

Lecture #32: Adiabatic ↔ Diabatic: Zewail

We are interested in wavepacket dynamics.

1. How to create a wavepacket with selected characteristics?
2. What are the basic features of wavepacket dynamics on a simple diatomic molecule potential energy curve with \mathbf{H} independent of time?
3. What are the additional features of a wavepacket on a $3N - 6$ dimensional potential energy surface?
4. intramode anharmonicity
intermode anharmonic interactions
curve crossings, surface crossings
stationary phase regions - where are they, what can happen as a wavepacket travels through or near one of them?
5. Landau-Zener inter-surface transition probability per crossing
6. How to probe wavepacket evolution?

Examples:

Zewail: I-CN dissociation

NaI dissociation via ionic covalent curve crossing

“Mechanism”

Diabatic vs. Adiabatic Potential Energy Curves

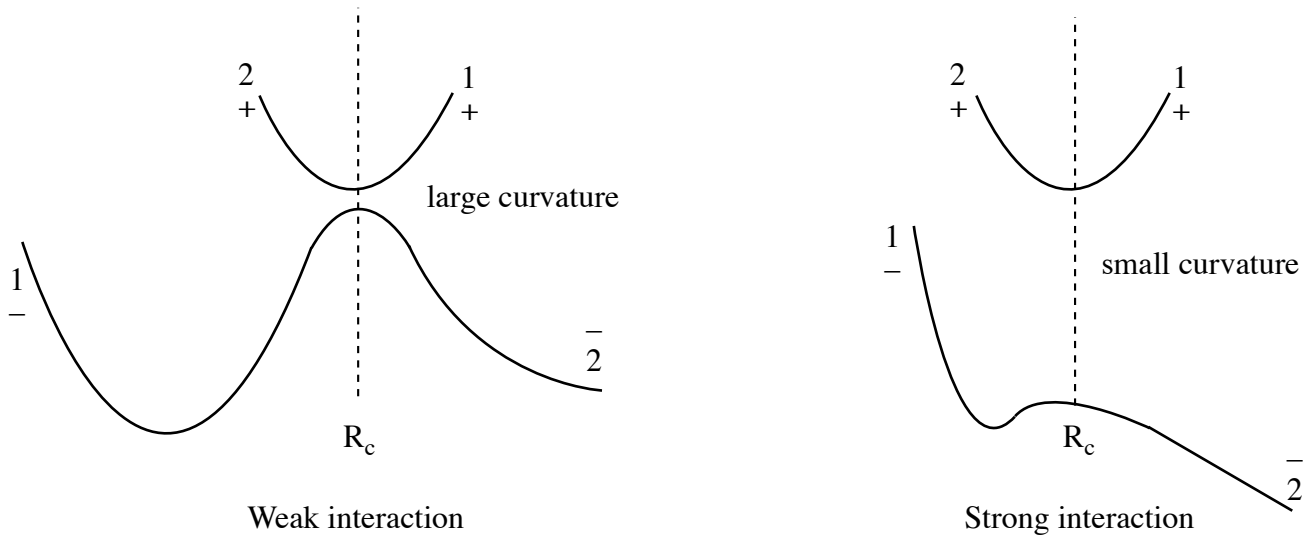
Ab Initio Potentials are “**clamped nuclei**” = adiabatic

exact solution of **electronic** Schrödinger Equation, ψ is parametrically dependent on \mathbf{R}

Non-Crossing Rule

Potential curves belonging to **same electronic symmetry** cannot cross because there are no symmetry restrictions on off-diagonal matrix elements between them.

If there is a will, molecules will find a way. There will be a non-zero interaction term.



$V_+(R_c) - V_-(R_c) = 2H_{12}$ This is an electronic interaction (usually $\frac{1}{r_{12}}$)

What is missing in the adiabatic representation? Clamped nuclei. Nuclear kinetic energy.

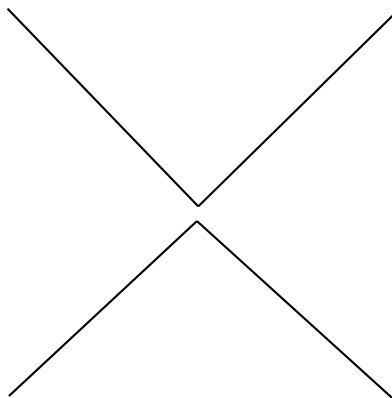
∇_R^2 nuclear kinetic energy (and rotation) must be treated as $H^{(1)}$.

