

Excited States with Time-Dependent Density Functional Theory and with Linear Vibronic Coupling Models

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Time-dependent density functional theory

What are people using to compute excited states?

Time-dependent density functional theory: Foundations

Regular DFT only works for a non-degenerate ground state,
based on the scope of the Hohenberg–Kohn theorems.

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Theoretical foundation of TDDFT:

- ▶ 1. Runge–Gross theorem: Correspondence between TD electron density $\rho(\vec{r}, t)$ and TD external potential.
- ▶ 2. Runge–Gross theorem: Least action principle, giving hints how the TD electron density should evolve.

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Thus, TDDFT is formally possible. It requires a TD functional, which has some additional requirements versus the Hohenberg–Kohn functional. E.g.,

- ▶ Causality (between external perturbation and density)
- ▶ Time non-locality (memory effect)
- ▶ Spatial non-locality (formally, local density approximation is incorrect in TDDFT)

Huix-Rotllant, Ferré, Barbatti: “Time-Dependent Density Functional Theory” in “Quantum Chemistry and Dynamics of Excited States” by González, Lindh (2021).

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Usually, TDDFT is based on the Kohn–Sham approach.

Time-dependent density functional theory: Kohn–Sham

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TD density taken as density of TD KS determinant:

$$\rho(\vec{r}, t) = \sum_i f_i |\phi_i(\vec{r}, t)|^2 \quad (1)$$

Time evolution according to TD-KS equations:

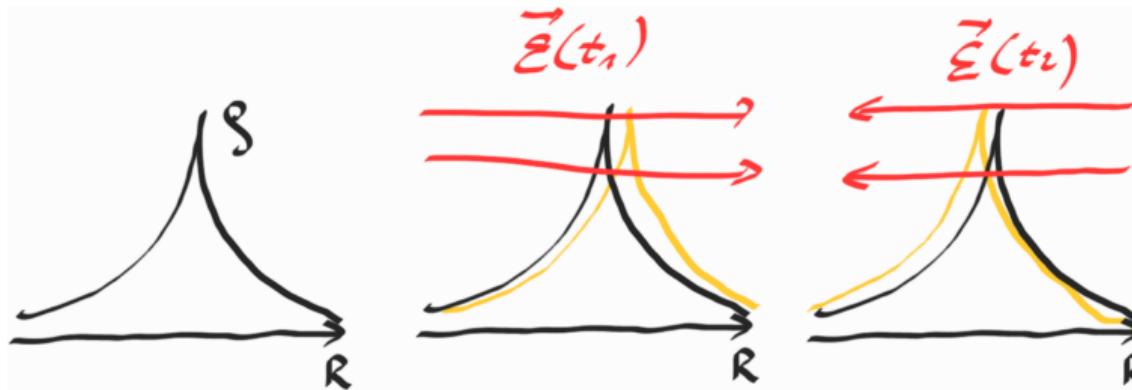
$$i\hbar \frac{\partial}{\partial t} \phi_i(\vec{r}, t) = \hat{h}^{\text{KS}}[\rho] \phi_i(\vec{r}, t) \quad (2)$$

Here, $\hat{h}^{\text{KS}}[\rho]$ should depend on $\rho(t') \forall t' \leq t$. In practice, it usually only depends on $\rho(t)$, called the **adiabatic local density approximation (ALDA)**.

Time-dependent density functional theory: Solving the TD Kohn–Sham equations

The first way to solve the TD-KS problem is real-time TDDFT (**RT-TDDFT**):

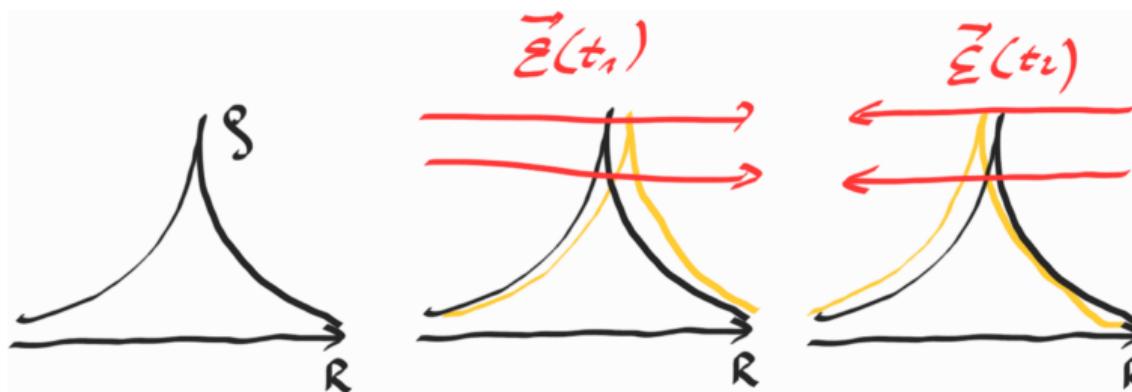
- ① Start with the initial electron density
- ② Introduce a periodic oscillating perturbing electric field $\vec{\mathcal{E}}(t) = \vec{\mathcal{E}}_0 \cos(\omega t)$
- ③ Simulate the temporal evolution of the electron density numerically
- ④ Obtain spectroscopic information from the Fourier transformation of the dipole moment autocorrelation function.



Time-dependent density functional theory: Solving the TD Kohn–Sham equations

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Very flexible (for weak and strong fields, good scaling with system size) but generally demanding.

