From Electronic Structure Theory to Simulating Electronic Spectroscopy

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Electronic Structure Methods for Excited States:

**General Multireference Methods:** Require expertise …

- CASPT2 / MR-PT: Many applications to sizeable molecules.
- MR-CI: *The* method for potential energy surfaces.

**Response methods:** Black box,

Applicable if well-behaved reference state.

- CIS, RPA
- TD-DFT: Choice of functionals; Not always reliable.
- CC-LRT / EOM-CC: Systematic accuracy, but rather expensive.
- SAC-CI: Widely applicable; additional approximations compared to CC.
- STEOM / FSCC: Efficient, but not quite as systematic as EOM-CC.
- Spin-Flip approaches.
## What is Calculated?

**Vertical transitions, e.g. ethylene:**

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</table>
What is measured?

**Ethylene:**
Two lowest states

Hudson et al.
Beyond vertical excitation energies for “sizeable” molecules:

Some type of “Harmonic” approximation to potential energy surfaces is required.

- Franck-Condon Approach: single surface.

- Non-adiabatic vibronic models: multiple surfaces.
What is best expansion point for harmonic approximation?

At equilibrium geometry of the absorbing state?

At equilibrium geometry of the excited state?

True excited state PES

Ground state PES
Potential problem with adiabatic FC: Excited state minimum may not exist!

Cationic states of ethylene along symmetric and asymmetric mode

Surfaces along symmetric mode
The broad features of the spectrum are obtained in a short time $T$.

\[ |\Phi_{ex}(q,t)\rangle = e^{-iH_{ext}t} \hat{X} |\Phi_0(q)\rangle \]

\[ P(\omega,T) = \int_{-T}^{T} \omega \langle \Phi_0(q)|\hat{X}|\Phi_{ex}(q,t)\rangle e^{i\omega t} dt \]
Going beyond the strict harmonic approximation in vertical FC

The treatment of double well potentials:

Potential energy surfaces of ethylene cationic states along torsion mode.
General 1-d Vertical Franck-Condon:

\[
\hat{H}_{ex} = \sum_{i \in \text{harmonic}} \hat{h}_{\text{harm}}(\tilde{q}_i) + \sum_{j \in \text{general}} \hat{h}_{\text{gen}}(\tilde{q}_j)
\]

\[
\hat{h}_{\text{harm}} \phi_n(\tilde{q}_i) = \omega_n \phi_n(\tilde{q}_i) \quad \hat{h}_{\text{gen}} \psi_n(\tilde{q}_j) = \epsilon_n \psi_n(\tilde{q}_j)
\]

How to calculate general Franck-Condon factors?

\[
\left\langle \phi_0(q_1)\phi_0(q_2)\ldots\phi_0(q_M)\left| \phi_n(\tilde{q}_1)\psi_m(\tilde{q}_2)\ldots\phi_z(\tilde{q}_M) \right. \right\rangle
\]

Introduce intermediate harmonic basis \( \left| \phi_n(\tilde{q}_j) \right\rangle \), \( \omega_n \) for trouble modes \( j \)

\[
\left| \psi_n(\tilde{q}_j) \right\rangle = \sum_k \left| \phi_k(\tilde{q}_j) \right\rangle \left\langle \phi_k(\tilde{q}_j) \left| \psi_n(\tilde{q}_j) \right. \right\rangle
\]

Calculate FC factors in intermediate, fully harmonic basis.
Transform FC factors to true basis states and obtain spectrum.

*General 1-d potentials, but decoupled in excited state normal modes.*
Ethylene UV absorption spectrum

Ethylene lowest Rydberg state PES along torsion mode

Harmonic approximation at ground state equilibrium geometry

Actual potential from electronic structure calculation
Ethylene Rydberg state:
Vertical Franck-Condon spectrum

Symmetric modes only. Harmonic vertical FC.

Torsion mode included General vertical FC.
Ethylene Valence state: Vertical Franck-Condon spectrum

Symmetric modes only.  
Harmonic vertical FC.  

Torsion mode included.  
General vertical FC.
Ethylene: Two lowest states

Experiment

General VFC calculation
STEOM-CC electronic structure
Summary Franck-Condon

- **Adiabatic Harmonic Franck-Condon:**
  - Optimize excited state geometries and frequencies.
  - Suitable for 0-0 transitions (if they exist !!).
  - Less appropriate for excitation spectra.

- **General 1-d Vertical Franck-Condon:**
  - No geometry optimization of excited states.
  - Requires full 1-d potentials for normal modes with negative force constants at ground state geometry.
  - Applicable only, if no degeneracies at ground state geometry.

