

ADIABATIC AND DIABATIC REPRESENTATIONS

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EXPANSION OF THE WAVE FUNCTION

$$\psi = \sum \varphi_i^{(a)}(\mathbf{r}, \mathbf{R}) \chi_i^{(a)}(\mathbf{R}, t) \quad (1)$$

- $\varphi_i^{(a)}$ adiabatic electronic wave functions,
- $\chi_i^{(a)}$ adiabatic nuclear wave functions,
- \mathbf{r} and \mathbf{R} electronic and nuclear coordinates, t time.

Assuming *independence* of $\varphi_i^{(a)}$ on \mathbf{R} : crude adiabatic approximation. Often leads to slow convergence of (1).

$$H = -\frac{\hbar^2}{2\mu} \nabla_{\text{nuc}}^2 + H_{\text{el}} = T_{\text{nuc}} + H_{\text{el}} \quad (2)$$

- ∇_{nuc} : nuclear gradient, T_{nuc} nuclear kinetic energy,
- H_{el} : all interaction and electronic kinetic energies.

COUPLED EQUATIONS

Let $\{\varphi_i^{(a)}\}$ orthonormal *complete* set of eigenfunctions of H_{el} :

$$\langle \varphi_j(\mathbf{r}, \mathbf{R}) | \varphi_i(\mathbf{r}, \mathbf{R}) \rangle_{\text{el}} = \delta_{ji}, \quad \sum_k |\varphi_k\rangle \langle \varphi_k| = 1, \quad (3)$$

$$H_{\text{el}} \varphi_i(\mathbf{r}, \mathbf{R}) = V_i(\mathbf{R}) \varphi_i(\mathbf{r}, \mathbf{R}). \quad (4)$$

$$H\psi = (T_{\text{nuc}} + H_{\text{el}}) \sum \varphi_i^{(a)} \chi_i^{(a)} \quad (5)$$

$$= -\frac{\hbar^2}{2\mu} \sum \nabla_{\text{nuc}}^2 \left(\varphi_i^{(a)} \chi_i^{(a)} \right) + \sum H_{\text{el}} \varphi_i^{(a)} \chi_i^{(a)} \quad (6)$$

$$= -\frac{\hbar^2}{2\mu} \sum \left[\left(\nabla^2 \varphi_i^{(a)} \right) \chi_i^{(a)} + 2 \left(\nabla \varphi_i^{(a)} \right) \left(\nabla \chi_i^{(a)} \right) \right. \\ \left. + \varphi_i^{(a)} \left(\nabla^2 \chi_i^{(a)} \right) \right] + \sum H_{\text{el}} \varphi_i^{(a)} \chi_i^{(a)} \quad (7)$$

multiply $\langle \varphi_j^{(a)} |$ from left:

$$\langle \varphi_j^{(a)} | H | \psi \rangle = [V_j^{(a)} + T_{\text{nuc}} + K_{jj}^{(a)}] \chi_j^{(a)} + \sum K_{j \neq i}^{(a)} \chi_i^{(a)}, \quad (8)$$

$$K_{jj}^{(a)} = -\frac{\hbar^2}{2\mu} \left[\langle \varphi_j^{(a)} | \nabla^2 \varphi_i^{(a)} \rangle + 2 \langle \varphi_j^{(a)} | \nabla \varphi_i^{(a)} \rangle \nabla \right]. \quad (9)$$

$$H\psi = E\psi \Rightarrow \langle \varphi_j^{(a)} | H | \psi \rangle = E \langle \varphi_j^{(a)} | \psi \rangle = E \chi_j^{(a)} \quad (10)$$

Then the steady-state Schrödinger equation is

$$\left[V_j^{(a)} + T_{\text{nuc}} + K_{jj}^{(a)} - E \right] \chi_j^{(a)} + \sum K_{ji}^{(a)} \chi_i^{(a)} = 0 \quad (11)$$

$$\left[\mathbf{V}^{(a)} + \mathbf{T}_{\text{nuc}} + \mathbf{K}^{(a)} - E \right] \chi^{(a)} = 0. \quad (12)$$

Neglect of $\mathbf{K}^{(a)}$ constitutes the *Born-Oppenheimer approximation*.

