# Time dependent vibrational electronic coupled cluster (VECC) theory

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## Motivations

**Non-adiabatic** dynamics is a research topic that has been intensively investigated. In a typical non-adiabatic system:

- There are multiple close-lying electronic states
- The Bohn-Oppenheimer approximation becomes invalid
- The nuclear wfn's have components along the multiple electronic states

**Non-adiabatic** dynamics problem can be decomposed into two parts:

- Part 1: Construction of the vibronic Hamiltonian

$$\hat{H}^{vibr}_{adiabats} = \begin{bmatrix} \hat{T}_1 & \text{N.A.C} \\ \text{N.A.C} & \hat{T}_2 \end{bmatrix} + \begin{bmatrix} E_1(\vec{R}) & 0 \\ 0 & E_2(\vec{R}) \end{bmatrix}$$

$\Downarrow$ diabatization (1)

$$\hat{H}^{vibr}_{diabats} = \begin{bmatrix} \hat{T}_1 & 0 \\ 0 & \hat{T}_2 \end{bmatrix} + \begin{bmatrix} \hat{V}_{11}(\vec{R}) & \hat{V}_{12}(\vec{R}) \\ \hat{V}_{21}(\vec{R}) & \hat{V}_{22}(\vec{R}) \end{bmatrix}$$

- Part 2: Solve the quantum dynamics problem of the vibronic model Hamiltonian

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}\tau} |\Psi(\tau)\rangle = \hat{H}^{vibr} |\Psi(\tau)\rangle \qquad (2)$$

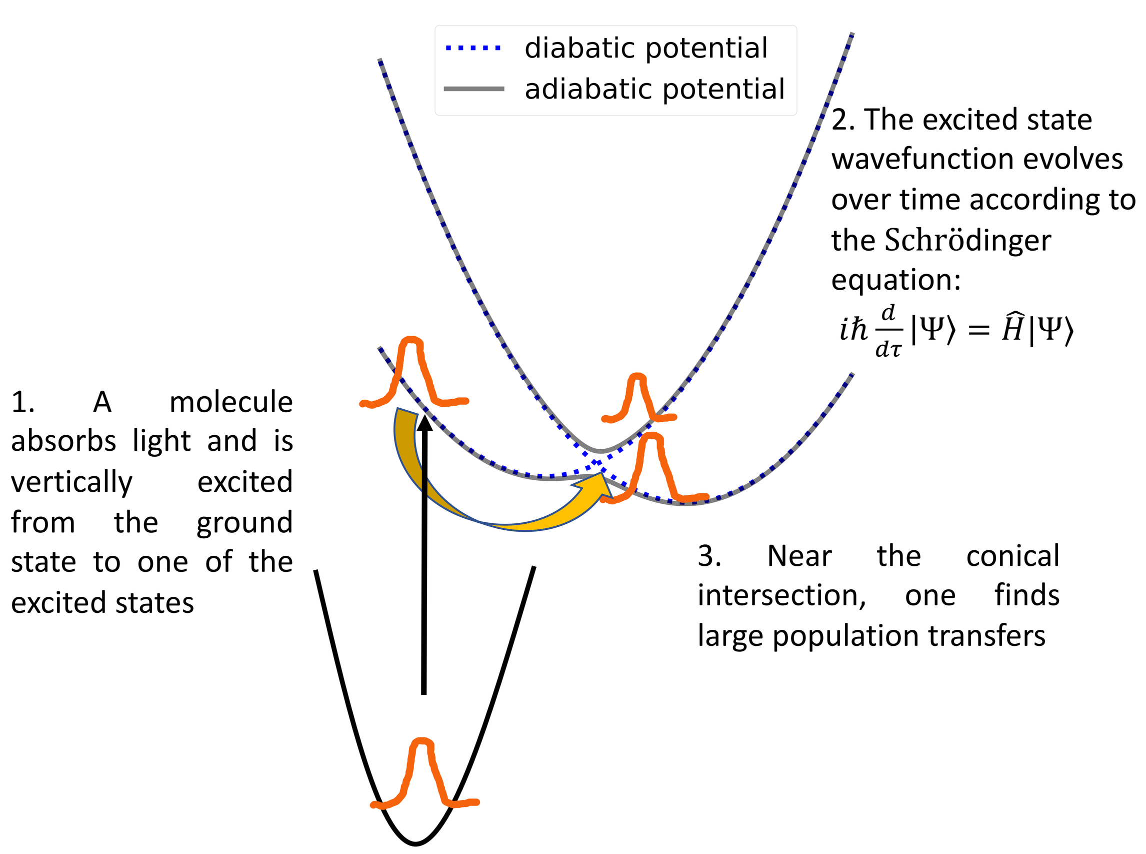



Figure 1: Diagram illustrates how excited state wavefunction involves over time

**Dynamics** simulation (part 2) of the problem is the focus of this research and we assume that the electronic structure calculations and the vibronic coupling constants are calculated somewhere else.

