Short-time dynamics through conical intersections

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2ème Journée de Théoriciens de Strasbourg 7/2/2011
Motivation

Experimental observation: no fluorescence in the first excited states of the monofluorobenzene cation, but optical transitions are dipole allowed.


→ Ultrafast electronic relaxation process due to Conical Intersections
   Simulations of the quantum dynamics
Schrödinger equation for a molecular system:

\[
H = H_{el} + T_N \quad \text{avec} \quad H_{el} = T_{el} + V(r, q)
\]

\[
H_{el} \phi_n(r; q) = V_n(q) \phi_n(r; q)
\]

\[
H \Psi(r, q) = E \Psi(r, q) \quad \text{avec} \quad \Psi(r, q) = \sum_n \chi_n(q) \phi_n(r; q)
\]

\[
[T_N + V_n(q) - E] \chi_n(q) = \sum_m \hat{\Lambda}_{nm} \chi_m(q)
\]

The BO approximation implies that \( \hat{\Lambda}_{nm} = 0 \) for \( n \neq m \).

\[
\hat{\Lambda}_{nm} = \sum_i \frac{\hbar^2}{M_i} \langle \phi_n | \frac{\partial \phi_m}{\partial q_i} \rangle \frac{\partial}{\partial q_i} - \langle \phi_n | T_N | \phi_m \rangle
\]

\[
\langle \phi_n | \frac{\partial \phi_m}{\partial q_i} \rangle = \frac{\langle \phi_n | \frac{\partial H_{el}}{\partial q_i} | \phi_m \rangle}{V_m(q) - V_n(q)} \rightarrow \infty \quad \text{pour} \quad V_m(q) \rightarrow V_n(q)
\]

The BO approximation is no more valid when two or more adiabatic electronic states are close in energy. (Vibronic coupling).
Conical intersections

- CIs correspond to particular topologies of potential energy surfaces:
  - adiabatic states are degenerate along the intersection seam $\rightarrow$ kinetic couplings diverge.
  - (quasi)diabatic representation is appropriate for quantum dynamics:

$$
H = T_N 1 + \begin{pmatrix}
    V_1(q) - \hat{\Lambda}_{11} & -\hat{\Lambda}_{12} \\
    -\hat{\Lambda}_{21} & V_2(q) - \hat{\Lambda}_{22}
\end{pmatrix}
$$

$$
\hat{\Lambda}_{nm} \rightarrow \infty \quad \text{for} \quad V_n(q) \rightarrow V_m(q)
$$

$\downarrow$ adiabatic towards diabatic: $\psi = S \phi$ $\downarrow$

$$
H = T_N 1 + \begin{pmatrix}
    W_{11}(q) & W_{12}(q) \\
    W_{21}(q) & W_{22}(q)
\end{pmatrix}
$$

Intersection space: hypersurface $(N_{vib} -2)$
Importance – abundance

Importance
- ultrafast non-radiative transitions (fs – ps)
- role in many photoinduced processes:
  - photo-induced charge transfer
  - photo-isomerization
  - electronic and vibrational relaxation, ...

Abundance
- exists already in triatomics (NO$_2$, O$_3$, H$_3$)
- have been found in
  - biomolecules: GFP, DNA bases, retinal chromophore,...
  - astrophysics: cumulenes,...
  - molecular switches: e.g. based on azobenzene chromophore, stilbene,...
  - polymer hetero-junctions
  - JT and PJT effects: fullerene, nanotubes,...

Abundance grows with the size of the molecular system → more difficult to describe
Vibronic coupling model

Expand the (generally smooth) potential energy matrix elements in a Taylor series about a reference geometry:

\[
W_{nn}(\mathbf{q}) = E_\alpha + V_0(\mathbf{q}) + \sum_i (\kappa_i^n q_i + \sum_j g_{ij}^n q_i q_j + \ldots)
\]

\[
W_{n \neq m}(\mathbf{q}) = \sum_i (\lambda_i^{(nm)} q_i + \ldots)
\]


Quantum dynamics:
limited to 20-25 modes for 2 electronic states / 10-12 for 5 electronic states.
(Multi-Configuration Time-Dependent Hatree -MCTDH)
→ large systems
Extended model Hamiltonian

large systems ⇔ many vibrational modes
treated as \textbf{SYSTEM-ENVIRONMENT} complexes

\textbf{SYSTEM} = a few modes supposed to dominate the dynamics.

