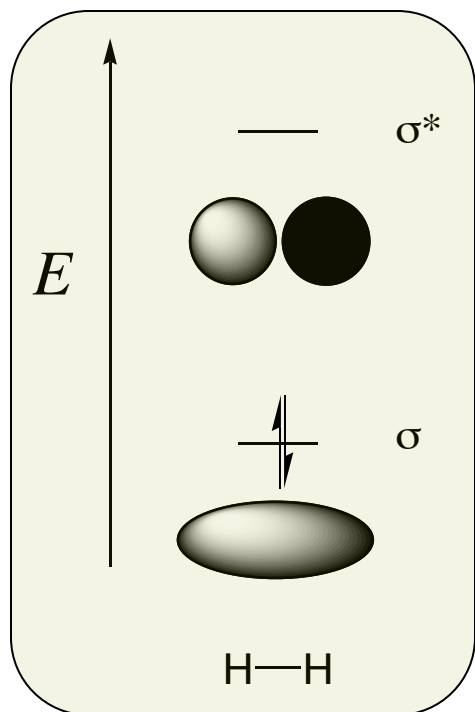
$$| \mathbf{F} - E\mathbf{S} | = 0 \quad \longrightarrow \quad \phi = \sum_{i=1}^N a_i \varphi_i$$

The HF many-electron wave function is the Slater determinant formed by occupation of lowest possible energy orbitals, *but, the HF orbitals are not "perfect" because of the HF approximation*

So, one way to improve things would be to treat the different Slater determinants that can be formed from *any occupation of HF orbitals* to *themselves* be a basis set to be used to create an improved many-electron wave function

$$| \mathbf{H} - E\mathbf{S} | = 0 \quad \longrightarrow \quad \Psi = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ.}} \sum_{r < s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

# Configuration Interaction (CI) Example: Minimal Basis H<sub>2</sub>



$$\Psi_{\text{CI}} = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ. vir.}} \sum_r a_i^r \Psi_i^r + \sum_{i < j}^{\text{occ. vir.}} \sum_{r < s} a_{ij}^{rs} \Psi_{ij}^{rs} + \dots$$

$$= a_{1(0)} |\sigma^2\rangle + 0 + a_2 |\sigma^{*2}\rangle$$

$$|\mathbf{H} - E\mathbf{S}| = 0 \longrightarrow \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$E^2 - (H_{11} + H_{22})E + (H_{11}H_{22} - H_{12}^2) = 0$$

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

Lowest energy eigenvalue is lower than  $E_{\text{HF}}$  if  $H_{12}$  is positive (as it is)

Higher energy eigenvalue corresponds to excited electronic state

Recall:

$$H_{ab} = \langle \Psi_a | H | \Psi_b \rangle, \quad \text{e.g., } H_{11} = E_{\text{HF}}, \quad H_{12} = K_{\sigma\sigma^*}$$

# CI in a Nutshell

	$\Psi_{\text{HF}}$	$\Psi_i^a$	$\Psi_{ij}^{ab}$	$\Psi_{ijk}^{abc}$
$\Psi_{\text{HF}}$	$E_{\text{HF}}$	<b>0</b>	dense	<b>0</b>
$\Psi_i^a$	<b>0</b>	dense	sparse	very sparse
$\Psi_{ij}^{ab}$	d e n s e	sparse	sparse	extremely sparse
$\Psi_{ijk}^{abc}$	<b>0</b>	very sparse	extremely sparse	extremely sparse

The bigger the CI matrix, the more electron correlation can be captured.

The CI matrix can be made bigger either by increasing basis-set size (each block is then bigger) or by adding more highly excited configurations (more blocks).

The ranked eigenvalues correspond to the electronic state energies.

Most common compromise is to include only single and, to lower ground state, double excitations (CISD)—not size extensive.

# CI Singles (CIS)

	$\Psi_{\text{HF}}$	$\Psi_i^a$
$\Psi_{\text{HF}}$	$E_{\text{HF}}$	0
$\Psi_i^a$	0	dense

There are  $m \times n$  singly excited configurations where  $m$  and  $n$  are the number of occupied and virtual orbitals, respectively.

Diagonalization gives excited-state energies *and* eigenvectors containing weights of singly excited determinants in the pure excited state

Quality of excited-state wave functions about that of HF for ground state.

Efficient, permits geometry optimization; semiempirical levels (INDO/S) optimized for CIS method.

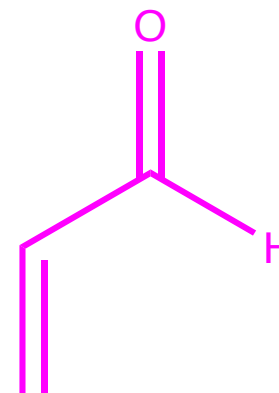
# CI Singles (CIS) — Acrolein Example

Excited State 1: Singlet-A" 4.8437 eV 255.97 nm f=0.0002  
 14 -> 16 0.62380 3.0329 408.79  
 14 -> 17 0.30035 3.73

Excited State 2: Singlet-A' 7.6062 eV 163.01 nm f=0.7397  
 15 -> 16 0.68354 6.0794 203.94  
 6.41

Excited State 3: Singlet-A" 9.1827 eV 135.02 nm f=0.0004  
 11 -> 16 -0.15957 6.6993 185.07  
 12 -> 16 0.55680  
 14 -> 16 -0.19752  
 14 -> 17 0.29331

Excited State 4: Singlet-A" 9.7329 eV 127.39 nm f=0.0007  
 9 -> 17 0.19146  
 10 -> 16 0.12993  
 11 -> 16 0.56876  
 12 -> 16 0.26026  
 12 -> 17 -0.11839  
 14 -> 17 -0.12343