Existing methods on the non-adiabatic dynamics simulations can be classified into to two types

- On-the-fly dynamics:
  ab initio multiple spawning (AIMS) method [1]
  surface hopping method [2]
- Wave-packet dynamics:
  multi-configurational time dependent Hartree (MCTDH) family of methods [3, 4]

## The VECC theory

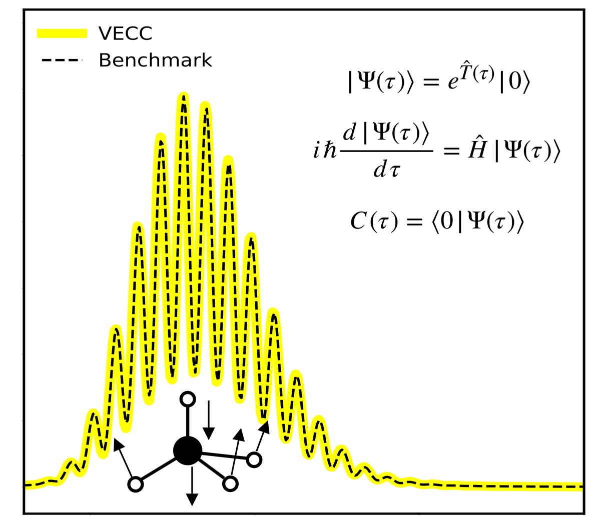



Figure 2: This year's SCP mug art: illustrate the key idea on the VECC method: applying second quantized coupled cluster ansatz to parameterize the time dependent wavefunction

- The vibronic model Hamiltonian can be expressed in terms of second quantized bosonic construction operators:

$$\hat{H} = \sum_{ab} |a\rangle\langle b| \Big( h^a_b + \sum_i h^{ai}_b \{\hat{a}^\dagger_i\} + \sum_i h^a_{bi}\{\hat{a}_i\} + \sum_{ij} h^{ai}_{bj}\{\hat{a}^\dagger_i \hat{a}_j\} + \frac{1}{2}\sum_{ij} h^{aij}_b \{\hat{a}^\dagger_i \hat{a}^\dagger_j\} + \frac{1}{2}\sum_{ij} h^a_{bij}\{\hat{a}_i \hat{a}_j\} \Big) \qquad (3)$$

- The full wavefunction is a linear combination of all electronic states:

$$|\Psi(\tau)\rangle = \sum_b \chi_b |\psi_b(\tau)\rangle \qquad (4)$$

- We apply the mixed CC / CI ansatz to parameterize the time dependent wavefunction:

$$|\psi_b(\tau)\rangle = \sum_x e^{\hat{T}(\tau)} \hat{Z}_x(\tau)|x,0\rangle\,,$$

$$\hat{T} = \sum_i t^i \hat{a}^\dagger_i \;;\; \hat{Z}_x = z^0_x + \sum_i z^i_x \hat{a}^\dagger_i + \frac{1}{2}\sum_{ij} z^{ij}_x \hat{a}^\dagger_i \hat{a}^\dagger_j + \ldots. \qquad (5)$$

- Substitute the ansatz into the TDSE and solve CC EOM:

$$i\langle y,0|\hat{\Omega}^\dagger_\nu \left(\frac{\mathrm{d}\hat{T}}{\mathrm{d}\tau}\hat{Z}_y + \frac{\mathrm{d}\hat{Z}_y}{\mathrm{d}\tau}\right)|y,0\rangle = \sum_x \langle y,0|\hat{\Omega}^\dagger_\nu \bar{H} \hat{Z}_x|x,0\rangle\,,$$

$$\bar{H} \equiv e^{-\hat{T}}\hat{H}e^{\hat{T}} = \left(\hat{H}e^{\hat{T}}\right)_{f.c.}. \qquad (6)$$

- Ehrenfest (taking state average) parameterization of the EOM for $\hat{T}$:

$$i\frac{\mathrm{d}t^i}{\mathrm{d}\tau} = \frac{\sum_{xy}(z^0_y)^* \langle y,0|\hat{a}_i e^{\hat{T}^\dagger}\bar{H}z^0_x|x,0\rangle}{\sum_x (z^0_x)^* z^0_x} \equiv R^i \qquad (7)$$

