

# Vibronic coupling

The most fundamental level of approximation is known as the crude adiabatic (CA) approximation. In this approximation the nuclear of the electronic wave function are fixed at a value  $Q_0$ .

$$\psi_{nv}^{CA}(r, Q) = \psi_n^0(r, Q_0)\chi_{nv}^{CA}(Q)$$

$Q_0$  is a reference geometry, which may be the equilibrium position or a transition state in some cases.

# The crude adiabatic approximation

The most fundamental level of approximation is known as the crude adiabatic (CA) approximation. In this approximation the nuclear of the electronic wave function are fixed at a value  $Q_0$ .

$$\psi_{nv}^{CA}(r, Q) = \psi_n^0(r, Q_0)\chi_{nv}^{CA}(Q)$$

$Q_0$  is a reference geometry, which may be the equilibrium position or a transition state in some cases.

$\chi_{nv}^{CA}(Q)$  is the vibration-rotation wave function calculated from an approximate Schrodinger equation:

$$\underbrace{[T(Q) + V(Q) + \varepsilon_n^0(Q_0) + \langle \psi_n^0(r, Q_0) | \Delta U(r, Q) | \psi_n^0(r, Q_0) \rangle]}_{\text{Effective potential}} \chi_{nv}^{CA}(Q) = E_{nv}^{CA} \chi_{nv}^{CA}(Q)$$

Effective potential

# Distortion along non-totally symmetric modes

The effective potential contains the term  $\Delta U$  that represents the energy change upon distortion along a non-totally symmetric vibrational mode.

$$[T(Q) + V(Q) + \varepsilon_n^0(Q_0) + \langle \psi_n^0(r, Q_0) | \Delta U(r, Q) | \psi_n^0(r, Q_0) \rangle] \chi_{nv}^{CA}(Q) = E_{nv}^{CA} \chi_{nv}^{CA}(Q)$$

The term  $\Delta U$  is defined as

$$\Delta U(r, Q) = U(r, Q) - U(r, Q_0)$$

We can expand  $\Delta U$  in powers of the non-totally symmetric mode coordinate,  $i$ :

$$\Delta U = \Delta U(r, Q_0) + \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i + \dots \textit{higher order}$$

# Distortion along non-totally symmetric modes

Note that  $\Delta U(r, Q_0) = 0$  since

$$\Delta U(r, Q) = U(r, Q) - U(r, Q_0)$$

And therefore

$$\Delta U(r, Q_0) = U(r, Q_0) - U(r, Q_0) = 0$$

We can also ignore the higher order terms. The expansion of  $\Delta U$  in powers of the non-totally symmetric mode coordinates becomes

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

The  $\Delta U$  integral is evaluated using  $\psi_n^0(r, Q_0)$ , which has a fixed nuclear coordinate and thus cannot contain the effect of distortion of the molecule. We can use perturbation theory present that effect:

$$\psi_{nv}(r, Q) = \psi_{nv}^{CA}(r, Q) + \sum_{mu \neq nv} \frac{\{\psi_{nv}^{CA} | \Delta U | \psi_{mu}^{CA}\}}{E_{nv}^{CA} - E_{mu}^{CA}} \psi_{mu}^{CA}(r, Q)$$

$$= \psi_{nv}^0(r, Q_0) \chi_{nv}^{CA}(Q) + \sum_u \sum_{mu \neq nv} \frac{(\chi_{nv}^{CA} \langle \psi_n^0 | \Delta U | \psi_m^0 \rangle \chi_{mu}^{CA})}{E_{nv}^{CA} - E_{mu}^{CA}} \psi_{mu}^{CA}(r, Q_0) \chi_{mu}^{CA}(Q)$$

{ } indicates an integral of r and Q (both electronic and nuclear)

( ) indicates an integral over Q (nuclear only)

< > Indicates an integral over r (electronic only)

This is known as the [Herzberg-Teller expansion](#).

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes,  $i$ .