Time-dependent density functional theory: Solving the TD Kohn–Sham equations

The second way to solve the TD-KS problem is linear-response TDDFT (**LR-TDDFT**):

- ① For weak external perturbations, use response theory in frequency domain
- ② Derivation: Start at linear density $\delta\rho(t)$, Fourier transform to frequency domain, derive response function, solve for poles of response function
- ③ This leads to the Casida LR-TDDFT equation:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \vec{\dot{X}} \\ \vec{\dot{Y}} \end{pmatrix} = \omega \begin{pmatrix} \vec{\dot{X}} \\ \vec{\dot{Y}} \end{pmatrix} \quad (3)$$

where matrices \mathbf{A} and \mathbf{B} have matrix elements:

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \iint \phi_i^*(r)\phi_a(r) \left[\frac{1}{|r - r'|} + \hat{f}_{xc} \right] \phi_b^*(r')\phi_j(r') dr dr' \quad (4)$$

$$B_{ia,jb} = \iint \phi_i^*(r)\phi_a(r) \left[\frac{1}{|r - r'|} + \hat{f}_{xc} \right] \phi_j^*(r')\phi_b(r') dr dr' \quad (5)$$

Time-dependent density functional theory: LR-TDDFT

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} \quad (6)$$

Some notes:

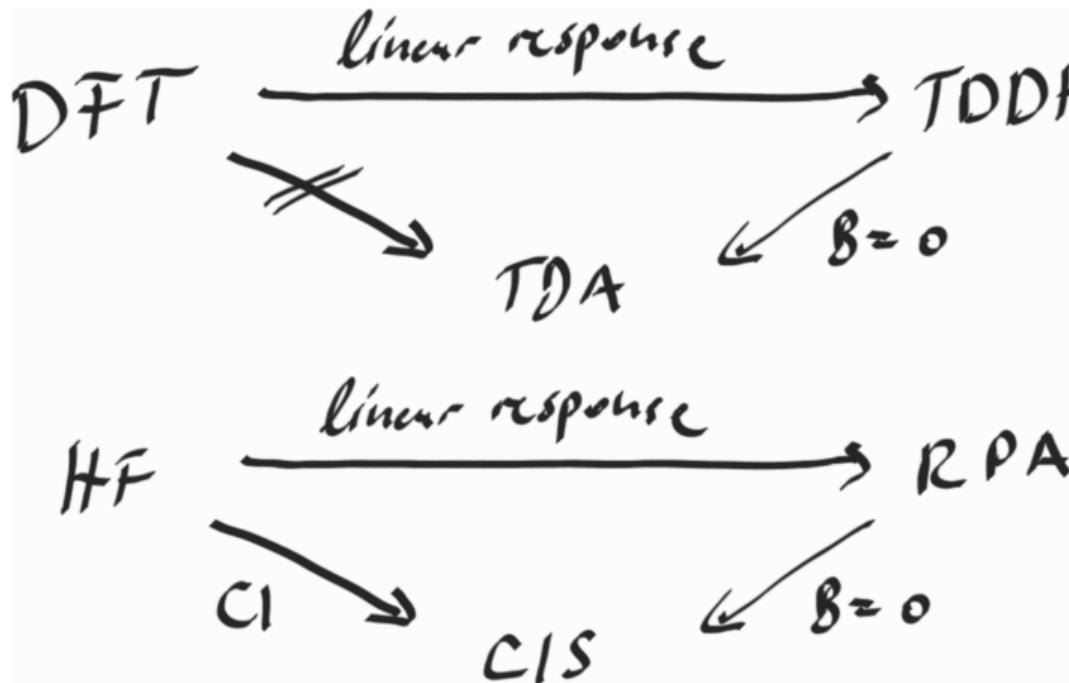
- ▶ \mathbf{A} and \mathbf{B} are formally depending on ω , but not when using the ALDA. This approximation is present in most TDDFT implementations.
- ▶ The equation has many eigenvalues ω that are the excitation energies of the system.
- ▶ For each ω , there will be a pair of \vec{X} and \vec{Y} vectors that describe the response of the density:

$$\delta\rho(r) = \sum_{ia} X_{ia} \phi_a^*(r) \phi_i(r) + Y_{ia} \phi_a(r) \phi_i^*(r) \quad (7)$$

- ▶ Here, the vector \vec{X} describes excitations $i \rightarrow a$ and \vec{Y} describes deexcitations $i \leftarrow a$.
- ▶ Often used is the Tamm-Dancoff approximation (**TDA**) that sets $\mathbf{B} = 0$ and thus $\vec{Y} = 0$:

$$\mathbf{A}\vec{X} = \omega\vec{X}. \quad (8)$$

Time-dependent density functional theory: Connection to HF and CIS



Starting from KS-DFT:

- ▶ derive LR-TDDFT via LR theory
- ▶ derive TDA from LR-TDDFT
- ▶ cannot go from KS-DFT directly to TDA

Starting from HF:

- ▶ derive RPA via LR theory
- ▶ derive CIS from RPA
- ▶ can also derive CIS directly via linear variational principle

TDDFT: How good is it? General points

These points are valid for LR-TDDFT with the ALDA (most TDDFT calculations):

- ▶ TDDFT naturally depends on the reference state, hence on the used XC functional
- ▶ Errors in the excitation energy are usually up to ± 0.5 eV, in good cases ± 0.2 eV
- ▶ Pure functionals tend to give too low excitation energies
- ▶ More sophisticated functionals tend to give better results:
LDA < GGA < Hybrid < Range-separated hybrid < Double hybrid

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The accuracy is also strongly dependent on the type of excitation:

- ▶ **Local excitations** ($n\pi^*$, $\pi\pi^*$, metal centered, ...): Often good with hybrids.
- ▶ **Rydberg excitations**: Often rather bad with errors $\gg 0.5$ eV (due to self-interaction error and too low ionization potentials).
- ▶ **Charge transfer excitations** (e.g., push–pull compounds or metal complexes): Requires range-separated hybrids, otherwise appear much too low and spurious ghost states appear. Can be identified by having little hole–electron overlap.
- ▶ **Core excitations** (for X-ray spectra): Similar to CT excitations, can be handled with empirical shifts, or with range-separated hybrids.
- ▶ **Higher excitations**: Can be very wrong, due to the neglect of doubly/higher excited determinants and the too low ionization potential of DFT.