- Apply modified projection manifold to parameterize EOM for $\hat{Z}$:

$$i\langle y,0|\hat{\Omega}^\dagger_\nu \boxed{e^{\hat{T}^\dagger}} \frac{\mathrm{d}\hat{Z}_y}{\mathrm{d}\tau}|y,0\rangle = \sum_x \langle y,0|\hat{\Omega}^\dagger_\nu \boxed{e^{\hat{T}^\dagger}} \left(\bar{H} - R^i\right)\hat{Z}_x|x,0\rangle \qquad (8)$$

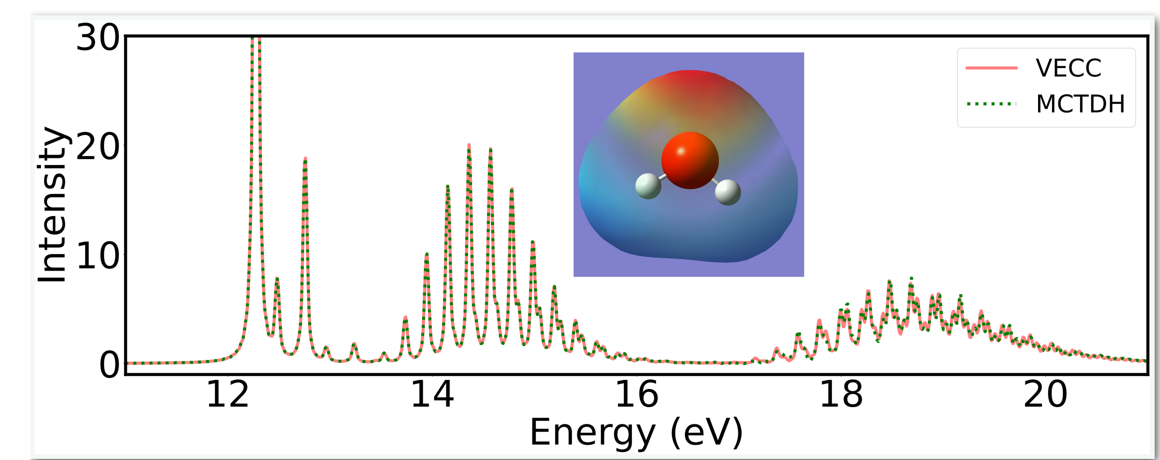
- Compute the auto-correlation function (ACF) from the CC amplitudes :

$$ACF(\tau) = \langle\Psi(0)|\Psi(\tau)\rangle = \sum_{ab} \chi_a z^0_b(\tau)\chi_b \qquad (9)$$

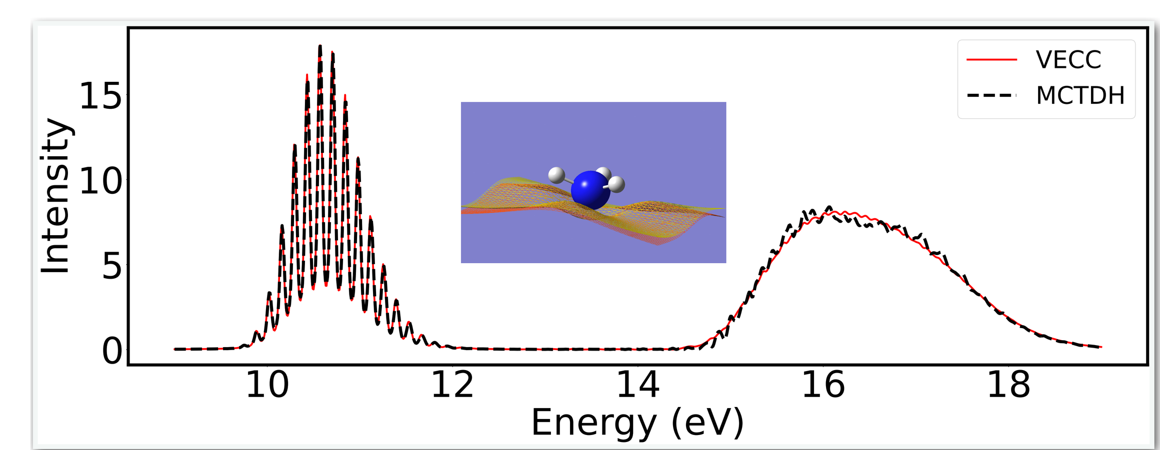
## Benchmark results

We implement the VECC method and benchmark against the MCTDH method. The open source code is available on the GitHub repository `t-amplitudes`.[5] The explicit working equations are generated through the open source software `termfactory` developed by Raymond et al. [6]