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv,mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, \mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{\mu}^{CA} \rangle}{E_{nv}^{CA} - E_{\mu}^{CA}}$$

The derivative  $\partial/\partial Q$  appears in the cross terms of the complete Hamiltonian that includes both electronic and nuclear motion. We invoke the **Born-Oppenheimer approximation** to eliminate the cross terms

$$H_{complete} = -\frac{\hbar^2}{2} \left( \frac{1}{m} \frac{\partial^2}{\partial r^2} + \frac{1}{\mu} \frac{\partial^2}{\partial Q \partial r} + \frac{1}{\mu} \frac{\partial^2}{\partial r \partial Q} + \frac{1}{M} \frac{\partial^2}{\partial Q^2} \right)$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

The derivative  $\partial/\partial Q$  appears in the cross terms of the complete Hamiltonian that includes both electronic and nuclear motion. We invoke the Born-Oppenheimer approximation to eliminate the cross terms

$$H_{\text{Born-Oppenheimer}} \approx -\frac{\hbar^2}{2} \left( \frac{1}{m} \frac{\partial^2}{\partial r^2} + \frac{1}{M} \frac{\partial^2}{\partial Q^2} \right)$$



We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

When the two separate equations have been solved term that contain the derivative  $\partial/\partial Q$  can be perturbations that couple states that are normally orthogonal.

$$H_{electronic} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \quad H_{nuclear} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Q^2}$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes,  $i$ .

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv,mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_n^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

The nuclear coordinate  $Q$  can couple two vibrational state wave functions if and only if they differ by one vibrational quantum. For example:

$$\langle 0 | Q | 1 \rangle = \int_{-\infty}^{\infty} \chi_0 Q \chi_1 dQ = \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha Q^2 / 2} Q \sqrt{2\alpha} Q e^{-\alpha Q^2 / 2} dQ$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

The nuclear coordinate  $Q$  can couple two vibrational state wave functions if and only if they differ by one vibrational quantum. For example:

$$\langle 0 | Q | 1 \rangle = \left( \frac{2}{\pi} \right)^{1/2} \alpha \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^2 dQ = \left( \frac{2}{\pi} \right)^{1/2} \alpha \left( \frac{\pi}{4\alpha^3} \right)^{1/2} = \frac{1}{\sqrt{2\alpha}}$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

The nuclear coordinate  $Q$  can couple two vibrational state wave functions if and only if they differ by one vibrational quantum. For example:

$$\langle 0 | Q | 1 \rangle = \left( \frac{2}{\pi} \right)^{1/2} \alpha \int_{-\infty}^{\infty} e^{-\alpha Q^2} Q^2 dQ = \left( \frac{2}{\pi} \right)^{1/2} \alpha \left( \frac{\pi}{4\alpha^3} \right)^{1/2} = \frac{1}{\sqrt{2\alpha}}$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

The nuclear coordinate  $Q$  can couple two vibrational state wave functions if and only if they differ by one vibrational quantum. For example:

$$\langle 0 | Q | 1 \rangle = \frac{1}{\sqrt{2\alpha}} = \sqrt{\frac{\hbar}{2\mu\omega}}$$

We substitute  $\Delta U$  in powers of the nuclear coordinate for the promoting modes, i.

$$\Delta U \approx \sum_i \frac{\partial \Delta U(r, Q)}{\partial Q_i} Q_i$$

We use  $\Delta U$  to define the vibronic mixing coefficient

$$\gamma_{nv, mu}^i = \frac{\langle \psi_n^0 | \frac{\partial \Delta U}{\partial Q_i} | \psi_m^0 \rangle \langle \chi_{nv}^{CA} | Q_i | \chi_{mu}^{CA} \rangle}{E_{nv}^{CA} - E_{mu}^{CA}}$$

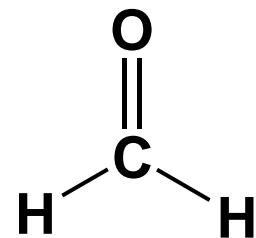
Substituting the coefficient into the expression above we can write it in a compact form.

$$\psi_{nv}(r, Q) = \psi_{nv}^0(r, Q_0) \chi_{nv}^{CA}(Q) + \sum_i \sum_u \sum_{mu \neq nv} \gamma_{nv, mu}^i \psi_{mu}^0(r, Q_0) \chi_{mu}^{CA}(Q)$$

The coefficient  $\gamma_{nv, mu}^i$  will vanish unless

$$\Gamma_{nv} \otimes \Gamma_{mu} \in \Gamma_{totally\ symmetric} \text{ and } Q_i \notin \Gamma_{non-totally\ symmetric}$$

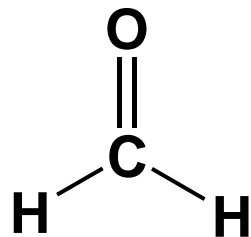
# Formaldehyde



In the case of formaldehyde there is one additional atom beyond the water example in  $C_{2v}$ . The symmetry of the C and O atoms are the same since they both lie along the symmetry axis. If we use group theory to construct SALCs we can use three different sets of symmetry adapted atomic orbitals and then combine them. However, we will use density functional theory in the next slide to obtain the states and energies.