- ▶ If DFT does not work, then TDDFT does not work
- ▶ Degenerate ground states: open-shell metal complexes, ...
- ▶ Degenerate ground states are also encountered in many dissociations

Problems in dissociation (attributed to KS-DFT, not TDDFT):

- ▶ RKS keeps electrons in pairs, precluding homolytic dissociation
- ▶ UKS allows unpaired electrons, but is spin-contaminated (very heavily in dissociation)

A conical intersection is a region where two PESs touch each other. They have a special, important topology:

$$\mathbf{H}^{\text{diab}}(x, y) = \begin{pmatrix} H_{11}(x, y) & H_{12}(x, y) \\ H_{12}(x, y) & H_{22}(x, y) \end{pmatrix} = \begin{pmatrix} x & y \\ y & -x \end{pmatrix}, \quad \mathbf{H}^{\text{adia}}(x, y) = \begin{pmatrix} -\sqrt{x^2 + y^2} & \\ & \sqrt{x^2 + y^2} \end{pmatrix}. \quad (9)$$

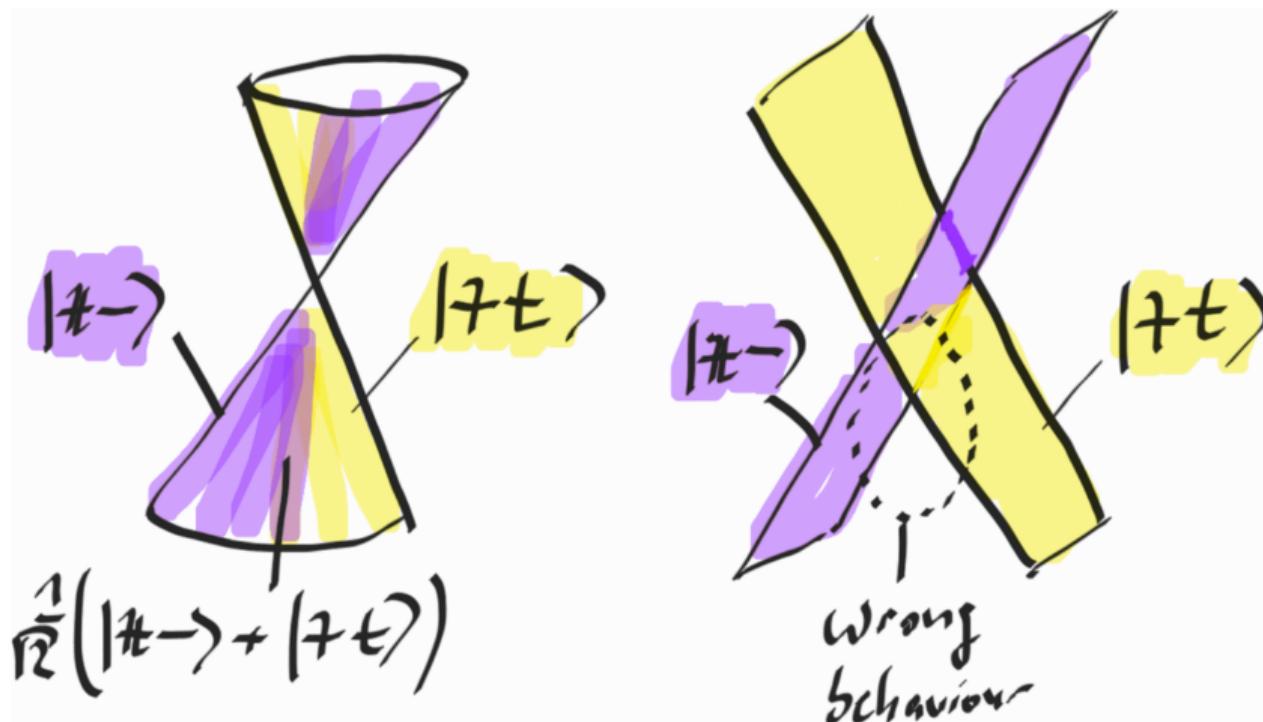
Conical intersection forms when two conditions hold along two different DOFs:

- ▶ $H_{11} = H_{22}$: here at $x = 0$
- ▶ $H_{12} = 0$: here at $y = 0$

In TDDFT there are two problems:

- ▶ If $H_{11} = H_{22}$, then KS-DFT is not well-defined and can produce instabilities.
- ▶ In TDDFT, the ground state is artificially fixed to one KS determinant and never mixes with the excited states. Hence, there is no coupling and $H_{12} = 0$ everywhere (not only at $y = 0$).

TDDFT: How good is it? Conical intersections II



TDDFT for nonadiabatic dynamics:

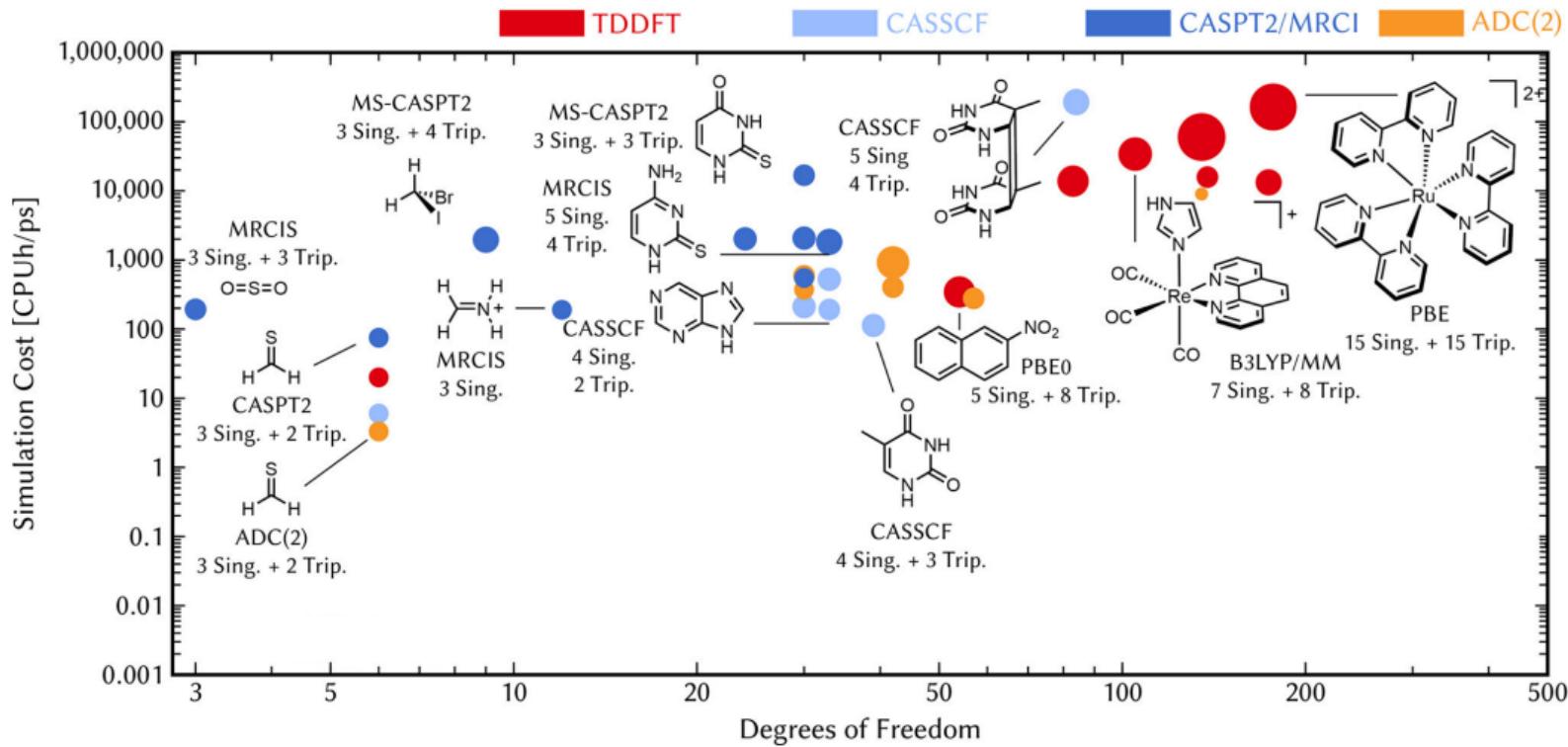
- ▶ Is one of the cheapest, easiest to use, most available methods
- ▶ Produces reasonable PESs for many cases
- ▶ Avoid transitions between TDDFT states and reference state (general caveat for single-reference methods)
- ▶ Pay attention to the system and kinds of states, choose functional wisely
- ▶ Avoid dissociation or extreme deformation of the molecule

Example of what works well:

- ▶ Dynamics that start in S_n , relaxes to S_1 , and then undergoes ISC to T_n and later to T_1

TDDFT: Computational cost of nonadiabatic dynamics

Computational Cost of Surface Hopping Simulations

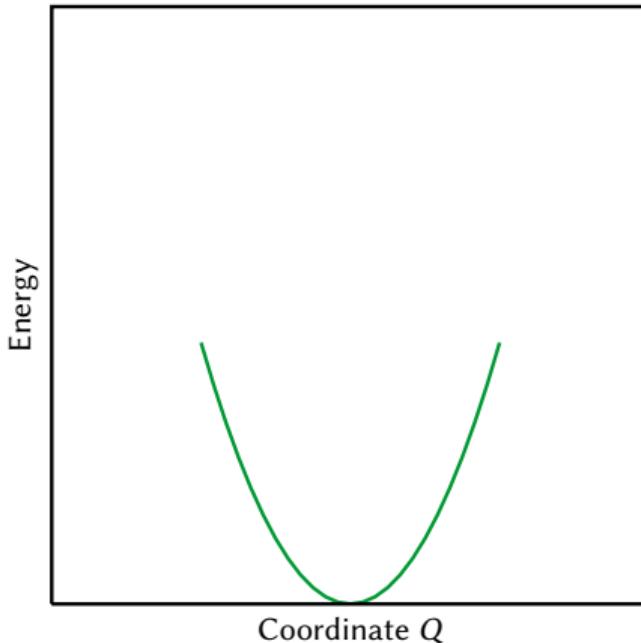


Linear vibronic coupling models

What can we do when ab initio methods are too expensive?

Linear vibronic coupling model

$$H = \left(\frac{\omega}{2} Q^2 \right) + \left(\quad \right)$$



Linear vibronic coupling (LVC)

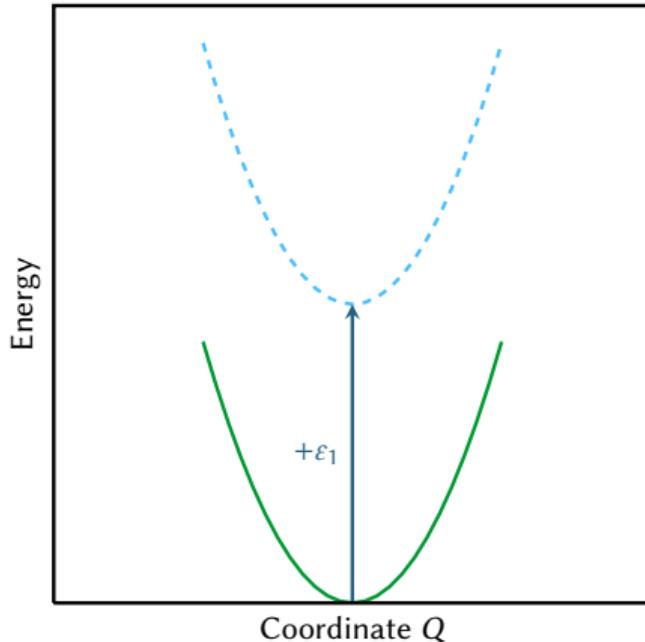
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Penfold et al., *Chem. Rev.* **118**, 6975 (2018).