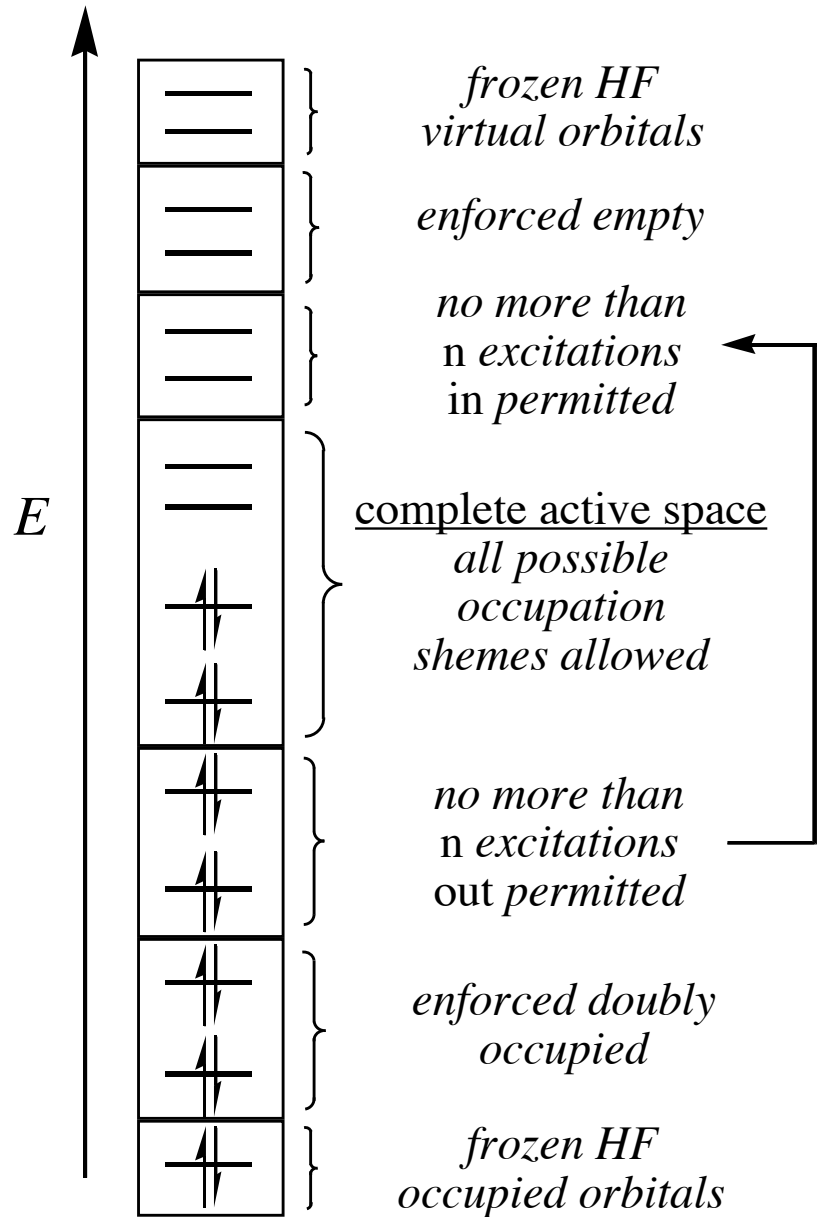


LUMO+1:  $\pi_4^*$   
 LUMO:  $\pi_3^*$   
 HOMO:  $\pi_2$   
 HOMO-1:  $n_O$

Expt

*Eigenvectors CIS/6-31G(d) and INDO/S*

# CI: Thème et Variation



If one chooses not to include *all* excited configurations (full CI) perhaps one should reoptimize the basis-function coefficients of the most important orbitals instead of using their HF values

Maybe *more* excitations into lower-energy orbitals is a better option than *any* excitations into higher-energy orbitals

The general term for this class of calculations is multiconfiguration self-consistent field (MCSCF)—special cases are CASSCF and RASSCF—**CASPT2** adds accuracy

Orbital optimization can be for an average of state energies so as not to bias the orbitals to any one state



# Excited Electronic States

Perturbation Theory and TD-DFT

Video VII.v

# Time-Dependent Perturbation Theory

Consider the time-dependent Schrödinger equation

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = H \Psi \quad \text{with eigenfunctions} \quad \Psi_j = e^{-iE_j t / \hbar} \Phi_j$$

*where  $\Phi_j$  is an eigenfunction of the time-independent Schrödinger equation*

Perturb the Hamiltonian with a radiation field

$$H = H^0 + e_0 \mathbf{r} \sin(2\pi\nu t)$$

The wave function evolves in the presence of the perturbation and may be expressed as a linear combination of the complete set of solutions to  $H$

$$\Psi = \sum_k c_k e^{-iE_k t / \hbar} \Phi_k$$

Termination of the radiation field will cause the wave function to collapse (upon sampling) to a stationary state with probability  $|c_k|^2$ . The  $c_k$  will evolve according to

$$-\frac{\hbar}{i} \frac{\partial}{\partial t} \sum_k c_k e^{-iE_k t / \hbar} \Phi_k = \left[ H^0 + e_0 \mathbf{r} \sin(2\pi\nu t) \right] \sum_k c_k e^{-iE_k t / \hbar} \Phi_k$$

# Time-Dependent Perturbation Theory (cont.)

$$-\frac{\hbar}{i} \frac{\partial}{\partial t} \sum_k c_k e^{-iE_k t / \hbar} \Phi_k = \left[ H^0 + e_0 \mathbf{r} \sin(2\pi\nu t) \right] \sum_k c_k e^{-iE_k t / \hbar} \Phi_k$$

*Taking the time derivative on the left and expanding on the right*

$$\begin{aligned} -\frac{\hbar}{i} \sum_k \frac{\partial c_k}{\partial t} e^{-iE_k t / \hbar} \Phi_k + \sum_k c_k E_k e^{-iE_k t / \hbar} \Phi_k \\ = \sum_k c_k E_k e^{-iE_k t / \hbar} \Phi_k + e_0 \mathbf{r} \sin(2\pi\nu t) \sum_k c_k e^{-iE_k t / \hbar} \Phi_k \end{aligned}$$

*Which simplifies to*

$$-\frac{\hbar}{i} \sum_k \frac{\partial c_k}{\partial t} e^{-iE_k t / \hbar} \Phi_k = e_0 \mathbf{r} \sin(2\pi\nu t) \sum_k c_k e^{-iE_k t / \hbar} \Phi_k$$

*Left multiplication by state of interest and integration yields*

$$-\frac{\hbar}{i} \sum_k \frac{\partial c_k}{\partial t} e^{-iE_k t / \hbar} \delta_{mk} = e_0 \sin(2\pi\nu t) \sum_k c_k e^{-iE_k t / \hbar} \langle \Phi_m | \mathbf{r} | \Phi_k \rangle$$

# Time-Dependent Perturbation Theory (cont.)

$$-\frac{\hbar}{i} \sum_k \frac{\partial c_k}{\partial t} e^{-(iE_k t/\hbar)} \delta_{mk} = e_0 \sin(2\pi\nu t) \sum_k c_k e^{-(iE_k t/\hbar)} \langle \Phi_m | \mathbf{r} | \Phi_k \rangle$$

*Evaluate Kronecker delta, rearrange, and assume perturbation is small, so ground state can be used for right-hand-side coefficients*

$$\frac{\partial c_m}{\partial t} = -\frac{i}{\hbar} e_0 \sin(2\pi\nu t) e^{-[i(E_m - E_0)t/\hbar]} \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle$$

*Integrating over time of perturbation*

$$\begin{aligned} c_m(\tau) &= -\frac{i}{\hbar} e_0 \int_0^\tau \sin(2\pi\nu t) e^{-[i(E_m - E_0)t/\hbar]} \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle dt \\ &= \frac{1}{2i\hbar} e_0 \left[ \frac{e^{i(\omega_{m0} + \omega)\tau} - 1}{\omega_{m0} + \omega} - \frac{e^{i(\omega_{m0} - \omega)\tau} - 1}{\omega_{m0} - \omega} \right] \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \end{aligned}$$

*where*

$$\omega = 2\pi\nu \qquad \omega_{m0} = \frac{E_m - E_0}{\hbar}$$



# Time-Dependent Density Functional Theory

*A similar mathematical formalism applied to density functional theory shows that excitation energies can be determined as poles of the polarizability matrix*

$$\langle \alpha \rangle_{\omega} = \sum_{m>0} \left[ \frac{|\langle \Phi_m | \mathbf{r} | \Phi_0 \rangle|^2}{\omega_{m0} + \omega} \pm \frac{|\langle \Phi_m | \mathbf{r} | \Phi_0 \rangle|^2}{\omega_{m0} - \omega} \right]$$

$$\omega = 2\pi\nu \qquad \omega_{m0} = \frac{E_m - E_0}{\hbar}$$

*Qualitative points:*

*TD DFT tends to be more accurate than CIS but this is sensitive to choice of functional and certain special situations*

*Charge-transfer transitions are particularly problematic*

*No wave function is created, but eigenvectors analogous to those predicted by CIS are provided*

# CI Singlet-GSA Acrolein Example

Excited State 1: Singlet-A" 3.8827 eV 323.93 nm f=0.0000  
~~15~~ -> 16 0.62380  
~~15~~ -> 17 0.30635

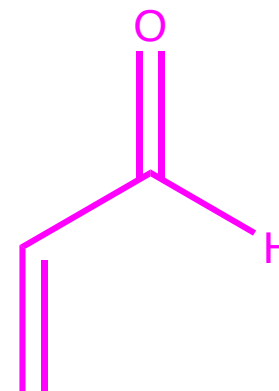
Excited State 2: Singlet-A' 6.6062 eV 183.66 nm f=0.3393  
~~14~~ -> 16 0.68350  
 14 -> 17 0.12143

Excited State 3: Singlet-A" 9.1827 eV 135.02 nm f=0.0004

Excited State 3: Singlet-A" 7.2723 eV 170.49 nm f=0.0004  
~~12~~ -> 16 0.55070  
~~15~~ -> 16 -0.19752  
~~15~~ -> 17 0.00306

Excited State 4: Singlet-A" 9.8029 eV 123.89 nm f=0.0006

~~13~~ -> 16 0.19708  
~~16~~ -> 16 -0.13990  
 11 -> 16 0.56876  
 12 -> 16 0.26026  
 12 -> 17 -0.11839  
 14 -> 17 -0.12343