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DERIVATIVE COUPLING

$$T_{ji}^{(1)} = \langle \varphi_j | \nabla_{\text{nuc}} \varphi_i \rangle \quad (13)$$

$$T_{ji}^{(2)} = \langle \varphi_j | \nabla_{\text{nuc}}^2 \varphi_i \rangle, \text{ so that} \quad (14)$$

$$\rightarrow K_{ji}^{(a)} = -\frac{\hbar^2}{2\mu} \left(2T_{ji}^{(1)} \nabla_{\text{nuc}} + T_{ji}^{(2)} \right), \quad (15)$$

$$\Rightarrow 0 = \left[-\frac{\hbar^2}{2\mu} \left(\nabla + \mathbf{T}^{(1)} \right)^2 + \mathbf{V}^{(a)} - E \right] \chi^{(a)} \quad (16)$$

$(\nabla + \mathbf{T}^{(1)})^2$ is called “dressed kinetic energy operator”^{1,2}.

¹G. A. Worth and L. S. Cederbaum *Beyond Born-Oppenheimer: Molecular dynamics through a conical intersection* Ann. Rev. Phys. Chem. **55** (2004) 127

²L. S. Cederbaum *Born-Oppenheimer approximation and beyond in: Conical Intersections*, ed. W. Domcke, D. R. Yarkony and H. Köppel, World Scientific (2004)

Elements of dressed kinetic energy $(\nabla + \mathbf{T}^{(1)})^2$:

$$\left(\nabla + \mathbf{T}^{(1)}\right)_{ji}^2 = \left(\nabla^2 + \mathbf{T}^{(1)}\nabla + \nabla\mathbf{T}^{(1)} + \mathbf{T}^{(1)2}\right)_{ji} \quad (17)$$

$$= \nabla^2 + 2 \underbrace{\langle \varphi_j | \nabla \varphi_i \rangle}_{T_{ji}^{(1)}} \nabla + \underbrace{\langle \varphi_j | \nabla^2 \varphi_i \rangle}_{T_{ji}^{(2)}} \\ + \langle \nabla \varphi_j | \nabla \varphi_i \rangle + \sum_k \langle \varphi_j | \nabla \varphi_k \rangle \langle \varphi_k | \nabla \varphi_i \rangle \quad (18)$$

$$\text{Now } \nabla \langle \varphi_j | \varphi_k \rangle = \langle \nabla \varphi_j | \varphi_k \rangle + \langle \varphi_j | \nabla \varphi_k \rangle = \nabla \delta_{jk} = 0,$$

$$\text{hence } \langle \varphi_j | \nabla \varphi_k \rangle = -\langle \nabla \varphi_j | \varphi_k \rangle \quad (19)$$

$\mathbf{T}^{(1)}$ is antihermitean. Since $\sum_k |\varphi_k\rangle \langle \varphi_k| = 1$, the last two terms in eq. (18) cancel. Corollary: $(\nabla \mathbf{T}^{(1)}) = \mathbf{T}^{(2)} - \mathbf{T}^{(1)2}$.

GROUP BORN-OPPENHEIMER APPROXIMATION

Usually, a group of states is considered only, denoted by superscript (g):

$$\left[-\frac{\hbar^2}{2\mu} \left(\nabla + \mathbf{T}^{(1,g)} \right)^2 + \mathbf{V}^{(g)} - E \right] \chi^{(a)} = 0, \quad (20)$$

This approximation can be corrected by replacing the $\mathbf{V}^{(g)}$ by $\mathbf{T}^{(3,g)}$ which contains the potential and all terms neglected in $\mathbf{T}^{(1,g)}$. Let $\hat{P}_g =$ projector on the selected group:

$$\rightarrow T_{ji}^{(3,g)}(\mathbf{R}) = V_i^{(g)}(\mathbf{R}) \delta_{ij} + \frac{\hbar^2}{2\mu} \left\langle \nabla \varphi_j \left| \left(1 - \hat{P}_g \right) \right| \nabla \varphi_i \right\rangle. \quad (21)$$

$\mathbf{T}^{(3,g)}$ is called “dressed potential”.