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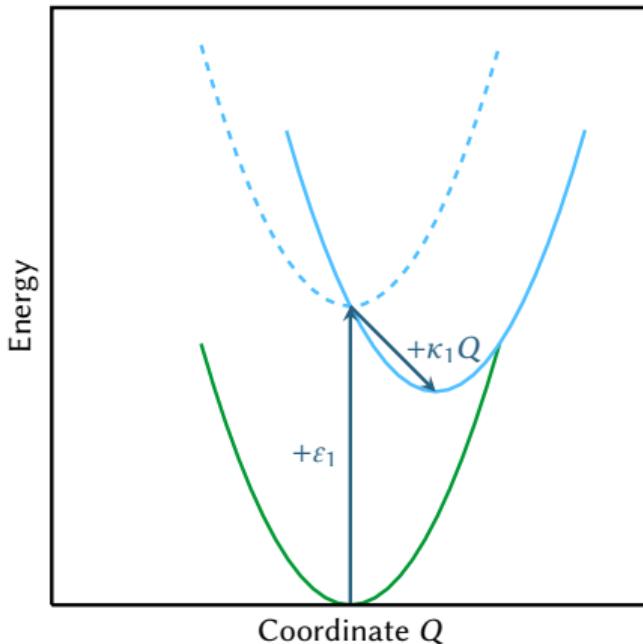
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$$H = \begin{pmatrix} \frac{\omega}{2} Q^2 & 0 \\ 0 & \varepsilon_1 + \kappa_1 Q \end{pmatrix}$$



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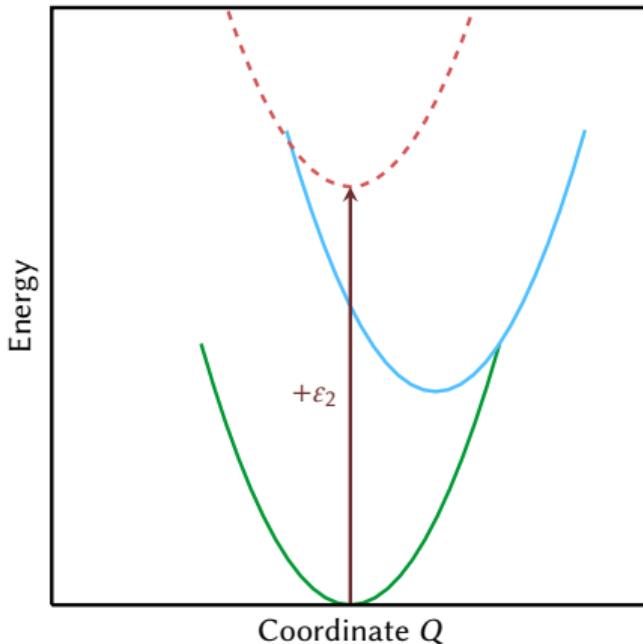
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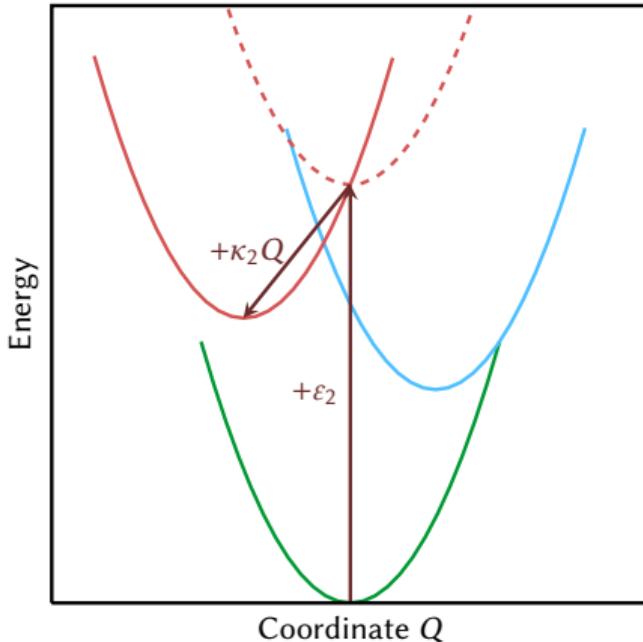
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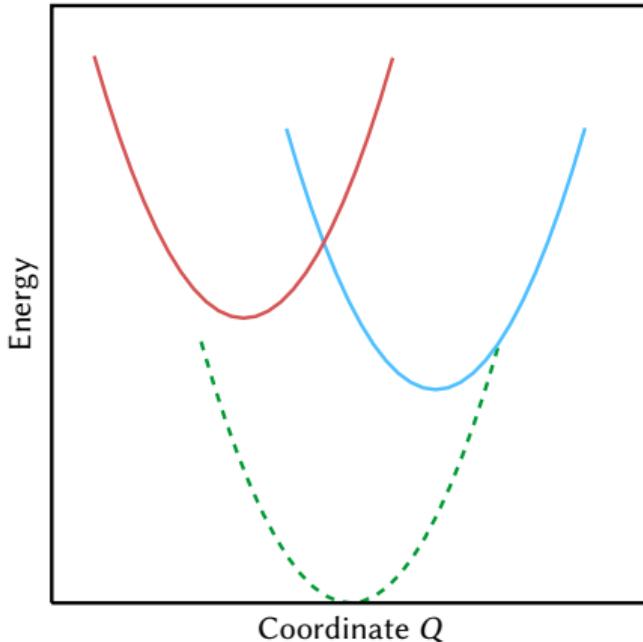
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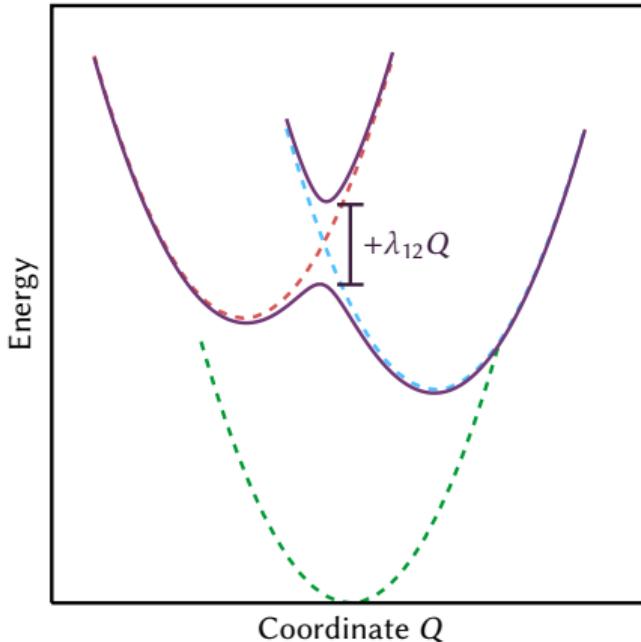
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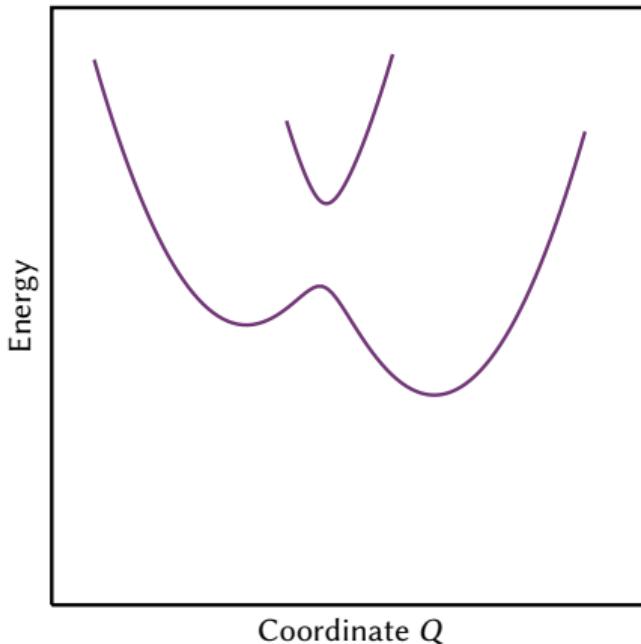
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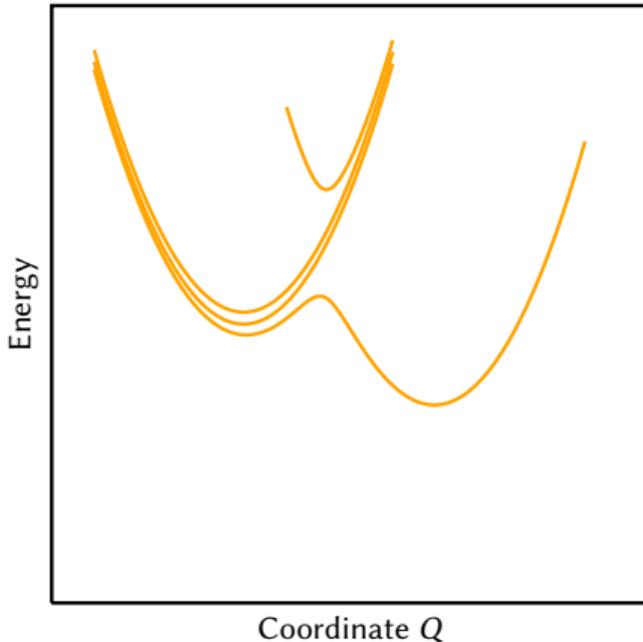
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- ▶ ... to get adiabatic states!