*Electronic structure calculations* determine computational costs.
The FC calculations themselves take negligible computer time.
Beyond Born-Oppenheimer: Vibronic models

• Short-time dynamics picture:

\[ P(\omega, T) = \int_{-T}^{T} \omega \langle \Phi_0(q) | \hat{X} e^{-iT\hat{H}} \hat{X} | \Phi_0(q) \rangle e^{i\omega t} dt \]

Requires accurate time-dependent wave-packet in Condon-region, for limited time.

Use multiple-surface model Hamiltonian \( \hat{H} \) that is accurate near absorbing state geometry.

E.g. Two-state Hamiltonian with symmetric and asymmetric mode

\[ \hat{H} = \begin{bmatrix}
  E_1 + \hat{h}_1^{\text{harm}} + k_s^1 q_s & k_a q_a \\
  k_a q_a & E_2 + \hat{h}_2^{\text{harm}} + k_s^2 q_s
\end{bmatrix} \]
Comparison of model FC and vibronic calculations

O=C=O symmetric and asymmetric stretch included.
Methane Photo-electron spectrum
Fully quadratic vibronic model
Calculating coupling constants in vibronic model

Construct model potential energy matrix in diabatic basis:

\[ V_{ab}(\mathbf{q}) = E_a \delta_{ab} + \sum_i E_{ab}^i \hat{q}_i + \frac{1}{2} \sum_i E_{ab}^{ij} \hat{q}_i \hat{q}_j \]

- Calculate geometry and harmonic normal modes of absorbing state.
- Calculate "excited" states in set of displaced geometries along normal modes.
- From adiabatic states construct set of diabatic states:
  - Minimize off-diagonal overlap:
    \[ \langle \Phi_a(\Delta \mathbf{q}) | \Psi_\mu(\mathbf{0}) \rangle = \sum_{\lambda} c_{a\lambda}(\Delta \mathbf{q}) \langle \Psi_{\lambda}(\Delta \mathbf{q}) | \Psi_\mu(\mathbf{0}) \rangle \]
  - Obtain non-diagonal diabatatic \( V_{ab}(\Delta q) \)
- Use finite differences to obtain linear and quadratic coupling constants.
- Impose Abelian symmetry.
Advantages of vibronic model in diabatic basis

• "Minimize" non-adiabatic off-diagonal couplings.
• Generate smooth Taylor series expansion for diabatic matrix. The adiabatic surfaces can be very complicated.
• No fitting required; No group theory.
• Fully automated / routine procedure.

• Model Potential Energy Surfaces  ⟷  Franck-Condon models.

• Solve for vibronic eigenstates and spectra in second quantization.
  Lanczos Procedure:
  - Cederbaum, Domcke, Köppel, 1980's
  - Stanton, Sattelmeyer: coupling constants from EOMCC calculations.
  - Nooijen:
    Automated extraction of coupling constants in diabatic basis.
    Highly efficient Lanczos for many electronic states.
Vibronic calculation in Second Quantization

\[ \hat{q}_i = \frac{1}{\sqrt{2}} (\hat{b}_i + \hat{b}^+_i) \quad \quad \quad \hat{T}_N + \frac{1}{2} \sum_i k_i q_i^2 \rightarrow \varepsilon_0 + \sum_i \omega_i b_i^+ b_i \]

- 2 x 2 Vibronic Hamiltonian (linear coupling)

\[ \hat{H} = \begin{pmatrix} E_1 + \varepsilon_0 & 0 \\ 0 & E_2 + \varepsilon_0 \end{pmatrix} + \sum_i \begin{pmatrix} \omega_i \hat{b}^+_i \hat{b}_i + \lambda_{11}^i \hat{q}_i & \lambda_{12}^i \hat{q}_i \\ \lambda_{12}^i \hat{q}_i & \omega_i \hat{b}^+_i \hat{b}_i + \lambda_{22}^i \hat{q}_i \end{pmatrix} \]

- Vibronic eigenstates \( |\Psi\rangle = \sum_{a,i,j,...,m} c_{i,j,...,m}^a |n_i,n_j,...,n_m\rangle \)

- Total number of basis states \( M_i M_j ... M_m \cdot N_a \)

- Dimension grows very rapidly (but a few million basis states can be handled easily).

- Efficient implementation: rapid calculation of \( HC \)
The many-electron problem for ground and excited states.

Elementary approach to electron correlation: **Configuration Interaction (CI).** "Diagonalize Hamiltonian over subset of configurations."