LUMO+1:  $\pi_4^*$   
 LUMO:  $\pi_3^*$   
 HOMO:  $\pi_2$   
 HOMO-1:  $\pi_2$

Eigenvectors EBE6/6-133(d)

Recall expt 3.73 / 6.41 eV

# Excited Electronic States

Conical Intersections and Dynamics

Video VII.vi



# Avoided Crossings and Conical Intersections

$$| \mathbf{H} - E\mathbf{S} | = 0 \longrightarrow \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

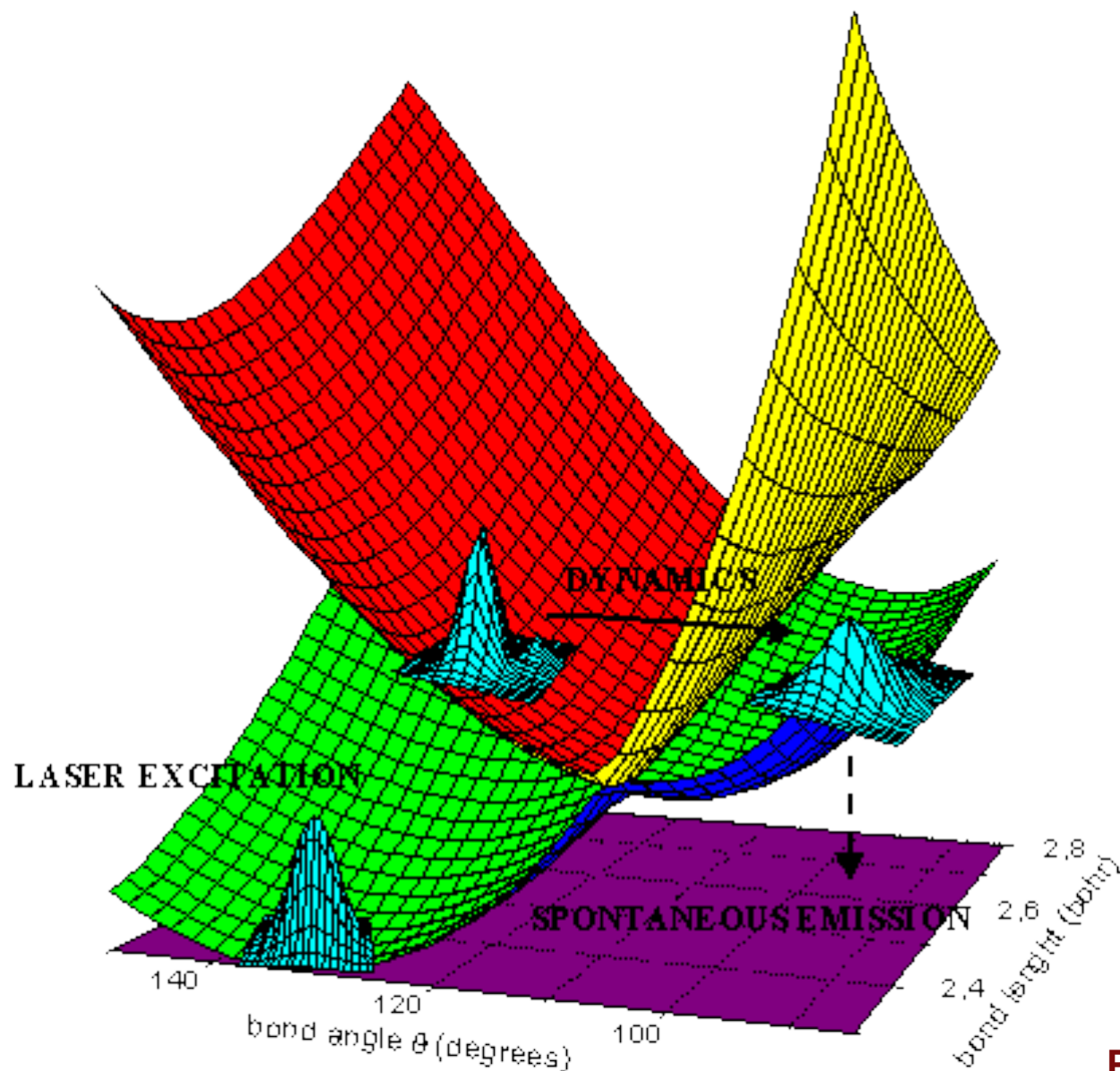
*Can two states have the same energy E?*

*Requires  $H_{11} = H_{22}$  and  $H_{12} = 0$*

*This restricts two degrees of freedom and is thus not possible in a diatomic (avoided crossing rule) but it is possible for larger molecules (conical intersection) and indeed multiple electronic states can be degenerate provided sufficient numbers of degrees of freedom are available to satisfy the necessary constraints.*

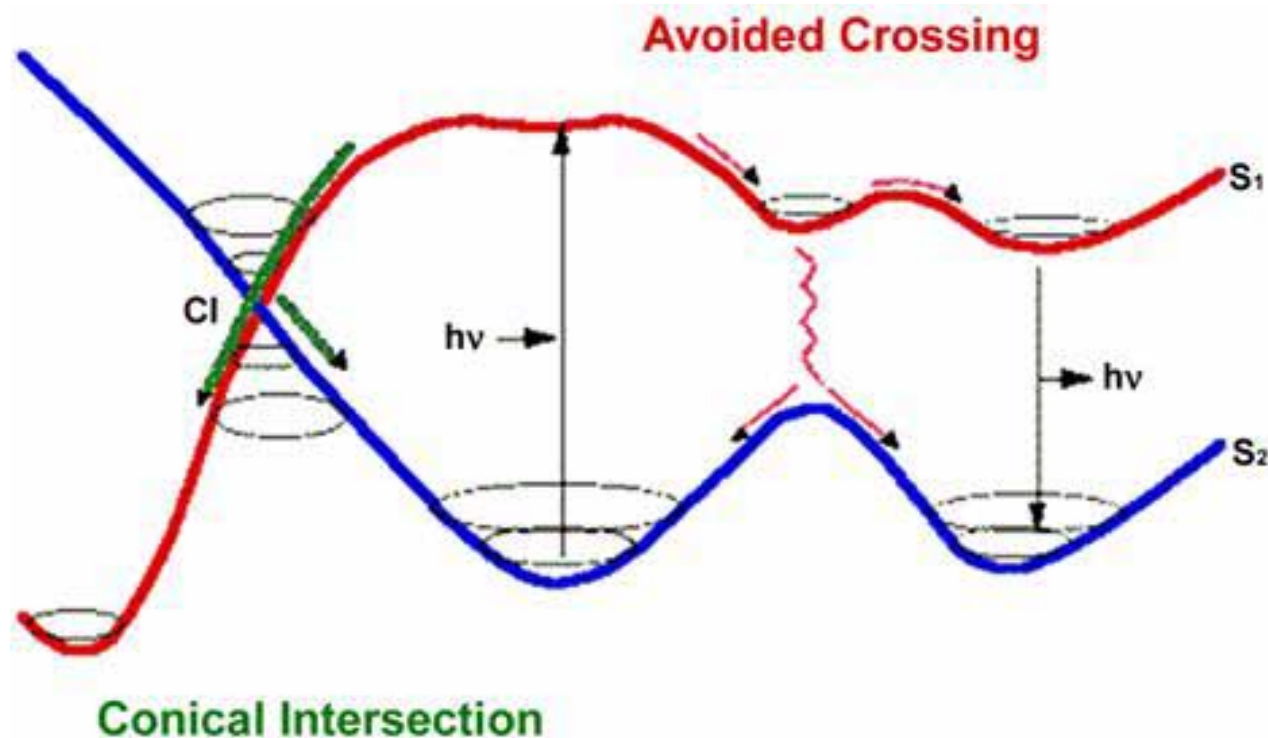
# Conical Intersection Example ( $\text{NO}_2$ )

*Note that 3 atoms leaves one final degree of freedom, so the CI is not a point, but a “seam” (that has a minimum)*