Seems harmless but the electronic Schrödinger Equation gives

$\frac{\partial^2}{\partial Q^2} + \frac{\partial}{\partial Q}$ operate on $\psi_i(q_i, Q)$

$\psi_i(q_i, Q)$
↑
parametric dependence on nuclear coordinates

so if we have a weakly avoided crossing



$V_+(R_c) - V_-(R_c) = 2H_{12}$

H_{12} is **very small**, can we ignore it?

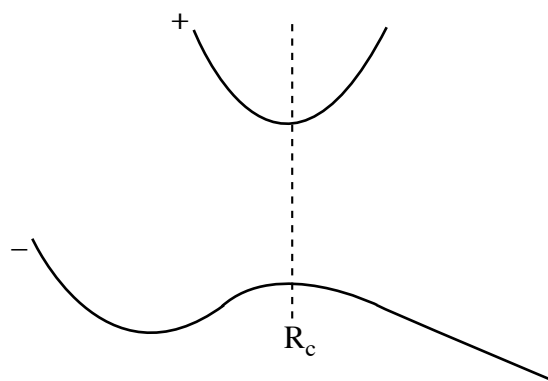
YES! But there is something else that we cannot ignore: matrix elements of ∇_R^2 between vibrational levels are enormous!

$\frac{\partial V_{\pm}}{\partial Q}$ is enormous. $\mathbf{H}^{(1)}$ is not small. Big trouble. Huge interaction between vibrational levels of the V_+ and V_- states.

The actual energy levels are very different from what are generated by $\mathbf{H}^{(0)}$. Why is this bad news?

The adiabatic representation is a very bad representation for the case of a weakly avoided crossing. It gives useless clues about how to assign the observed vibrational levels.

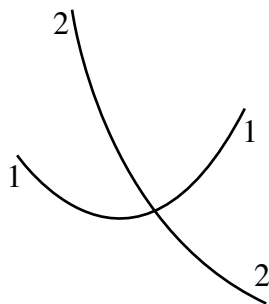
Strongly avoided crossing



$V_+(R_c) - V_-(R_c) = 2H_{12}$ huge. But H_{12} is explicitly taken into account in the *ab initio* computation of $V_-(R)$ and $V_+(R)$ potentials. We solve for the vibrational levels of $V_+(R)$ and $V_-(R)$ and we see close relationships between the vibrational levels and $\mathbf{H}^{(0)}$.

What about $\frac{\partial \psi(r; R)}{\partial R}$ near R_c ? Very small because electronic character is changing slowly.

Diabatic Curves do cross

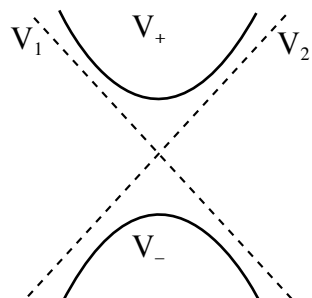


How is this possible? We exclude some term in $\mathbf{H}^{\text{electronic}}$ which enables the electronic wavefunctions to remain orthogonal. Electronic character does not change near R_c .

But there is no such explicit term that we can exclude from $\mathbf{H}^{(0)}$ and treat as $\mathbf{H}^{(1)}$!

Quantum Chemists do not like the diabatic representation even though it is what we like as Chemists. Why?

There are ways to construct a diabatic representation from the *ab initio* adiabatic representation



Solid curves are *adiabatic*
Dashed curves are *diabatic*

Adiabatic gives R_c and H_{12}

Make linear approximation for diabatic potential in region of curve crossing. We have an R-dependent 2-level problem.

$$\mathbf{H}(R) = \mathbf{T}^\dagger \begin{pmatrix} \text{DIABATIC} \\ V_1(R) & H_{12}(R_c) \\ H_{12}(R_c) & V_2(R) \end{pmatrix} \mathbf{T} = \begin{pmatrix} \text{ADIABATIC} \\ V_+(R) & 0 \\ 0 & V_-(R) \end{pmatrix}$$

We know $V_\pm(R)$ and $H_{12}(R_c)$. This is sufficient to generate $V_1(R)$ and $V_2(R)$. We do a least squares fit by varying the slope of V_1 and V_2 at R_c .

Once we have V_1 and V_2 or V_+ and V_- we can fit the spectrum.

H_{12} large: adiabatic representation is best.

H_{12} small: diabatic representation is best.