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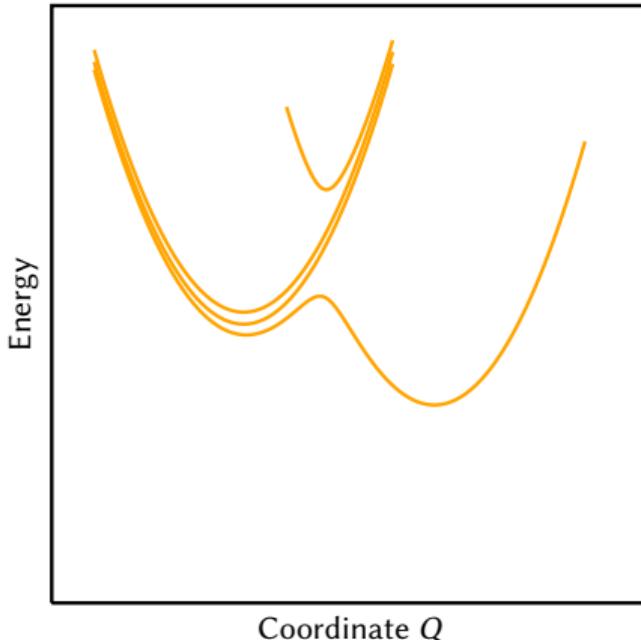
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- + Speed up: 3–5 orders of magnitude vs. ab initio
- Only for rigid molecules and short time scales

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Linear vibronic coupling model: Multidimensional models

$$\mathbf{H}^{\text{diab}}(\vec{Q}) = \underbrace{\sum_i Q_i^2 \frac{\omega_i}{2} \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ & & & \ddots \end{pmatrix}}_{\text{harmonic oscillator}} + \underbrace{\begin{pmatrix} \varepsilon^1 & & & \\ & \varepsilon^2 & & \\ & & \varepsilon^3 & \\ & & & \ddots \end{pmatrix}}_{\text{vertical shifts}} + \underbrace{\sum_i Q_i \begin{pmatrix} \kappa_i^1 & & & \\ & \kappa_i^2 & & \\ & & \kappa_i^3 & \\ & & & \ddots \end{pmatrix}}_{\text{gradients}}$$
$$+ \underbrace{\sum_i Q_i \begin{pmatrix} \lambda_i^{12} & \lambda_i^{13} & \dots \\ \lambda_i^{23} & \lambda_i^{23} & \dots \\ \lambda_i^{13} & \lambda_i^{23} & \ddots \end{pmatrix}}_{\text{linear couplings}} + \underbrace{\begin{pmatrix} \eta^{12} & \eta^{13} & \dots \\ \eta^{23} & \eta^{23} & \dots \\ \eta^{13} & \eta^{23} & \ddots \end{pmatrix}}_{\text{constant couplings}} + \underbrace{\sum_d \mathcal{E}_d \begin{pmatrix} \mu_d^{11} & \mu_d^{12} & \mu_d^{13} & \dots \\ \mu_d^{12} & \mu_d^{22} & \mu_d^{23} & \dots \\ \mu_d^{13} & \mu_d^{23} & \mu_d^{33} & \dots \\ \vdots & & & \ddots \end{pmatrix}}_{\text{electric field-dipole couplings}}$$

Superscripts: indices of diabatic states, subscripts: normal modes.