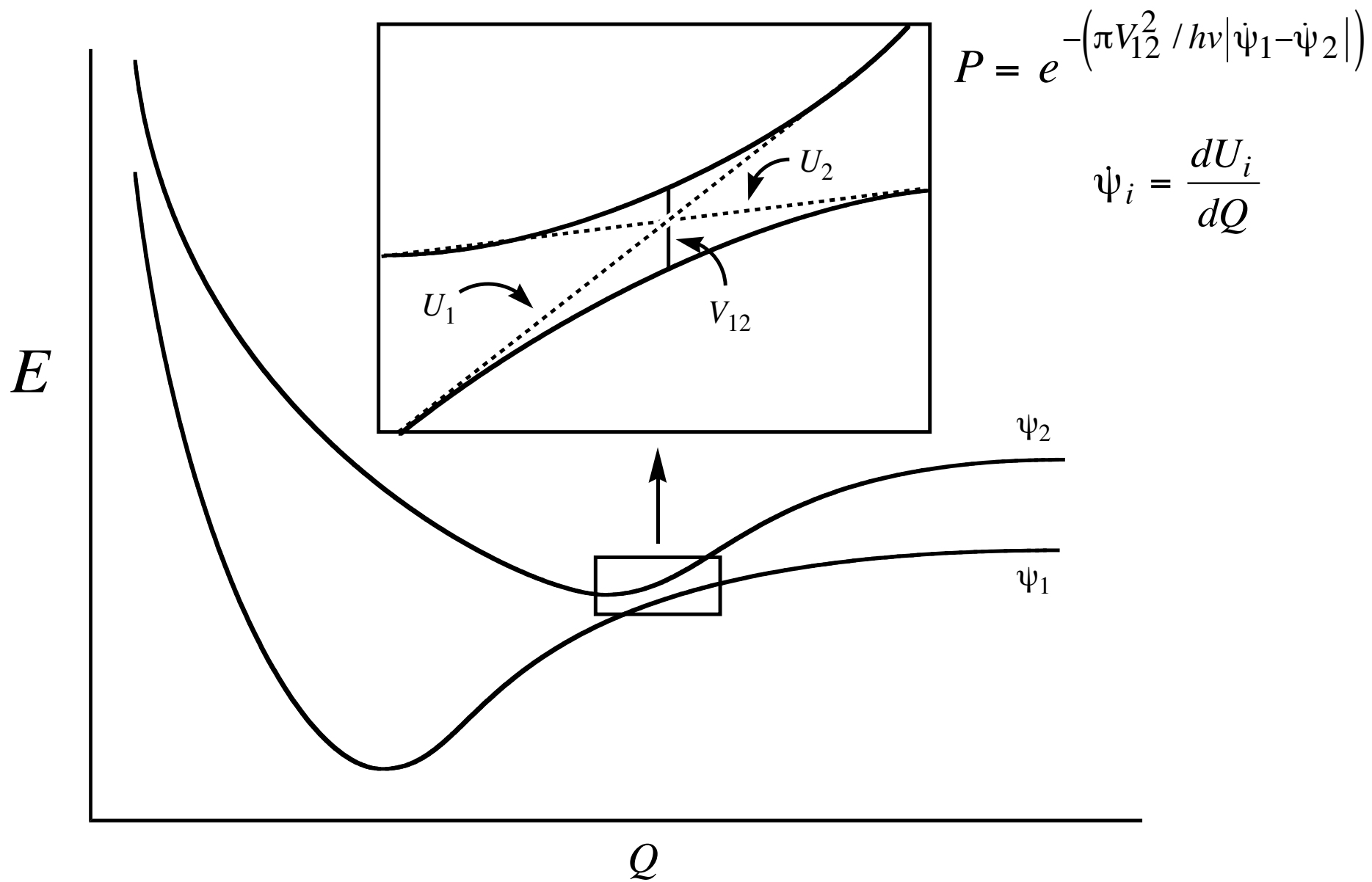
**Professor Carlo Petrongolo**

# Conical Intersection Example 1D Projection



*Conical intersections permit radiationless transitions from one state to another. Kasha's rule says that such internal conversions among excited states will be very fast until one reaches  $S_1$  (the first state above the ground state  $S_0$ )*