- Benchmark on small molecular compounds



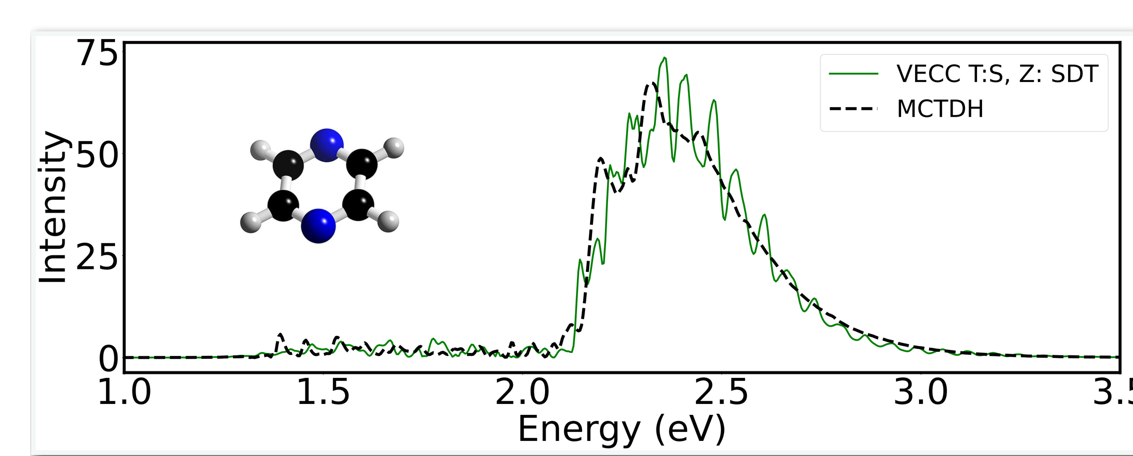

(a) Absorption spectra for water with 100 fs propagation



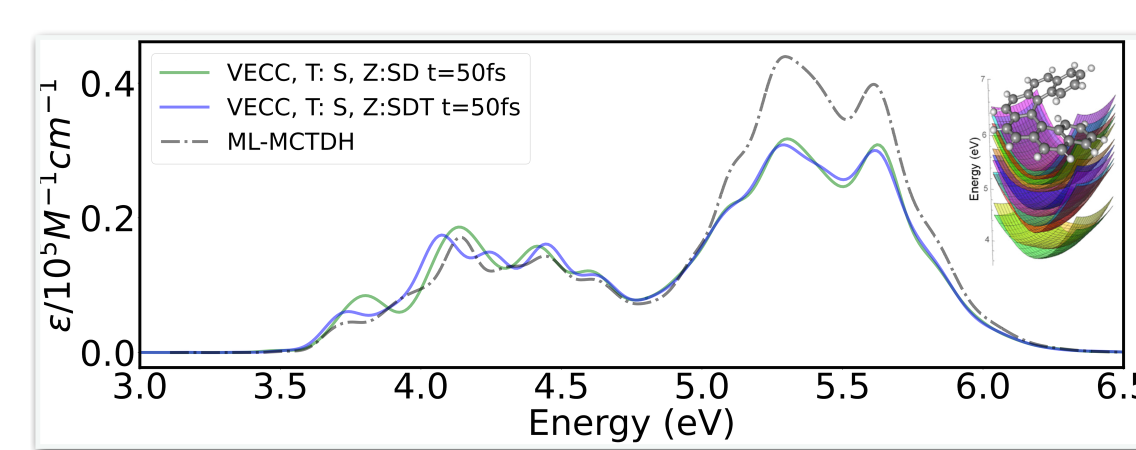

(b) Absorption spectra for 'Jahn-Teller' ammonia with 100 fs propagation

Figure 3: To verify the validity of the VECC method, we firstly benchmark against a few small molecular compounds: water (3 state, 3 modes) and 'Jahn-Teller' ammonia (3 states, 6 modes) [7] .

- Benchmark on large molecular compounds




(a) Absorption spectra for pyrazine with 300 fs propagation




(b) Absorption spectra for hexalicene with 50 fs propagation

Figure 4: To show the full potential of the VECC method, we benchmark against a few large molecular compounds: pyrazine (2 states, 24 modes)[8], hexahelicene(14 states, 63 modes)[9].

- The VECC method has tremendous advantage in terms of the computational runtime:
  For the pyrazine model above, it takes $\sim$ 2.5 min.
  For the hexahelicene model above, it takes $\sim$ 6h (with double $Z$ trunction) and $\sim$ 9h (with triple $\hat{Z}$ truncation).

## Conclusion

- We develop the VECC method for the non-adiabatic dynamics simulations.
- From the benchmark studies, we verified that the VECC method is robust and efficient.
- The VECC method can be widely applied for the spectra simulations.
- We are currently working on the VECC scheme to calculate the diabatic state populations which could facilitate the understandings of the pathways of the photo-chemical reactions.

## References

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