For polyatomic molecules we have potential surfaces, not curves.

Two adiabatic surfaces can have **different symmetries**. This permits them to cross at the high symmetry point. But as you move away from R_{sym} , the 2 states interact and the surfaces repel. They look like a pair of cones that are joined at the apex.

“Conical Intersection”
“Vibronic Coupling”

Many things that violate chemical intuition are “explained” by vibronic coupling.

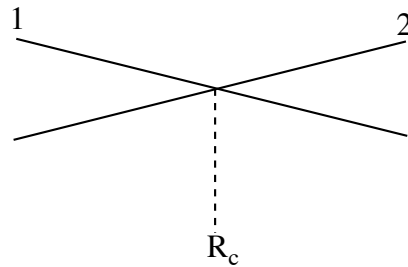
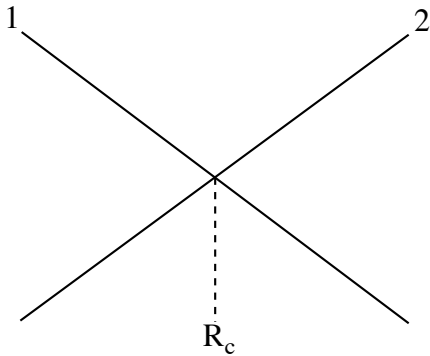
How is this related to Landau-Zener? Transition Probability.

$P_{12} = 1 - e^{-2\pi\gamma}$ transition probability $1 \rightarrow 2$ at each passage through R_c .

$$\gamma = \frac{V_{12}^2}{\hbar v |s_1 - s_2|} \quad P_{12} = 0 \text{ when } \gamma = 0, P_{12} = 1 \text{ when } \gamma \text{ large}$$

γ small when v large (P_{12} small), v is velocity at R_c

γ large when $s_1 \approx s_2$, s is slope of diabatic curve at R_c .



Look at examples from the Zewail experiments.

Off-Diagonal Matrix Elements in the Diabatic and Adiabatic Representation

In the diabatic representation, the electronic-vibration matrix elements are

$$H_{e_1, v_1; e_2, v_2}^{\text{diab}} = \left\langle \chi_{v_1}^{\text{d}} \left| \left\langle \Phi_{e_1}^{\text{d}} \left| H^{\text{el}} \left| \Phi_{e_2}^{\text{d}} \right\rangle_r \right| \chi_{v_2}^{\text{d}} \right\rangle_R$$

where right subscripts specify integration over electronic (r) or nuclear (R) coordinates. This matrix element simplifies to the product of two integrals

$$\left\langle \chi_{v_1}^{\text{d}} \left| \chi_{v_2}^{\text{d}} \right\rangle \left\langle \Phi_{e_1}^{\text{d}} \left| H(R_c) \left| \Phi_{e_2}^{\text{d}} \right\rangle \right.$$

or, more simply,

$$\left\langle \chi_{v_1}^{\text{d}} \left| \chi_{v_2}^{\text{d}} \right\rangle_R H_{1,2}(R_c).$$

The vibrational overlap integral is calculated using the vibrational wavefunctions of electronic states 1 and 2. The electronic matrix element is evaluated at R_c because that is the stationary phase point at which the vibrational integral accumulates to its final value.

The matrix elements in the adiabatic representation are the result of a lengthy derivation, given on pages 168-172 of H. Lefebvre-Brion and R. W. Field (see end of Lecture 32 Supplement #2).

The term that is neglected in the “clamped nuclei” calculation is

$$\mathbf{T}^N = -\frac{\hbar^2}{2\mu} \left[\frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right] + \frac{\hbar^2}{2\mu R^2} \mathbf{R}^2 \quad (1)$$

The last term is nuclear rotation and we will ignore it. Since the electronic wavefunctions depend parametrically on R , we need to operate with \mathbf{T}^N on the product of the electronic wavefunction, $\psi_e(r; R)$ and the vibrational wavefunction, $\chi_v(R)$. After some algebra we get

$$\begin{aligned} \mathbf{H}_{e_1, v_1; e_2, v_2}(\text{cm}^{-1}) = & -\frac{16.8576}{\mu(\text{amu})} \left\langle \xi_{v_1}^{\text{ad}} \left| \left\langle \Phi_{e_1}^{\text{ad}} \left| \frac{\partial^2}{\partial R^2} \left| \Phi_{e_2}^{\text{ad}} \right\rangle_r \right. \right. \right. (\hat{A}^{-2}) \left. \left. \left. \xi_{v_2}^{\text{ad}} \right\rangle_R \right. \right. \\ & - \frac{33.7152}{\mu(\text{amu})} \left\langle \xi_{v_1}^{\text{ad}} \left| \left\langle \Phi_{e_1}^{\text{ad}} \left| \frac{\partial}{\partial R} \left| \Phi_{e_2}^{\text{ad}} \right\rangle_r \right. \right. \right. (\hat{A}^{-1}) \left. \left. \left. \frac{d}{dR} \xi_{v_2}^{\text{ad}} \right\rangle_R \right. \right. \end{aligned} \quad (2)$$