Linear vibronic coupling model: Multidimensional models

$$\mathbf{H}^{\text{diab}}(\vec{Q}) = \sum_i Q_i^2 \frac{\omega_i}{2} \underbrace{\begin{pmatrix} 1 & & \\ & 1 & \\ & & \ddots \end{pmatrix}}_{\text{harmonic oscillator}} + \underbrace{\begin{pmatrix} \varepsilon^1 & & \\ & \varepsilon^2 & \\ & & \varepsilon^3 \\ & & & \ddots \end{pmatrix}}_{\text{vertical shifts}} + \sum_i Q_i \underbrace{\begin{pmatrix} \kappa_i^1 & & \\ & \kappa_i^2 & \\ & & \kappa_i^3 \\ & & & \ddots \end{pmatrix}}_{\text{gradients}}$$

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Superscripts: indices of diabatic states, subscripts: normal modes.

Definition of normal mode coordinates:

$$Q_i = \sqrt{\omega_i} \sum_a^{\text{atoms}} \sum_d^3 K_{ad,i} \sqrt{M_a} (r_{ad} - r_{ad}^{\text{ref}}) \quad (10)$$

Linear vibronic coupling model: Parameters

Set of parameters for harmonic oscillators:

- ▶ Normal mode frequencies ω_i : $3N_{\text{atom}} - 6$ parameters
- ▶ Normal mode transformation matrix with elements $K_{ad,i}$: $(3N_{\text{atom}} - 6)(3N_{\text{atom}})$ parameters
- ▶ Normal mode reference geometry with coordinates r_{ad}^{ref} : $3N_{\text{atom}}$ parameters
- ▶ Atom masses M_a : N_{atom} parameters

In SHARC, these parameters are contained in the file V0.txt.

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Set of parameters for excited states:

- ▶ Vertical shifts ε^α : N_{states} parameters
- ▶ Gradient terms κ_i^α : $(3N_{\text{atom}} - 6)N_{\text{states}}$ parameters
- ▶ Linear vibronic couplings $\lambda_i^{\alpha\beta}$: $(3N_{\text{atom}} - 6)N_{\text{states}}^2$ parameters
- ▶ Constant spin-orbit couplings $\eta^{\alpha\beta}$: $N_{\text{SO states}}^2$ parameters
- ▶ Dipole moment terms $\mu_d^{\alpha\beta}$: $3N_{\text{states}}^2$

In SHARC, these parameters are contained in the file LVC.template.

Linear vibronic coupling model: Obtaining parameters

Parameters for the harmonic oscillators:

- ① Choose desired reference state (often S_0 , PES should look similar to relevant states)
- ② Optimize minimum of reference state
- ③ Do frequency calculation of reference state

The SHARC script `wigner.py` can then produce the file `V0.txt`.

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Parameters for excited states:

- ① Run a single point calculation at reference geometry:
 - ▶ Excitation energies: ε^α
 - ▶ (Transition) dipole moments: $\mu_d^{\alpha\beta}$
 - ▶ Spin-orbit couplings: $\eta^{\alpha\beta}$
 - ▶ Gradients transformed into normal mode coordinates: κ_i^α
- ② Run $6N_{\text{atom}}$ displaced single point calculations
 - ▶ Compute numerical derivatives of diabatic Hamiltonian: $\lambda_i^{\alpha\beta}$

This involves three steps, (i) using `setup_LVCparam.py`, (ii) running calculations in all created folders, (iii) using `create_LVCparam.py` to extract parameters and write the file `LVC.template`.

Complex LVC model

- ▶ Model for $n3p$ Rydberg and $\pi\pi^*$ states (grey box)
- ▶ Ab initio level of theory:
SOS-ADC(2)/cc-pVTZ
+aug(10s8p6d4f) on O