# Probability of Surface Hopping—Landau-Zener Model

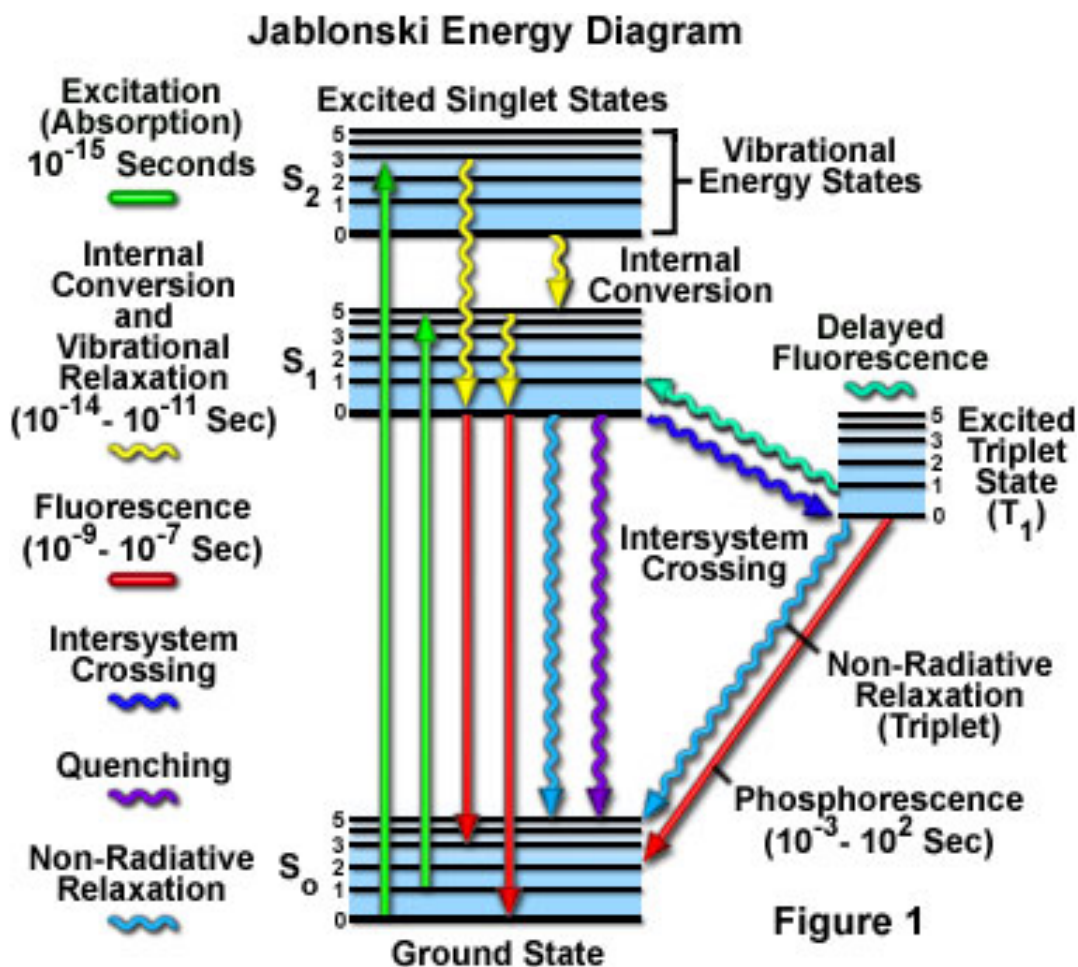


## What If Two States Have Different Spin Multiplicity?

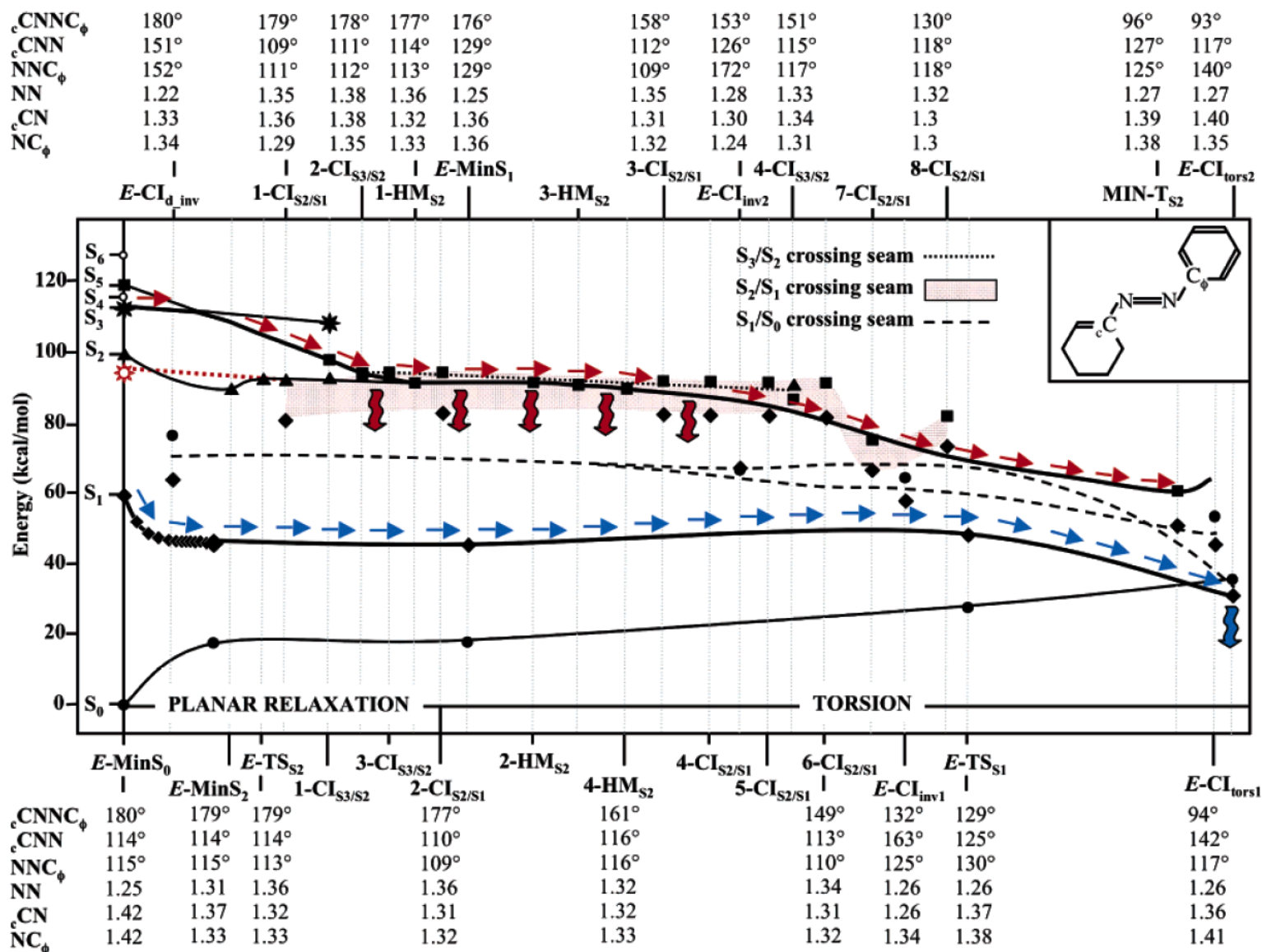
- In non-relativistic quantum mechanics, transitions between two states of different spin multiplicity are strictly forbidden (although it is mildly paradoxical to refer to spin at all if one is imagining non-relativistic QM)
- However, a relativistic Hamiltonian includes operators that affect spin, including the spin-orbit operator, the spin-spin dipole operator (coupling two electrons) and the hyperfine operator (coupling electronic and nuclear spins)
- Spin-orbit coupling increases with the 4th power of the atomic number, so with heavier nuclei, this process can be very efficient

$$H_{\text{SO}} \approx \frac{1}{c^2} \sum_{i=1}^N \sum_{k=1}^M \frac{Z_k^4}{|r_{ik}|^3} l_j \cdot s_j$$

# Nondynamical Photophysical Processes for a Single Geometry

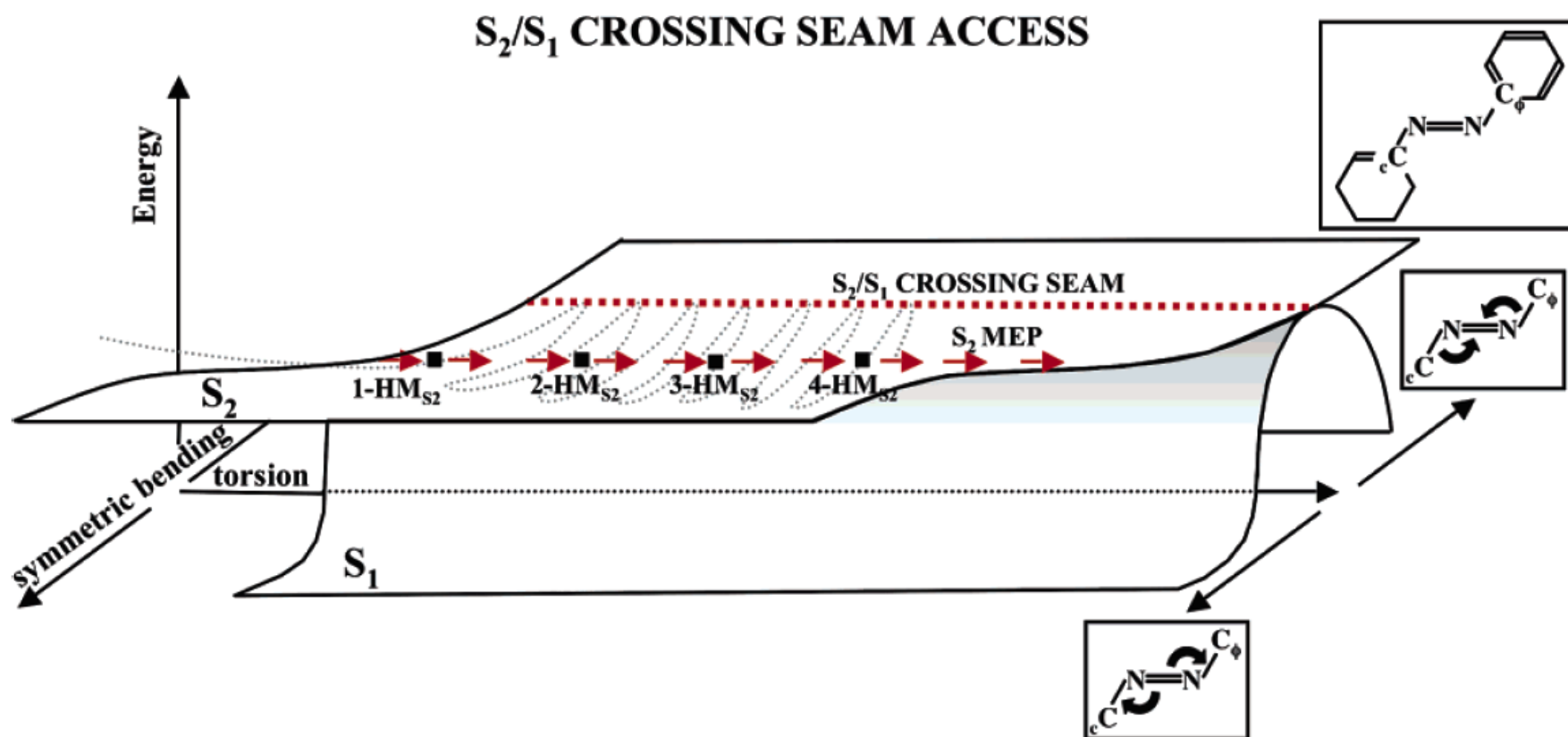


*Dynamics adds substantial complication by changing relative state energies. Solvation compounds the difficulty by changing state energies in a time-dependent fashion as non-equilibrium solvation decays to equilibrium solvation*