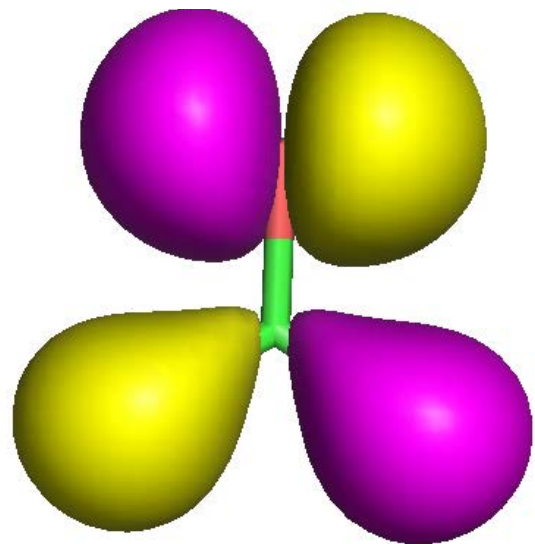
# Formaldehyde



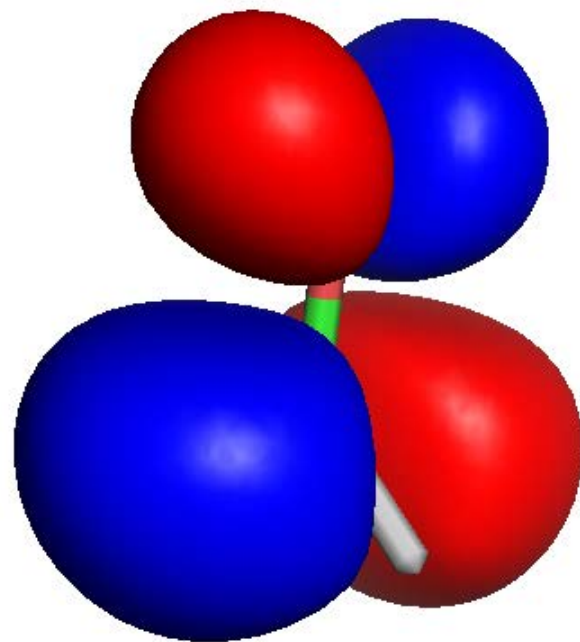
We can see that the HOMO ( $B_1$ ) to LUMO ( $B_2$ ) Transition is forbidden. The direct product is  $A_2$ .

$C_{2v}$	E	$C_2$	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1
$A_2$	1	1	-1	-1

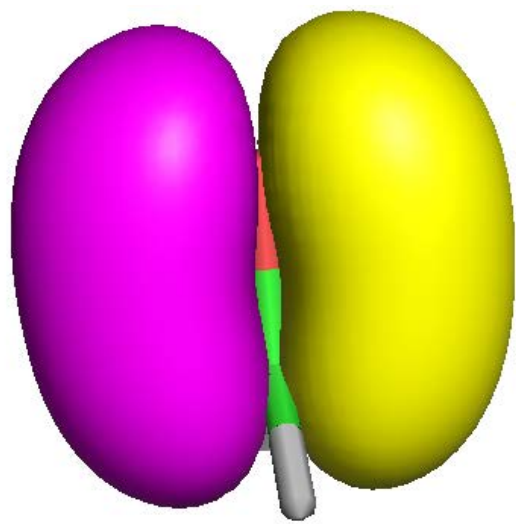
MO	Irrep	eV	Occupation
1	$a_1$	-510.777	2.000
2	$a_1$	-271.620	2.000
3	$a_1$	-26.478	2.000
4	$a_1$	-15.675	2.000
5	$b_1$	-12.056	2.000
6	$a_1$	-10.884	2.000
7	$b_2$	-9.924	2.000
8	$b_1$	-6.190	2.000
9	$b_2$	-2.569	0.000
10	$a_1$	1.918	0.000
11	$b_1$	3.613	0.000
13	$b_2$	9.266	0.000



