Libra Summer School and Workshop 2024

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Defining Hamiltonians in Libra

Wavefunction and selection of representation

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$|\Psi\rangle$ Abstract wavefunction

$\{|\boldsymbol{r}\rangle : \hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle\}$ Position states (Hilbert space)

$\{|\boldsymbol{k}\rangle : \hat{\boldsymbol{k}}|\boldsymbol{k}\rangle = \boldsymbol{k}|\boldsymbol{k}\rangle\}$ Momentum states (Hilbert space)

$\Psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\Psi\rangle$ Wavefunction in a **position representation** – representation in the basis of position states

$$1 = \int d\boldsymbol{r}'|\boldsymbol{r}'\rangle\langle \boldsymbol{r}'| \quad \text{Complete basis}$$

Indeed

$$|\Psi\rangle = \int d\boldsymbol{r}'|\boldsymbol{r}'\rangle\,\langle \boldsymbol{r}'|\Psi\rangle = \int d\boldsymbol{r}'\,|\boldsymbol{r}'\rangle\Psi(\boldsymbol{r}')$$

$\Psi(\boldsymbol{r}')$ is essentially an expansion coefficient in the basis of coordinate states $\{|\boldsymbol{r}\rangle\}$
Can be regarded as DVR (grid representation of the wavefunction)

$\Psi(\boldsymbol{k}) = \langle \boldsymbol{k}|\Psi\rangle$ Likewise, the **momentum representation** of a wavefunction

Different Hilbert spaces:

$\Psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\Psi\rangle$; $|\boldsymbol{r}\rangle, |\Psi\rangle \in \mathcal{H}_{\boldsymbol{r}}$ only electrons

$\Psi(\boldsymbol{R}) = \langle \boldsymbol{R}|\Psi\rangle$; $|\boldsymbol{R}\rangle, |\Psi\rangle \in \mathcal{H}_{\boldsymbol{R}}$ only nuclei

$\Psi(\boldsymbol{r}, \boldsymbol{R}) = \langle \boldsymbol{r}, \boldsymbol{R}|\Psi\rangle$; $|\Psi\rangle \in \mathcal{H}_r \otimes \mathcal{H}_{\boldsymbol{R}}$ both electrons and nuclei

$\Psi(\boldsymbol{r}) = \langle \boldsymbol{R}|\Psi\rangle$; $|\Psi\rangle \in \mathcal{H}_r \otimes \mathcal{H}_{\boldsymbol{R}}$ projection on $|\boldsymbol{R}\rangle \in \mathcal{H}_{\boldsymbol{R}}$; $\Psi(\boldsymbol{r}; \boldsymbol{R}) \in \mathcal{H}_r$ operator of electronic DOF (electronic coordinate operator), but a function of nuclear DOF - $\boldsymbol{R}$

Working in Different Hilbert Spaces: Exact-Factorization Example

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Han, D.; Akimov, A.V. *J. Chem. Theory Comput.* **2024,** 20, 5022–5042

electron-nuclear state $|\Psi(t)\rangle \in \mathcal{H}_{\boldsymbol{r}\times\boldsymbol{R}} = \mathcal{H}_{\boldsymbol{r}} \otimes \mathcal{H}_{\boldsymbol{R}}$

Electronic Hilbert space Electronic Hilbert space

$|\Psi(t)\rangle = |\chi(t), \Phi(t)\rangle$

$|\boldsymbol{R}\rangle \in \mathcal{H}_{\boldsymbol{R}}$

$|\boldsymbol{r}\rangle \in \mathcal{H}_{\boldsymbol{r}}$

Using the resolution-of-identity: $|\Psi(t)\rangle = \int d\,\boldsymbol{R}|\boldsymbol{R}\rangle\langle\boldsymbol{R}|\Psi(t)\rangle = \int d\,\boldsymbol{R}|\boldsymbol{R}\rangle\langle\boldsymbol{R}|\chi(t), \Phi(t)\rangle = \int d\,\boldsymbol{R}|\boldsymbol{R}\rangle\langle\boldsymbol{R}|\chi(t)\rangle|\Phi_{\boldsymbol{R}}(t)\rangle$

marginal nuclear state $|\chi(t)\rangle \in \mathcal{H}_{\boldsymbol{R}}$

conditional electronic state $|\Phi_{\boldsymbol{R}}(t)\rangle \in \mathcal{H}_{\boldsymbol{r}}$

Nuclear wavefunction in position representation: $\chi(\boldsymbol{R}, t) = \langle\boldsymbol{R}|\chi(t)\rangle$