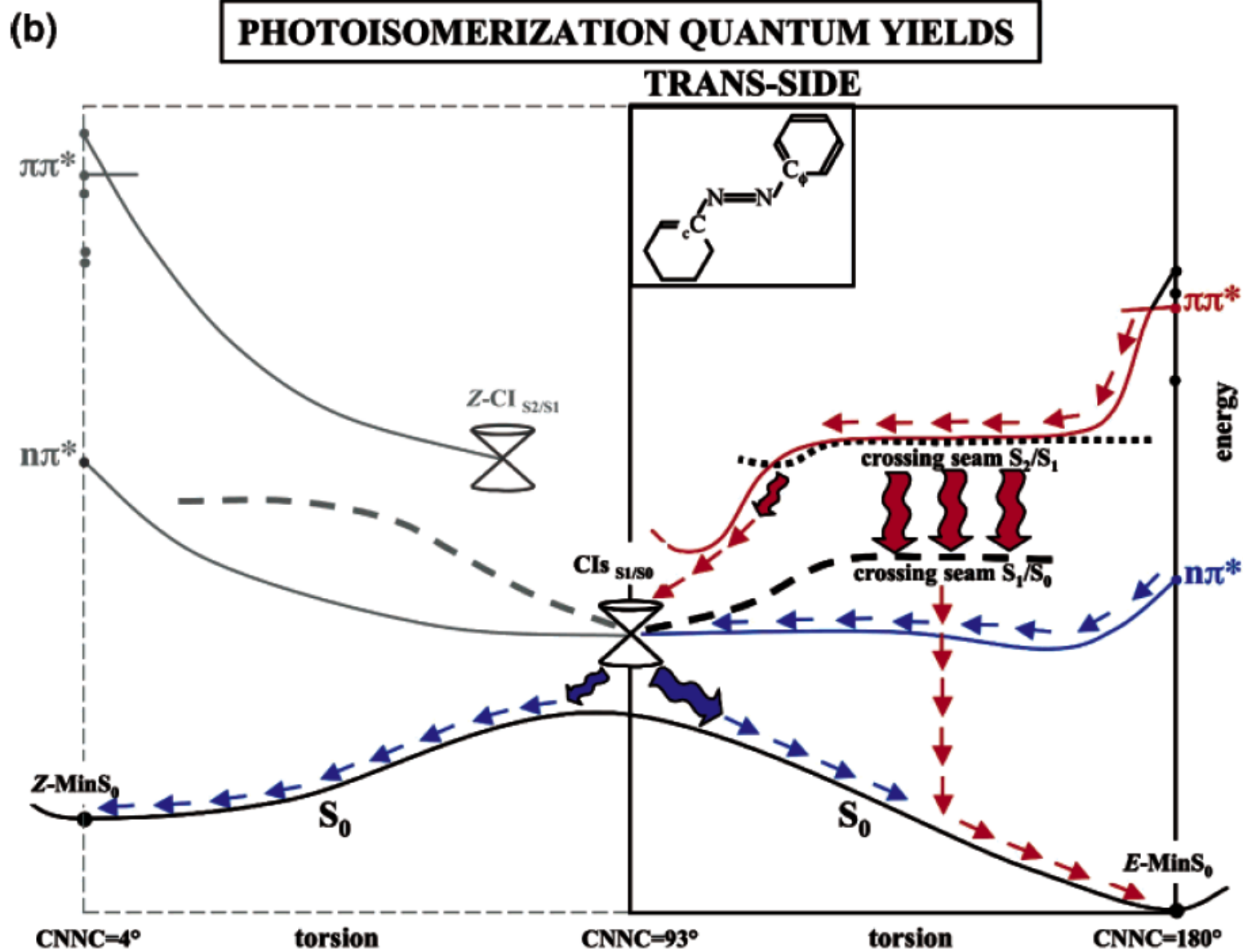
**Figure 4.** E-CPD computed reaction paths upon  $n\pi^*$  and  $\pi\pi^*$  excitations. Blue arrows show the  $n\pi^*$  state (solid diamonds) MEP from the Franck–Condon region to the low-energy  $S_1/S_0$  crossing point ( $-N=N-$  torsions are mainly involved); red arrows show the MEP from the bright  $\pi\pi^*$  state (solid asterisks). The higher double-excitation state (solid squares) suddenly crosses the  $\pi\pi^*$  state and drives the relaxation of the excited molecule. The dotted red points zone represents the extended  $S_2/S_1$  crossing seam. The red dotted line is the bright  $\pi\pi^*$  state scaled to match the experimental absorption value. All the energy profiles have been scaled to match CASPT2 values (Table 2).

# Dynamics Occurs in All Degrees of Freedom



<sup>a</sup> The crossing seam can be accessed by vibrations (e.g., symmetric CNN bending modes) orthogonal to the MEP.





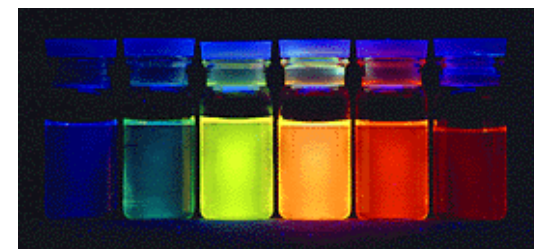
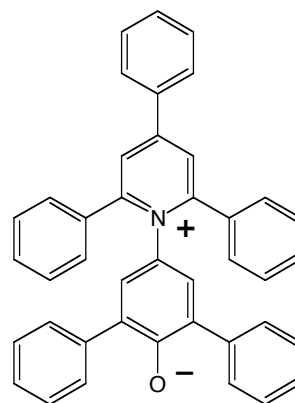
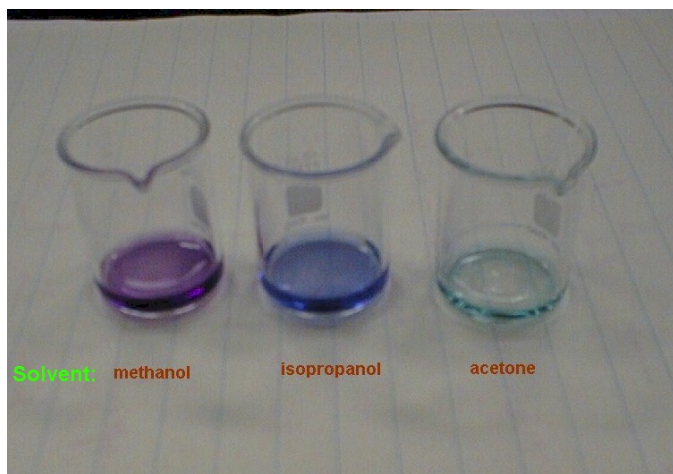
<sup>a</sup> Bigger arrows show the most favorite paths. The red color identifies  $\pi\pi^*$  decay paths, while the blue color identifies  $n\pi^*$  decay paths.