Hartree Fock: $|\Phi_0\rangle$

Single excitations: $|\Phi_i^a\rangle = \hat{a}^\dagger i |\Phi_0\rangle$

Double excitations: $|\Phi_{ij}^{ab}\rangle = \hat{a}^\dagger \hat{b}^\dagger j |\Phi_0\rangle$

\[
\begin{array}{cccccc}
0 & S & D & T & Q \\
0 & x & x & x & 0 & 0 \\
S & x & x & x & x & 0 \\
D & x & x & x & x & x \\
T & 0 & x & x & x & x \\
Q & 0 & 0 & x & x & x \\
\end{array}
\]

CI Hamiltonian:

Ground state: At least include singles and doubles.  
Singly excited states: Include up to (selected) triples!
**Coupled Cluster theory for ground states:**

Exponential parameterization: 
\[ |\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle = (1 + \hat{T} + \frac{1}{2} \hat{T}^2 + ...) |\Phi_0\rangle \]
\[ \hat{T} = \hat{T}_1 + \hat{T}_2 + ... = \sum_{i,a} t_i^a \hat{a}^\dagger_i + \frac{1}{4} \sum_{i,j,a,b} t_{ab}^{ij} \hat{a}^\dagger_i \hat{b}^\dagger_j + ... \]

Coupled Cluster equations: 
\[ \hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{\hat{T}} |\Phi_0\rangle \]
\[ e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = e^{-\hat{T}} E e^{\hat{T}} |\Phi_0\rangle = E |\Phi_0\rangle \]

Transformed Hamiltonian: 
\[ \hat{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \]

Hartree Fock \( |\Phi_0\rangle \) eigenstate of \( \hat{H} \) with “exact” energy \( E \)

CCSD equations: 
\[ \langle \Phi_{i}^{a} | \hat{H} | \Phi_{0}\rangle = \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{0}\rangle = 0 \]

*Highly accurate method, especially CCSD(T), Size-consistent*
**Equation of Motion Coupled Cluster theory:**
*electronically excited states.*

"Configuration Interaction" using the transformed Hamiltonian \( \hat{H} = e^{-\hat{t}} \hat{H} e^{\hat{t}} \)

CCSD equations: \( \overline{h}_a^i = \overline{h}_{ab}^{ij} = 0 \)

<table>
<thead>
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**EOM-CCSD Hamiltonian**

**EOM-CC: Much improved accuracy compared to CI**
Similarity Transformed EOM-CCSD (STEOM).

One more transformation of the Hamiltonian

\[ G = \left\{ e^{\hat{S}} \right\}^{-1} e^{-\hat{t}} \hat{H} e^{\hat{t}} \left\{ e^{\hat{S}} \right\} \]

\[ \hat{S} = \frac{1}{2} \sum_{a,b,e} s_{ab}^{ie} \left\{ \hat{a}^{\dagger} \hat{b}^{\dagger} \hat{e} \right\} + \frac{1}{2} \sum_{i,j,a,m} s_{am}^{ij} \left\{ \hat{a}^{\dagger} \hat{m}^{\dagger} \hat{j} \right\} \]

Solve for \( \hat{S} \) such that \( g_{ab}^{ie} = g_{am}^{ij} = 0 \)

\[
\begin{array}{cccccc}
0 & S & D & T & Q \\
0 & E & x & x & 0 & 0 \\
S & 0 & x & x & x & 0 \\
D & 0 & ~ & x & x & x \\
T & ~ & ~ & ~ & x & x \\
Q & ~ & ~ & ~ & ~ & x \\
\end{array}
\]

STEOM Hamiltonian:

STEOM-CC: Diagonalize \( G \) over single excited states only!
Extended STEOM: Diagonalize \( G \) over single and double excited states.
Comparison Full CI / (Extended) STEOM for CH₂

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<td>94%</td>
<td>95%</td>
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</table>
UV absorption spectrum of ketene: \( \text{CH}_2=\text{C}=\text{O} \)

Lowest \( A_1 \) Rydberg state

Adiabatic

Franck-Condon

Vibronic
UV absorption spectrum of ketene

Four higher-lying Rydberg states

Adiabatic
Franck-Condon
Vibronic
Absorption into 1 B2 state at 8.00 eV

Absorption into 4 B1 state at 8.00 eV

Absorption into 4 A1 state at 8.15 eV

Absorption into 3 A1 state at 7.73 eV

Relative Intensity

Absorption Energy (nm)
Summary

- Vibronic models are a convenient tool to simulate electronic spectra.
- Coupling constants that define the vibronic model can routinely be obtained from electronic structure calculations & diabatization procedure.

- Full Lanczos diagonalizations can be very expensive. Hard to converge.

- Vibronic model defines electronic surfaces:
  - Can be used in (vertical and adiabatic) Franck-Condon calculations.
  - No geometry optimizations; No surface scans.

- Other possibilities to use vibronic models (in the future):
  - Investigate short-time photochemical processes.
  - Resonance Raman processes and other spectroscopies.
  - Studies of transition metal chemistry.
  - Coupling constants from Amsterdam Density Functional program.
Anirban Hazra    Hannah Chang    Alexander Auer

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