- Hamiltonian of the complex (diabatic) : \( H = H_S + H_B \)

\begin{itemize}
  \item \textbf{SYSTEM} \((N_S \text{ modes})\):
  \[ H_S = \begin{pmatrix}
  E_1 + T_S + W_{11}(q_S) & W_{12}(q_S) \\
  W_{21}(q_S) & E_2 + T_S + W_{22}(q_S)
  \end{pmatrix} \]

  \item \textbf{ENVIRONMENT} \((N_B \text{ modes})\):
  \[ H_B = \sum_{i=1}^{N_B} \frac{\omega_i}{2} \left( p_i^2 + q_i^2 \right) 1 + \begin{pmatrix}
  \sum_{i=1}^{N_B} \kappa_i^{(1)} q_i & \sum_{i=1}^{N_B} \lambda_i q_i \\
  \sum_{i=1}^{N_B} \lambda_i q_i & \sum_{i=1}^{N_B} \kappa_i^{(2)} q_i
  \end{pmatrix} \].
\end{itemize}

- transform the Hamiltonian of the environment.
Effective Hamiltonian

Unitary transformation (\( q = TQ \)): \( H_B \to H_1 + H_{r1} \)

- **effective Hamiltonian** \( H_1 \) (3 modes):

\[
H_1 = \sum_{i=1}^{3} \frac{\Omega_i}{2} (P_i^2 + Q_i^2) 1
\]

\[
= \left( \begin{array}{ccc}
\bar{\kappa}^{(1)} & \sum_{i=1}^{3} K_i^{(1)} Q_i & \bar{\lambda} \sum_{i=1}^{3} \Lambda_i Q_i \\
\bar{\lambda} \sum_{i=1}^{3} \Lambda_i Q_i & \bar{\kappa}^{(2)} & \sum_{i=1}^{3} K_i^{(2)} Q_i \\
\sum_{i=1}^{3} K_i^{(2)} Q_i & \end{array} \right)
\]

with \( \bar{\kappa}^{(1,2)^2} = \sum_i \kappa_i^{(1,2)^2} \) and \( K_i^{(1,2)}, \Lambda_i \) orthonormalization constants.

- **residual Hamiltonian** \( H_{r1} \) (\( N_B - 3 \) modes):

\[
H_{r1} = \sum_{j=4}^{N_B} \frac{\Omega_j}{2} (P_j^2 + Q_j^2) 1 + \sum_{i=1}^{3} \sum_{j=4}^{N_B} d_{ij} (P_i P_j + Q_i Q_j) 1
\]

- \( H_{r1} \) diagonal: does not couple the electronic states.
Moments, dynamics and spectra

First approximation, we replace \( H = H_S + H_B \) by \( H_S + H_1 \).
Quantum dynamics manageable.

This approximation is related to the moments of \( H \).
- autocorrelation function: \( P(t) = \langle 0 | e^{-iHt} | 0 \rangle \).
- moments: \( P(t) = \sum_{k=0}^{\infty} \frac{(-it)^k}{k!} M_k \); \( M_k = \langle 0 | H^k | 0 \rangle \)
- spectrum: Fourier transform of \( P(t) \)

\( H_S + H_1 \) reproduce exactly the moments \( M_0, \ldots, M_3 \) of \( H \)
→ short-time dynamics and band shapes of the complex.

- short-time dynamics \( \rightarrow H_1 \) is enough
- dynamics at longer times \( \rightarrow \) include \( H_{r1} \) \((N_B - 3 \text{ modes!})\)
Hierarchy of effective Hamiltonians

- idea: constructing additional effective modes for $H_{r1}$:

$$H_{r1} = \sum_{j=4}^{N_B} \frac{\Omega_j}{2} (P_j^2 + Q_j^2) 1 + \sum_{i=1}^{3} \left[ P_i \left( \sum_{j=4}^{N_B} d_{ij} P_j \right) + Q_i \left( \sum_{j=4}^{N_B} d_{ij} Q_j \right) \right] 1$$

- thus $H_{r1}(N_B - 3) = H_2(3) + H_{r2}(N_B - 6)$

- property: $H_{r2}$ have the same mathematical form as $H_{r1}$!