# Excited Electronic States

Solvatochromism

Video VII.vii

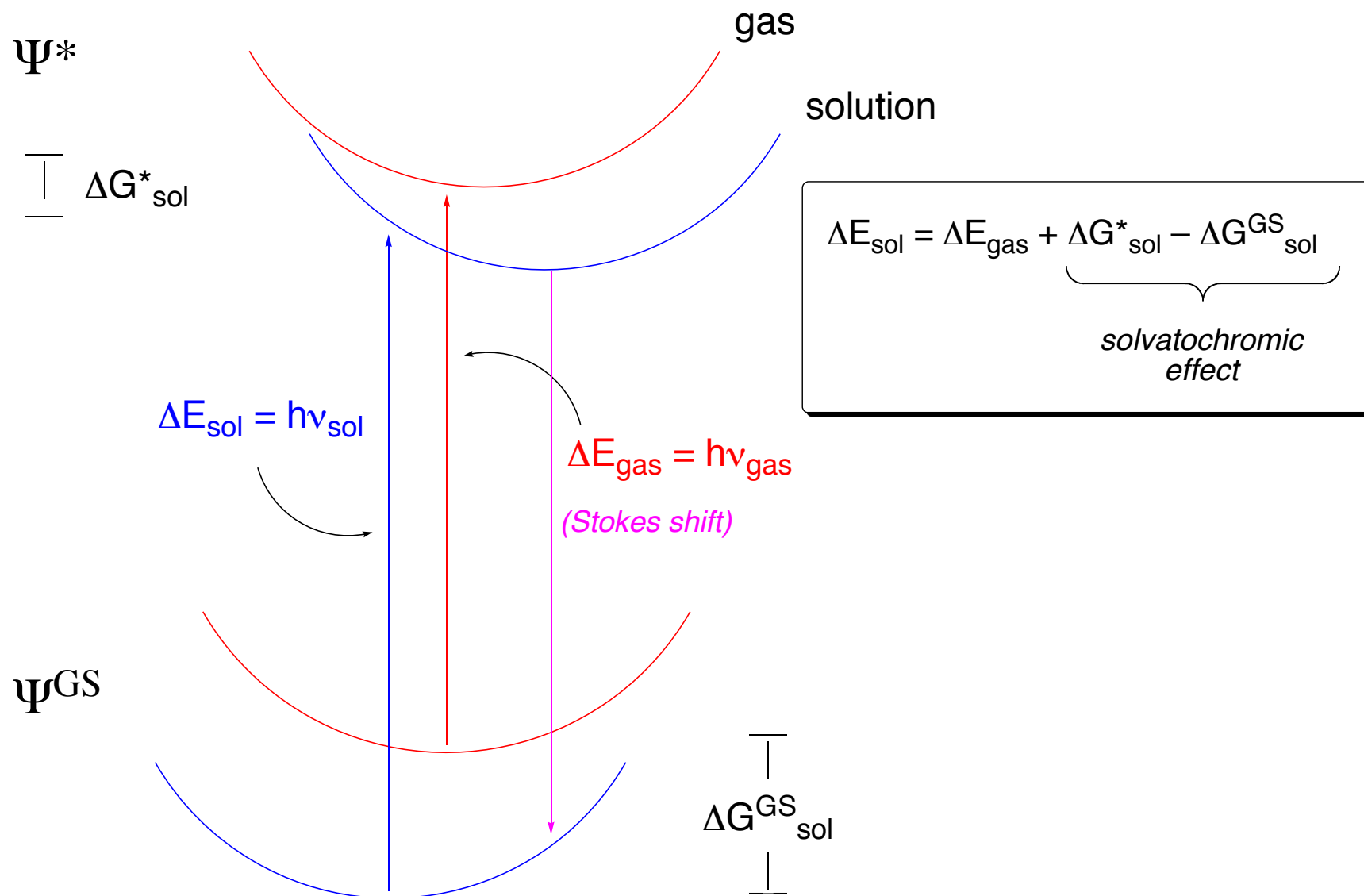
# Solvatochromism of Dye E<sub>T</sub>-30 (S<sub>1</sub> – S<sub>0</sub>)



Solvent	Color	$\lambda_{\text{max}}$ , nm
anisole	yellow	769
acetone	green	677
2-pentanol	blue	608
ethanol	violet	550
methanol	red	515