The r, R right subscripts specify integration over the electron (r) and nuclear coordinates (R).

The vibrational wavefunction

$$|\xi_v^{\text{ad}}(R)\rangle \equiv R|\chi_v^{\text{ad}}(R)\rangle \quad (3)$$

where $\xi(R)$ and $\chi(R)$ are normalized as

$$\langle \chi_v(R) | R^2 | \chi_v(R) \rangle_R = 1 \quad (4a)$$

$$\langle \xi_v(R) | \xi_v(R) \rangle_R = 1. \quad (4b)$$

The diabatic curves cross and the 2×2 configuration interaction secular equation is

$$\begin{vmatrix} E_{e_1}^d(R) - E & \mathbf{H}_{12}^e(R) \\ \mathbf{H}_{12}^e(R) & E_{e_2}^d(R) - E \end{vmatrix} = 0 \quad (5)$$

where the diabatic potential energy curves are

$$E_{e_1}^d(R) = V_1^d(R), \quad E_{e_2}^d(R) = V_2^d(R), \quad (6)$$

and we get the adiabatic wavefunctions from the diabatic electronic wavefunctions

$$\Phi_{e_1}^{\text{ad}} = \cos \theta(R) \Phi_{e_1}^d - \sin \theta(R) \Phi_{e_2}^d \quad (7a)$$

$$\Phi_{e_2}^{\text{ad}} = \sin \theta(R) \Phi_{e_1}^d + \cos \theta(R) \Phi_{e_2}^d. \quad (7b)$$

Note that the mixing angle, θ , is dependent on R .

At the crossing point, R_c , between the diabatic potential curves, $R = R_c$ and $\theta = \pi/4$. The vertical energy difference at R_c between the adiabatic potential curves is

$$E_{e_1}^{\text{ad}}(R_c) - E_{e_2}^{\text{ad}}(R_c) = 2H_{12}^e(R_c) \quad (8)$$

and the slopes of the *assumed linear* diabatic potentials near $R = R_c$ are

$$E_{e_1}^d(R) - E_{e_2}^d(R) = a(R - R_c). \quad (9)$$

Since the diabatic electronic wavefunctions are, by definition, independent of R , $\frac{\partial}{\partial R}$ applied to equation (7) operates only on $\cos \theta(R)$ and $\sin \theta(R)$, thus

$$\left\langle \Phi_{e_1}^{\text{ad}} \left| \frac{\partial}{\partial R} \right| \Phi_{e_2}^{\text{ad}} \right\rangle = \left(\frac{\sin^2 \theta + \cos^2 \theta}{=1} \right) \frac{\partial \theta}{\partial R} = \frac{\partial \theta}{\partial R}. \quad (10)$$

By expanding the determinant in Eq. (5), we obtain the R -dependence of θ near R_c

$$\frac{\sin \theta \cos \theta}{\cos^2 \theta - \sin^2 \theta} = \frac{1}{2} \tan 2\theta = \frac{H_{12}^e(R_c)}{E_{e_2}^d - E_{e_1}^d} = -\frac{H_{12}^e(R_c)}{a(R - R_c)}. \quad (11)$$

Thus

$$\theta(R) = \frac{1}{2} \tan^{-1} \left[\frac{-2H_{12}^e(R_c)}{a(R - R_c)} \right] = \frac{1}{2} \cot \left[\frac{a(R - R_c)}{-2H_{12}^e(R_c)} \right]. \quad (12)$$

Since

$$\frac{d}{dx} \cot^{-1} \left(\frac{x}{c} \right) = \frac{-c}{c^2 + x^2} \quad (13)$$

$$\left\langle \Phi_{e_1}^{\text{ad}} \left| \frac{\partial}{\partial R} \right| \Phi_{e_2}^{\text{ad}} \right\rangle = \frac{\partial \theta}{\partial R} = \frac{aH_{12}^e(R_c)}{4(H_{12}^e(R_c))^2 + a^2(R - R_c)^2}. \quad (14a)$$