- successive transformations: $H_{r2}(N_B - 6) = H_3(3) + H_{r2}(N_B - 9)$, etc.
Hierarchy of effective Hamiltonians

- full transformation of $H$:

$$H = H_S + \sum_{m=1}^{\mathcal{N}} H_m$$

with $\mathcal{N}$ the total number of effective Hamiltonians, with

$$H_1 = \sum_{i=1}^{3} \frac{\Omega_i}{2} (P_i^2 + Q_i^2) 1 + \begin{pmatrix}
\kappa^{(1)} & K^{(1)} & \lambda \Lambda_i Q_i \\
\bar{K}^{(1)} & \bar{\lambda} \sum_{i=1}^{3} \Lambda_i Q_i & \kappa^{(2)} \sum_{i=1}^{3} K_i^{(2)} Q_i
\end{pmatrix}$$

and $H_m, m > 1$,

$$H_m = \sum_{j=3(m-1)+1}^{3m} \frac{\Omega_j}{2} (P_j^2 + Q_j^2) 1 + \sum_{i=3(m-2)+1}^{3(m-1)} \sum_{j=3(m-1)+1}^{3m} d_{ij} (P_i P_j + Q_i Q_j) 1$$

- each $H_m$ is comprised of 3 effective modes only and couples to $H_{m-1}$.
- only $H_1$ couples directly to $H_S$, via the electronic subsystem.

Approach valid for $n_{el}$ states → each $H_m$ is comprised of $n_{el}(n_{el} + 1)/2$ modes
Sequential dynamics

- in practice: truncate the hierarchy at the order \( n \).

\[
H = H_S + \sum_{m=1}^{n<N} H_m
\]

- moment analysis: Using the Hamiltonian truncated at the order \( n \), \( H_S + \sum_{m=1}^{n} H_m \), suffices to reproduce exactly all the moments of \( H \) up to the order \( 2n + 1 \) included.

Analytical proof, valid for \( n_{el} \) electronic states, whatever \( H_S \) is, and for an arbitrary large value of \( N_B \). E. Gindensperger and L.S. Cederbaum, J. Chem. Phys. 127, 124107 (2007)

- sequential dynamics: each \( H_m \) comes into play at a later time than \( H_{m-1} \).
Sequential dynamics

The **HIERARCHY OF EFFECTIVE HAMILTONIANS** subsumes all the environment on a given time-scale.

- System (few modes)
- Environment (many modes)
- Primary effective modes
- Secondary effective modes

...
Illustration: model complex

- model complex: 2 states – 22 modes
  - system, $H_S$: prototype of CI (2 modes $\nu_g, \nu_u$)
  - environment, $H_B$: 20 modes (weakly coupled)
- calculations up to 22 dimensions (MCTDH).
Illustration: results
Application: FBz$^+$


- 5 lowest electronic states of the cation, $\tilde{X}^2 B_1$, $\tilde{A}^2 A_2$, $\tilde{B}^2 B_2$, $\tilde{C}^2 B_1$, $\tilde{D}^2 A_1$, (divided in two bands: $\tilde{X} - \tilde{A}$ and $\tilde{B} - \tilde{C} - \tilde{D}$).

- 30 vibrational modes $\rightarrow$ use of effective modes:
  2 system modes (tuning, for quadratic contributions) $+$ 10 effective modes (for the 28 remaining modes)
**Linear vibronic model** (I. Bâldea, et al., Chem. Phys. 329, 65 (2006)).

\[
\begin{pmatrix}
\tilde{X} & \tilde{A} & \tilde{B} & \tilde{C} & \tilde{D} \\
9.23 & 9.68 & 16.55 & 27.87 & 16.17 \\
9.68 & 13.75 & 23.89 & 15.95 & \\
12.02 & 12.25 & 12.60 & \\
12.23 & 12.48 & \\
12.48 & \\
\end{pmatrix}
\rightarrow Cl(\tilde{A} - \tilde{B}) \text{ inactive.}
\]

**Linear model augmented by quadratic contributions for totally symmetric modes**

\[
\begin{pmatrix}
\tilde{X} & \tilde{A} & \tilde{B} & \tilde{C} & \tilde{D} \\
9.22 & 9.69 & 12.84 & 30.73 & 14.40 \\
9.69 & 12.29 & 22.40 & 14.54 & \\
11.91 & 12.24 & 12.58 & \\
12.22 & 12.45 & \\
12.43 & \\
\end{pmatrix}
\rightarrow Cl(\tilde{A} - \tilde{B}) \text{ energetically accessible.}
MATI spectrum

Mass-analyzed threshold ionization spectrum, $\tilde{X} \rightarrow \tilde{A}$ band, (C. H. Kwon et al., J. Chem. Phys. 116, 10367 (2002))
Photoelectron spectrum

Population dynamics
Conclusion

- quantum dynamics through CIs manageable on a given time scale with effective modes.

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- Pr. Lorenz S. Cederbaum (Heidelberg)
- Dr. Irene Burghardt (CNRS/ENS, Paris)
- Pr. Horst Köppel (Heidelberg)
- Pr. H.-Dieter Meyer (Heidelberg): MCTDH
- Dr. S. Faraji (Heidelberg / Frankfurt)

Thank you!