SINGULARITIES AT CONICAL INTERSECTIONS

$$H_{\text{el}}\varphi_i(\mathbf{r}, \mathbf{R}) = V_i(\mathbf{R})\varphi_i(\mathbf{r}, \mathbf{R}) \quad (22)$$

$$(\nabla_{\text{nuc}} H_{\text{el}})\varphi_i + H_{\text{el}}(\nabla_{\text{nuc}}\varphi_i) = (\nabla_{\text{nuc}} V_i)\varphi_i + V_i(\nabla_{\text{nuc}}\varphi_i) \quad (23)$$

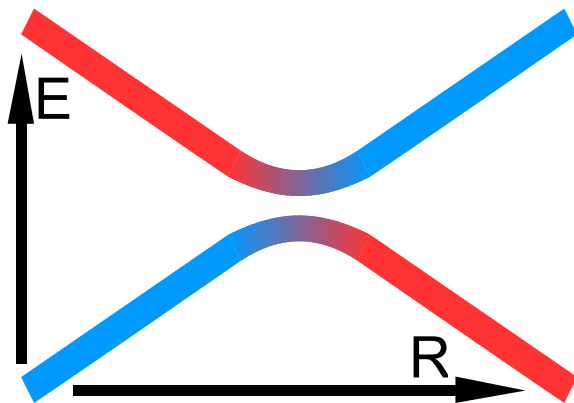
$$\begin{aligned} \langle \varphi_j | (\nabla H_{\text{el}}) | \varphi_i \rangle + \langle \varphi_j | H_{\text{el}} | \nabla \varphi_i \rangle \\ = \langle \varphi_j | (\nabla V_i(\mathbf{R})) | \varphi_i \rangle_{\text{el}} + \langle \varphi_j | V_i | \nabla \varphi_i \rangle \end{aligned} \quad (24)$$

$$\begin{aligned} \langle \varphi_j | (\nabla H_{\text{el}}) | \varphi_i \rangle + V_j \langle \varphi_j | \nabla \varphi_i \rangle \\ = (\nabla V_i(\mathbf{R})) \delta_{ji} + V_i \langle \varphi_j | \nabla \varphi_i \rangle \end{aligned} \quad (25)$$

$$\rightarrow T_{ji}^{(1)} = \langle \varphi_j | \nabla_{\text{nuc}} \varphi_i \rangle = \frac{\langle \varphi_j | (\nabla_{\text{nuc}} H_{\text{el}}) | \varphi_i \rangle_{\text{el}}}{V_i(\mathbf{R}) - V_j(\mathbf{R})}. \quad (26)$$

Denominator small close to avoided crossings \rightarrow Born-Oppenheimer breaks down, as derivative coupling large.
Conical intersection: $T_{ji}^{(1)}$ singular.

DIABATIC REPRESENTATION³




SHOWN

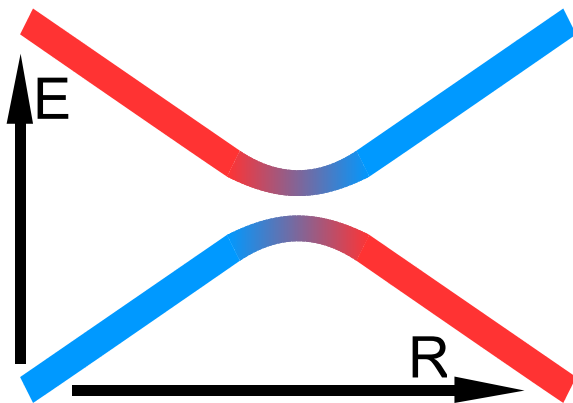
Adiabatic states around an avoided crossing.

IDEA

Connect like colours.

³M. Desouter-Lecomte, J. C. Leclerc, J. C. Lorquet Chem. Phys. **9** (1975) 147. 

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UNITARY TRANSFORMATION

A unitary transformation $\mathbf{U}(\mathbf{R})$ in the vector space of electronic states does not change the wave function ψ .

$$\psi = \sum \varphi_i^{(a)} \chi_i^{(a)} = \varphi^{a+} \chi^{(a)} = \varphi^{a+} \mathbf{U} \cdot \mathbf{U}^+ \chi^{(a)} \quad (27)$$

$$= (\mathbf{U}^+ \varphi^a)^+ (\mathbf{U}^+ \chi^{(a)}) = \varphi^{d+} \chi^{(d)}. \quad (28)$$

Transformed wave functions are denoted $\varphi^{(d)}$ and $\chi^{(d)}$.