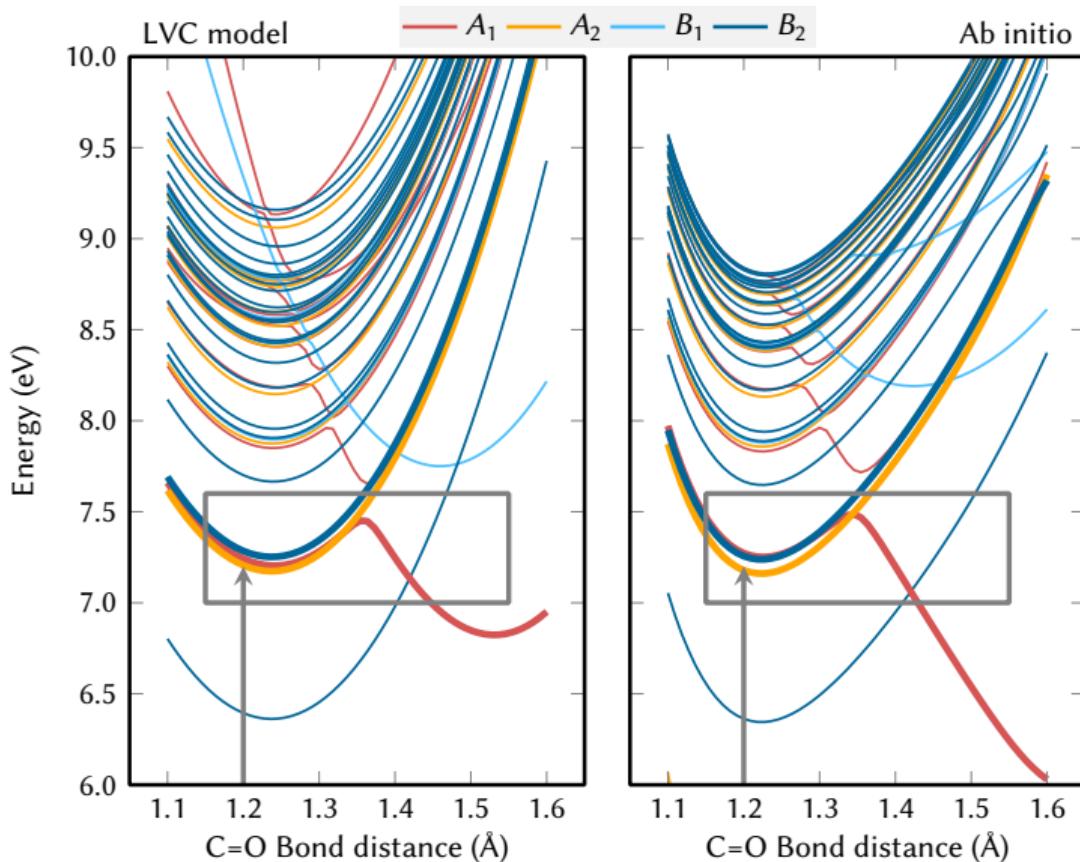
Complex LVC model

- ▶ Model for $n3p$ Rydberg and $\pi\pi^*$ states (grey box)
- ▶ Ab initio level of theory:
SOS-ADC(2)/cc-pVTZ
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- ▶ $720 K_{ad,i}$
- ▶ $30 r_{ad}^{\text{ref}}$
- ▶ $10 M_a$
- ▶ $49 \varepsilon^\alpha$
- ▶ 392 nonzero κ_i^α
- ▶ 7280 nonzero $\lambda_i^{\alpha\beta}$

Linear vibronic coupling model: Acetone

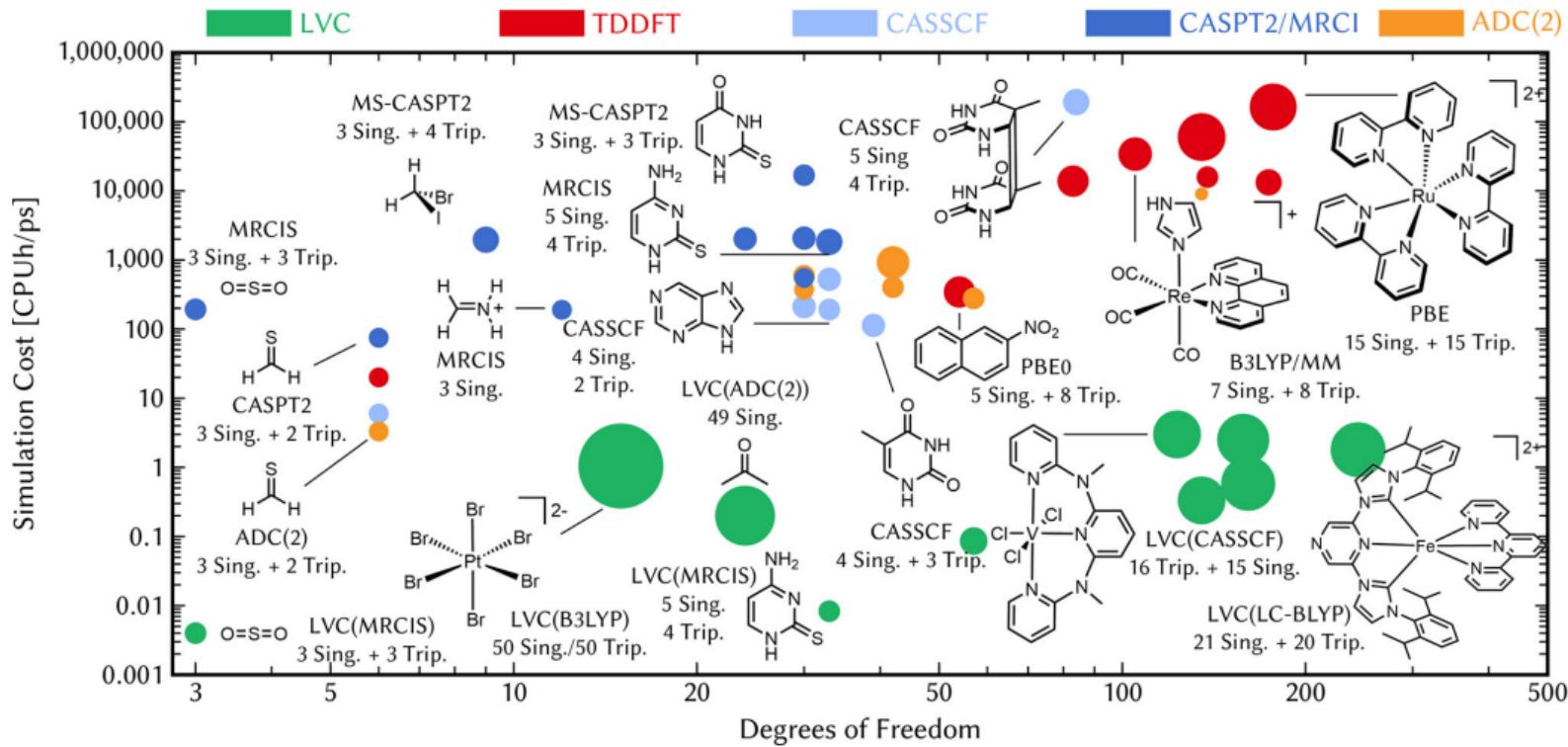
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LVC: Computational cost of nonadiabatic dynamics

Computational Cost of Surface Hopping Simulations



Time-dependent density functional theory (TDDFT)

- ▶ A lot of formal math and derivations
- ▶ Practical LR-TDDFT with ALDA works like CIS, but is more accurate
- ▶ Cheap and easy to use, but errors depend strongly on system, state, and functional
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Linear vibronic coupling (LVC) models

- ▶ Analytical model for coupled PESs
- ▶ Shifted and coupled multi-dimensional harmonic oscillators in normal mode coordinates
- ▶ Works well for rigid molecules with similar states and extremely easy to parametrize
- ▶ Extremely efficient (3–5 orders of magnitude faster than ab initio)

Thank you for your attention!

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My further thanks goes to:



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