For convenience, define $b = H_{12}^e(R_c)/a$

$$\left\langle \Phi_{e_1}^{\text{ad}} \left| \frac{\partial}{\partial R} \right| \Phi_{e_2}^{\text{ad}} \right\rangle_r = \frac{b}{4b^2 + (R - R_c)^2} \equiv W^e(R) \quad (14b)$$

It is reasonable to treat H_{12}^e as independent of R , because the integral over R accumulates only near R_c . Then Eq. (14b) requires that $W^e(R)$ is a Lorentzian in R with a full width at half-maximum of $4b = 4H^e(R_c)/a$ where a is the difference in slope between $H_{e_1}^d$ and $H_{e_2}^d$ near R_c .

Recall that the Landau-Zener formula for the probability of jumping from the $V_+(R)$ to the $V_-(R)$ adiabatic curve is

$$P_{+-} = 1 - e^{-2\pi\gamma}$$

$$\gamma = \frac{H^e(R_c)^2}{\hbar v |s_1 - s_2|}$$

$$\text{where } |s_1 - s_2| = \left| \frac{dH_{e_1}^d}{dR} - \frac{dH_{e_2}^d}{dR} \right|$$

Vibrational Matrix Elements

Our goal is to derive the matrix elements between the vibrational levels of adiabatic potential curves $E_{e_1}^{\text{ad}}(R)$ and $E_{e_2}^{\text{ad}}(R)$ that result from ∇_R^2 .

If it is possible to ignore vibronic interactions of state Φ_1^{ad} and Φ_2^{ad} with other electronic states, the two terms in Eq. (2) reduce to

$$\mathbf{H}_{e_1v_1;e_2v_2}(\text{cm}^{-1}) = -\frac{16.8576}{\mu(\text{amu})} \left\langle \xi_{v_1}^{\text{ad}} \left| \frac{dW^e}{dR} \right| \xi_{v_2}^{\text{ad}} \right\rangle_R - \frac{33.7152}{\mu(\text{amu})} \left\langle \xi_{v_1}^{\text{ad}} \left| W^e(R) \frac{d}{dR} \right| \xi_{v_2}^{\text{ad}} \right\rangle_R.$$

Since both R -integrals accumulate near R_c ,

$$W^e(R_c) = \frac{1}{4b} = \frac{a}{4H_{12}^e}$$

$$\left. \frac{dW^e}{dR} \right|_{R_c} = 0$$

and the dominant term in the inter-electronic vibrational matrix elements is

$$\mathbf{H}_{e_1v_1;e_2v_2}(\text{cm}^{-1}) = -\frac{33.7152}{\mu(\text{amu})} \left\langle \xi_{v_1}^{\text{ad}} \left| \frac{a}{4H_{12}^e} \frac{d}{dR} \right| \xi_{v_2}^{\text{ad}} \right\rangle_R$$

where

$$\left. \frac{d}{dR} \right| \xi_{v_2}^{\text{ad}} \rangle \propto \left| \xi_{v_2 \pm 1}^{\text{ad}} \right\rangle$$

because $\frac{d}{dR} \propto (\mathbf{a} - \mathbf{a}^\dagger)$.

Note that when H_{12}^e is small (weakly avoided crossing) and the difference in slope of the diabatic potential curves is large (also weakly avoided crossing), the vibrational matrix elements are large. If the adiabatic potential curves are very different in shape, the vibrational matrix elements will not follow any sort of restrictive propensity rule. This means that the interaction matrix elements between the vibrational levels of two adiabatic potential energy curves will be large and involve many simultaneous interactions. An enormously non-diagonal interaction matrix will have to be diagonalized in the adiabatic representation. At the opposite extreme, if the crossing is strongly avoided, H_{12}^e will be large and the difference in slopes near R_c will be very small. All of the off-diagonal vibrational matrix elements will be very small.

In the diabatic representation, the opposite behavior of the off-diagonal matrix elements is expected.

For a weakly avoided crossing, H_{12}^{el} is small, the difference in slopes is large, and the only interactions between vibrational levels of diabatic states 1 and 2 that need to be considered will be between pairs of

near-degenerate vibrational levels. For a strongly avoided crossing, H_{12}^{el} is enormous and many vibrational overlap integrals will be large.

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