KINETIC TERMS

\mathbf{T}_{nuc} and $\mathbf{K}^{(a)}$ applied to *adiabatic* nuclear wave fn. $\chi^{(a)} = \mathbf{U}\chi^{(d)}$:

$$\mathbf{T}_{\text{nuc}}\chi^{(a)} = -\frac{\hbar^2}{2\mu} \nabla_{\text{nuc}}^2 (\mathbf{U}\chi^{(d)}) \quad (29)$$

$$= -\frac{\hbar^2}{2\mu} \left[(\nabla^2 \mathbf{U}) + 2(\nabla \mathbf{U}) \nabla + \mathbf{U} \nabla^2 \right] \chi^{(d)} \quad (30)$$

$$\mathbf{K}^{(a)}\chi^{(a)} = -\frac{\hbar^2}{2\mu} \left[2\mathbf{T}^{(1)} \nabla + \mathbf{T}^{(2)} \right] \chi^{(a)} \quad (31)$$

$$= -\frac{\hbar^2}{2\mu} \left[2\mathbf{T}^{(1)} (\nabla \mathbf{U}) + 2\mathbf{T}^{(1)} \mathbf{U} \nabla + \mathbf{T}^{(2)} \mathbf{U} \right] \chi^{(d)} \quad (32)$$

SCHRÖDINGER EQUATION

$$0 = \left[\mathbf{V}^{(a)} - E + \left(\mathbf{T}_{\text{nuc}} + \mathbf{K}^{(a)} \right) \right] \mathbf{U} \chi^{(d)} \quad (33)$$

$$= \left[\left(\mathbf{V}^{(a)} - E \right) \mathbf{U} - \frac{\hbar^2}{2\mu} \left(\nabla^2 \mathbf{U} + 2\mathbf{T}^{(1)} (\nabla \mathbf{U}) + \mathbf{T}^{(2)} \mathbf{U} \right) - \frac{\hbar^2}{2\mu} 2 \left(\nabla \mathbf{U} + \mathbf{T}^{(1)} \mathbf{U} \right) \nabla - \frac{\hbar^2}{2\mu} \mathbf{U} \nabla^2 \right] \chi^{(d)}. \quad (34)$$

Apart from being unitary, \mathbf{U} has not been restricted yet, so it can be chosen such as to solve the differential equation

$$\nabla \mathbf{U} + \mathbf{T}^{(1)} \mathbf{U} = 0. \quad (35)$$

This makes the coefficient of the first derivative zero.

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If eq. (35), $\nabla \mathbf{U} + \mathbf{T}^{(1)} \mathbf{U} = 0$, and $\{\varphi_n^{(a)}\}$ is a complete set, then

$$2\mathbf{T}^{(1)} (\nabla \mathbf{U}) + 2\mathbf{T}^{(2)} \mathbf{U} + \nabla^2 \mathbf{U} = 0. \quad (36)$$

PROOF

The first derivative of equation (35) is

$$\nabla^2 \mathbf{U} + (\nabla \mathbf{T}^{(1)}) \mathbf{U} + \mathbf{T}^{(1)} \nabla \mathbf{U} = 0 \quad (37)$$

If $\{\varphi_n^{(a)}\}$ is a complete set, $(\nabla \mathbf{T}^{(1)}) = \mathbf{T}^{(2)} - \mathbf{T}^{(1)2}$, so (37) takes the form

$$\nabla^2 \mathbf{U} + \mathbf{T}^{(2)} \mathbf{U} - \mathbf{T}^{(1)2} \mathbf{U} + \mathbf{T}^{(1)} \nabla \mathbf{U} = 0. \quad (38)$$

On the other hand, application of $\mathbf{T}^{(1)}$ to the given restricting equation (35) gives $-\mathbf{T}^{(1)2} \mathbf{U} = \mathbf{T}^{(1)} \nabla \mathbf{U}$ so finally

$$\nabla^2 \mathbf{U} + 2\mathbf{T}^{(1)} \nabla \mathbf{U} + \mathbf{T}^{(2)} \mathbf{U} = 0, \quad (39)$$

which is the desired result.

If eq. (35), $\nabla\mathbf{U} + \mathbf{T}^{(1)}\mathbf{U} = 0$, and $\{\varphi_n^{(a)}\}$ is a complete set, then

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DIABATIC POTENTIAL

Fixing the diabatic transformation thus, the Schrödinger equation simplifies to

$$\left[\left(\mathbf{V}^{(a)} - E \right) \mathbf{U} - \frac{\hbar^2}{2\mu} \mathbf{U} \nabla^2 \right] \chi^{(d)} = 0. \quad (40)$$

Applying \mathbf{U}^+ from the left gives

$$\left[\left(\mathbf{V}^{(d)} - E \right) - \mathbf{T}_{\text{nuc}} \right] \chi^{(d)} = 0 \text{ with } \boxed{\mathbf{V}^{(d)} = \mathbf{U}^+ \mathbf{V}^{(a)} \mathbf{U}} \quad (41)$$

which has the form of a simple Schrödinger equation.