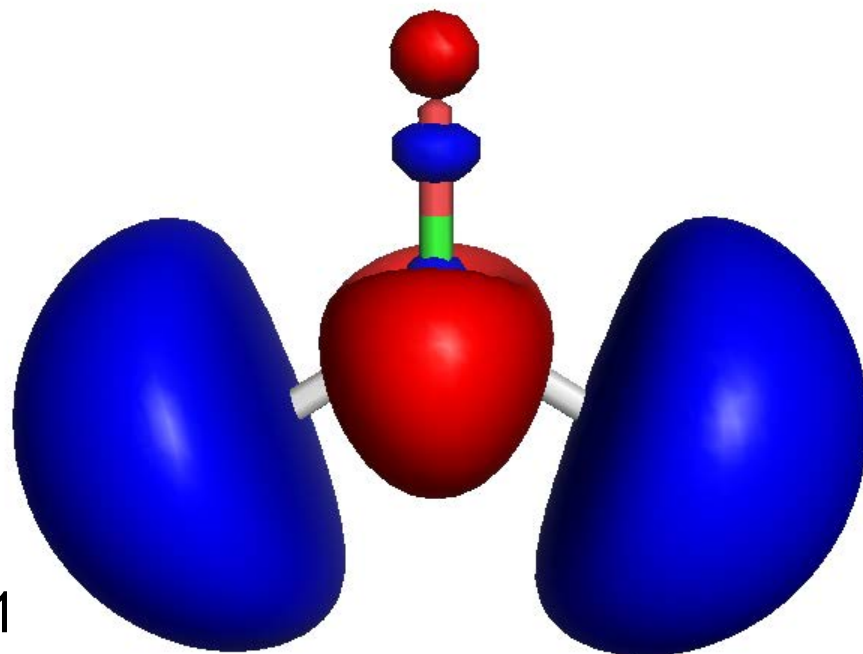
8 B<sub>1</sub>



9 B<sub>2</sub>



7 B<sub>2</sub>



10 A<sub>1</sub>

However, the HOMO ( $B_1$ ) to NLUMO ( $A_1$ ) is allowed. In that case the excitation radiation must be polarized along x ( $B_1$ ), since

$$B_1 \otimes B_1 \otimes A_1 = A_1$$

Other allowed transitions include 7  $\rightarrow$  9 and 8  $\rightarrow$  11. The direct products are,

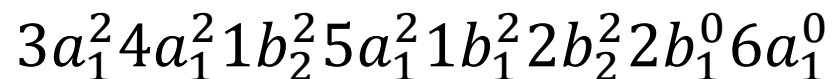
$$B_1 \otimes B_1 = A_1 \quad \text{are} \quad B_2 \otimes B_2 = A_1$$

Note that  $a_1$  corresponds to z-polarization in  $C_{2v}$ . Thus, these products tells us that the  $\pi-\pi^*$  transition and  $n-\pi^*$  transitions are allowed.

$C_{2v}$	E	$C_2$	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$	Rot	IR	Raman
$A_1$	1	1	1	1		z	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$		
$B_1$	1	-1	1	-1	$R_y$	x	
$B_2$	1	-1	-1	1	$R_x$	y	

# Formaldehyde – an example of vibronic coupling

The electronic configuration is



The configurations and transitions are given in Table 1

$\tilde{X}^1A_1$	Transition	Type	eV
$\tilde{A}^1A_2$	$2b_1 \leftarrow 2b_2$	$\pi^* \leftarrow n_0$	3.5
$\tilde{B}^1B_2$	$6a_1 \leftarrow 2b_2$	$\sigma^* \leftarrow n_0$	7.1
$^1A_1$	$2b_1 \leftarrow 1b_1$	$\pi^* \leftarrow \pi$	8.0
$^1B_1$	$2b_1 \leftarrow 5a_1$	$\pi^* \leftarrow n\sigma$	9.45

The transition  $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$  is a  $\pi^* \leftarrow n_0$  and is forbidden. The other three transitions are allowed.



# Using the direct product to assess vibronic mechanism

The  $\tilde{A} \leftarrow \tilde{X}$  transition can borrow oscillator strength from the other allowed transitions. One way to see this is to find if there is a mode whose direct product with the forbidden electronic excited state gives an irrep, which is the same as an allowed electronic excited state. We find that there are two possibilities:

$$A_2 \otimes b_1 = B_2$$

$$A_2 \otimes b_2 = B_1$$

The  $b_2$  mode is  $\nu_4$ , an out-of-plane bending mode.