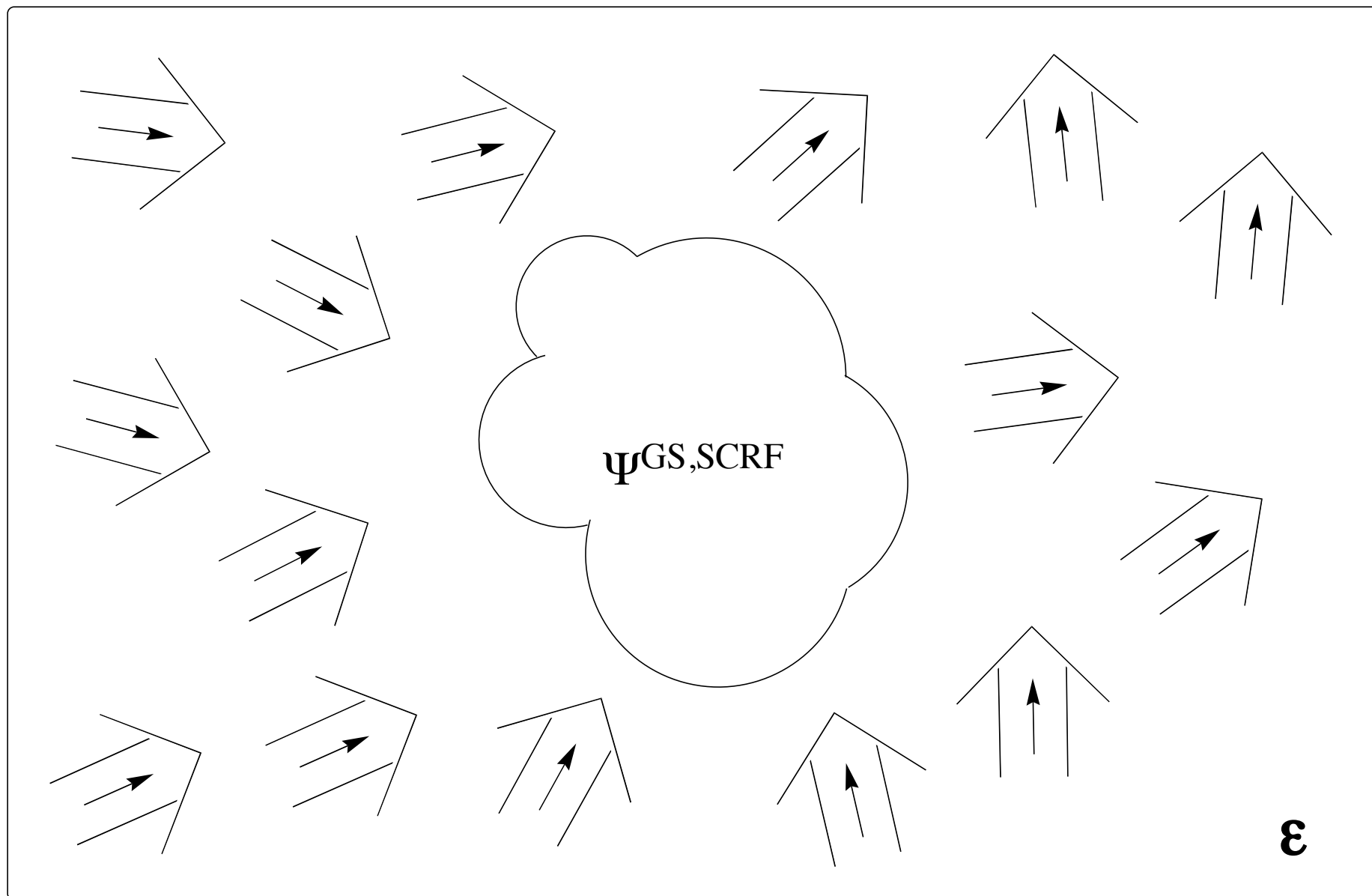
# Solvatochromism Redux

## Equilibrium vs. Nonequilibrium Solvation



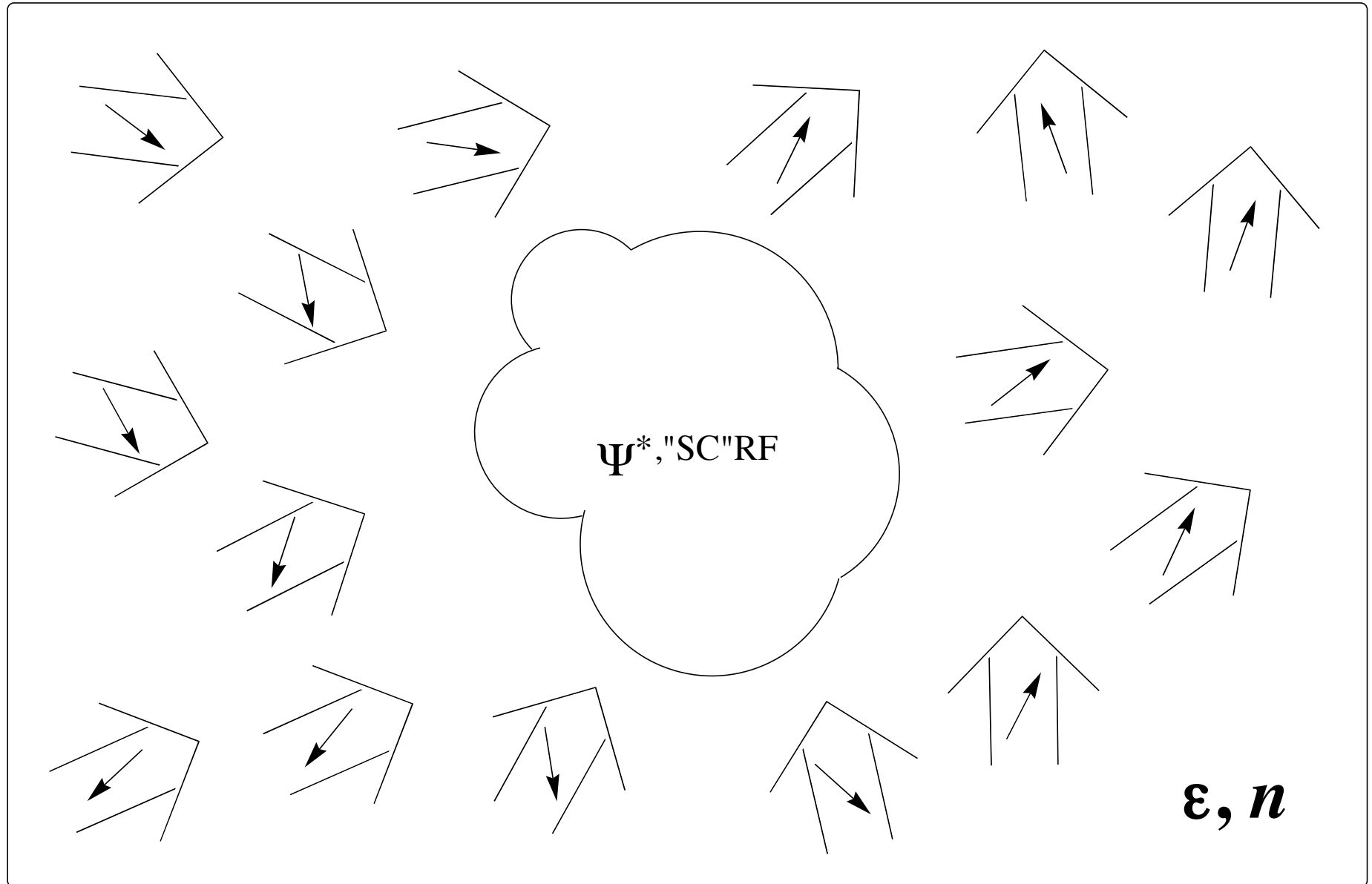
# QM Self-Consistent Reaction Field (SCRf)

$\Psi$  minimizes  $H_{\text{gas}} + V_{\text{int}} + G_{\text{cost}}$  — equilibrium quantity



# QM "SC"RF for Excited State

$\Psi^*$  minimizes a non-equilibrium quantity



# Ground State Solvation Free Energy Polarization Component

*Generalized Born Approach*

$$\Delta G_P^{\text{GS}} = -\frac{1}{2} \left( 1 - \frac{1}{\epsilon} \right) \sum_{k,k'}^{\text{atoms}} q_k^{\text{GS}} q_{k'}^{\text{GS}} \gamma_{kk'}$$

$\epsilon$  is the bulk dielectric constant of the medium

$q$  is a partial atomic charge (from  $\Psi^{\text{SCRF}}$ )

## Excited State Polarization Free Energy

$$\Delta G_P^* = -\frac{1}{2} \left(1 - \frac{1}{n^2}\right) \sum_{k,k'}^{\text{atoms}} q_k^* q_{k'}^* \gamma_{kk'} \quad (\text{electronic SCRF})$$

$$-\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \sum_{k,k'}^{\text{atoms}} q_k^* q_{k'}^{\text{GS}} \gamma_{kk'} \quad (\text{elec/orient inter})$$

$$+\frac{1}{2} \left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \sum_{k,k'}^{\text{atoms}} q_k^{\text{GS}} q_{k'}^{\text{GS}} \gamma_{kk'} \quad (\text{orient cost})$$

$$+\frac{1}{2} \left(1 - \frac{1}{n^2}\right) \left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \sum_{k,k'}^{\text{atoms}} \left(q_k^* - q_k^{\text{GS}}\right) q_{k'}^{\text{GS}} \gamma_{kk'} \quad (\text{cross term})$$

Li et al. *Int. J. Quantum Chem.* **2000**, 77, 264

Marenich et al. *Chem. Sci.* **2011**, 2, 2143



## Excited State SCRF

CI Singles formalism

$$\Psi^* = \sum_{m=1}^M c_m \Phi_m, \quad \Phi_1 = \Psi^{\text{GS}}, \quad \Phi_{m>1} = \Psi^{\text{GS}} \uparrow_a^i$$

form CI Matrix

$$H_{mn} = \langle \Phi_m | \mathbf{H}^0 + \mathbf{H}_{\text{int}}^* | \Phi_n \rangle$$

where the one-electron operator is defined

$$\mathbf{H}_{\text{int}}^* = \sum_{i=1}^N \sum_{\mu\nu} |\phi_\mu(i)\rangle \left( -\delta_{\mu\nu} V_{k_\mu}^* \right) \langle \phi_\nu(i)|$$

and

$$V_{k_\mu}^* = - \left( 1 - \frac{1}{n^2} \right) \sum_l q_l^* \gamma_{k_\mu l} - \left( \frac{1}{n^2} - \frac{1}{\epsilon} \right) \sum_l q_l^{\text{GS}} \gamma_{k_\mu l}$$

## Solvatochromism of Acetone $n \rightarrow \pi^*$

Solvent	$\epsilon$	$n$	$\Delta\nu, \text{cm}^{-1}$	
			VEM42	Experiment
(gas phase)	(1.0)	(1.0)		(36,165)
Heptane	1.91	1.3878	-241	195
Cyclohexane	2.04	1.4266	-264	440
$\text{CCl}_4$	2.23	1.4601	-294	440
Diethyl Ether	4.24	1.3526	-530	65
Chloroform	4.71	1.4459	-515	-125
Ethanol	24.85	1.3611	-736	-680
Methanol	32.63	1.3288	-769	-880
Acetonitrile	37.5	1.3442	-763	-335
Water	78.3	1.3330	-787	-1670

Not so exciting...

## Other Solvation Components!

1) Dispersion (largely responsible for red shifts in non-polar solvents)

$$\Delta\nu_D = D \frac{n^2 - 1}{2n^2 + 1}$$

Optimized value for  $D = 3448 \text{ cm}^{-1}$

2) Hydrogen bonding (explicit solvation effect)

$$\Delta\nu_H = H\alpha$$

Optimized value for  $H = -1614 \text{ cm}^{-1}$

## Solvatochromism of Acetone $n \rightarrow \pi^*$

Solvent	$\epsilon$	$n$	$\alpha$	$\Delta\nu, \text{cm}^{-1}$	
				EPDH	Experiment
(gas phase)	(1.0)	(1.0)	(0.0)		(36,165)
Heptane	1.91	1.3878	0.0	417	195
Cyclohexane	2.04	1.4266	0.0	440	440
$\text{CCl}_4$	2.23	1.4601	0.0	447	440
Diethyl Ether	4.24	1.3526	0.0	84	65
Chloroform	4.71	1.4459	0.15	-31	-125
Ethanol	24.85	1.3611	0.37	-708	-680
Methanol	32.63	1.3288	0.43	-880	-880
Acetonitrile	37.5	1.3442	0.07	-273	-335
Water	78.3	1.3330	0.82	-1522	-1670

Mean unsigned error  $65 \text{ cm}^{-1}$