- $\mathbf{V}^{(d)}$ is **not** a diagonal matrix.
- Kinetic coupling elements $\mathbf{T}^{(1/2)}$ extinguished but reflected in off-diagonal elements of $\mathbf{V}^{(d)}$.
- Difficulty now in calculation of transformation matrix.
- \mathbf{U} unitary \rightarrow expectation values of observables unaffected.

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SOLUTION OF EQUATION (35)

Formal solution of equation (35), $\nabla \mathbf{U} + \mathbf{T}^{(1)} \mathbf{U} = 0$:

$$\mathbf{U}(\mathbf{R}) = \hat{R} e^{-\int_{\gamma} \mathbf{T}^{(1)}(\mathbf{R}') d\mathbf{R}'} \mathbf{U}(\mathbf{R}_0), \quad (42)$$

- Note:**
- γ is (linear) path $\mathbf{R}_0 \rightarrow \mathbf{R}$,
 - \hat{R} = space ordering operator.

Do propagation⁴ (space order satisfied), stepsize $\Delta \mathbf{R}$:

$$-\int_{\gamma} \mathbf{T}^{(1)}(\mathbf{R}') d\mathbf{R}' \approx -\sum_n \mathbf{T}^{(1)}(\mathbf{R}_0 + n \cdot \Delta \mathbf{R}) \Delta \mathbf{R} \quad (43)$$

$$\Rightarrow \mathbf{U}(\mathbf{R}) \approx \prod_n e^{-\mathbf{T}^{(1)}(\mathbf{R}_0 + n \cdot \Delta \mathbf{R}) \Delta \mathbf{R}} \mathbf{U}(\mathbf{R}_0) \quad (44)$$

- Choose \mathbf{R}_0 away from crossing, so $U(\mathbf{R}_0)$ can be set to 1.
- Calculate $e^{-\mathbf{T}^{(1)}(\mathbf{R}_0 + n \cdot \Delta \mathbf{R}) \Delta \mathbf{R}}$ by diagonalising exponent.

⁴M. Baer in Cheuk-Yiu Ng, M. Baer State-selected and State-to-State Ion-Molecule Reaction Dynamics, Adv. in Chem. Phys. vol. LXXXII part 2, 187.

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EXAMPLE: TWO ELECTRONIC STATES.

$\mathbf{T}^{(1)}$ antihermitian, i.e. only one independent element: $T_{12}^{(1)}$.

Let $A_{12} = - \int_{\gamma} T_{12}^{(1)}(\mathbf{R}') d\mathbf{R}$. **A** eigenvalues: $\lambda = \pm i\alpha = \pm i|A_{12}|$.

$$\mathbf{U}(\mathbf{R}) = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \begin{pmatrix} e^{i\alpha} & 0 \\ 0 & e^{-i\alpha} \end{pmatrix} \begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \quad (45)$$

$$= \begin{pmatrix} \cos \alpha(\mathbf{R}) & \sin \alpha_{12}(\mathbf{R}) \\ -\sin \alpha(\mathbf{R}) & \cos \alpha(\mathbf{R}) \end{pmatrix} \quad (46)$$

$\alpha(\mathbf{R})$ = mixing angle. If $T_{12}^{(1)}$ approximated by a Lorentzian

$$T_{12}^{(1)} \approx \frac{\Gamma_{12}/4}{[\mathbf{R} - \mathbf{R}_{12}^c]^2 + \Gamma_{12}^2/4} \quad (47)$$

the mixing angle can be found analytically to be⁵

$$\alpha = -\frac{1}{2} \arctan \left[\frac{2|\mathbf{R} - \mathbf{R}_{12}^c|}{\Gamma_{12}} \right] - \frac{\pi}{4}. \quad (48)$$

⁵P. Saalfrank Chem. Phys. **193** (1995) 119.

DIABATISATION BY ANSATZ

FITTING PROCEDURE

Circumventing the calculation of derivative coupling elements.

- 1 Construct physical parametric form for diabatic potential.
- 2 Guess initial parameters.
- 3 Diagonalise diabatic potential matrix (numerically).
- 4 Evaluate least square deviation from adiabatic potentials.
- 5 Change parameters along direction of steepest descent.
- 6 Go back to step 3.

This procedure converges to a diabatic potential which, when diagonalised, reproduces the given adiabatic potential. \mathbf{U} is the diagonalising transformation .

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