Electronic wavefunction for fixed nuclear geometry: $\Phi(\boldsymbol{r}, t; \boldsymbol{R}) = \langle\boldsymbol{r}|\Phi_{\boldsymbol{R}}(t)\rangle$

$$|\Psi(t)\rangle = \int d\boldsymbol{R}|\boldsymbol{R}\rangle\chi(\boldsymbol{R}, t)|\Phi_{\boldsymbol{R}}(t)\rangle \in \mathcal{H}_{\boldsymbol{r}\times\boldsymbol{R}}$$

molecular state $|\Psi(\boldsymbol{R}, t)\rangle$

$$|\Psi(\boldsymbol{R}', t)\rangle = \langle\boldsymbol{R}'|\Psi(t)\rangle = \int d\boldsymbol{R}\langle\boldsymbol{R}'|\boldsymbol{R}\rangle\chi(\boldsymbol{R}, t)|\Phi_{\boldsymbol{R}}(t)\rangle = \int d\boldsymbol{R}\delta(\boldsymbol{R}' - \boldsymbol{R})\chi(\boldsymbol{R}, t)|\Phi_{\boldsymbol{R}}(t)\rangle$$
$$= \chi(\boldsymbol{R}', t)|\Phi_{\boldsymbol{R}'}(t)\rangle \in \mathcal{H}_{\boldsymbol{r}}$$

Shorthand notation. Adiabatic and Diabatic Representations

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$\psi_i(\boldsymbol{r}) = \langle \boldsymbol{r}|i\rangle = \langle \boldsymbol{r}|\psi_i\rangle$ electronic coordinates, i-th basis state

Shorthand notation for the entire basis: $|\boldsymbol{\psi}\rangle = (|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle)$

Matrix elements (scalars) → $A_{ij} = \langle \psi_i|\hat{A}|\psi_j\rangle \leftrightarrow A = \langle \boldsymbol{\psi}|\hat{A}|\boldsymbol{\psi}\rangle$ ← Matrix

Basis:

Adiabatic (Hamiltonian is diagonal):
$\langle \psi_{adi,i}|\hat{H}_{el}|\psi_{adi,j}\rangle = 0, \forall i \neq j$

Diabatic (NACs are exactly zero):
$\langle \psi_{dia,i}|\nabla_{\boldsymbol{R}}|\psi_{dia,j}\rangle = 0, \forall \boldsymbol{R}$

$$|\boldsymbol{\psi}_{adi}\rangle = |\boldsymbol{\psi}_{dia}\rangle U$$

$H_{adi} = \langle \boldsymbol{\psi}_{adi}|\hat{H}_{el}|\boldsymbol{\psi}_{adi}\rangle$ Hamiltonians $H_{dia} = \langle \boldsymbol{\psi}_{dia}|\hat{H}_{el}|\boldsymbol{\psi}_{dia}\rangle$

Transformation between bases $H_{dia}U = SUH_{adi}$ $H_{adi} = U^{+}H_{dia}U = \widetilde{H}_{dia}$

Wavefunction should be invariant w.r.t. the basis representation $|\Psi(t)\rangle = |\boldsymbol{\psi}_{adi}(t)\rangle C_{adi}(t) = |\boldsymbol{\psi}_{dia}(t)\rangle C_{dia}(t)$

TD-SE in the Shorthand notation

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Wavefunction should be invariant w.r.t. the basis representation

$$|\Psi(t)\rangle = |\boldsymbol{\psi}_{adi}(t)\rangle C_{adi}(t) = |\boldsymbol{\psi}_{dia}(t)\rangle C_{dia}(t)$$

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$$

$$|\boldsymbol{\psi}\rangle = \left(|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle\right)$$

$$C = (c_1, c_2, \dots, c_N)^T$$

$$i\hbar \frac{\partial}{\partial t}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep} + i\hbar|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle \frac{\partial}{\partial t} C_{rep} = \hat{H}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep}$$

Projecting:

$$i\hbar\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\frac{\partial}{\partial t}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep} + i\hbar\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle \frac{\partial}{\partial t} C_{rep} = \langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\hat{H}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle C_{rep}$$

$$\boxed{i\hbar S_{rep}\frac{\partial}{\partial t} C_{rep} = \left[\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\hat{H}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle - i\hbar\langle\boldsymbol{\psi}_{\boldsymbol{rep}}(t)|\frac{\partial}{\partial t}|\boldsymbol{\psi}_{\boldsymbol{rep}}(t)\rangle\right] C_{rep}}$$

Implementation in Libra classes

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Wavefunction language $|\Psi(t)\rangle = |\boldsymbol{\psi}_{adi}(t)\rangle \boldsymbol{C}_{adi}(t) = |\boldsymbol{\psi}_{dia}(t)\rangle \boldsymbol{C}_{dia}(t)$

Density matrix language $\hat{\rho} = |\Psi\rangle\langle\Psi|$

$$P_{adi} = \langle\boldsymbol{\psi}_{adi}|\hat{\rho}|\boldsymbol{\psi}_{adi}\rangle = \langle\boldsymbol{\psi}_{adi}|\boldsymbol{\psi}_{adi}\rangle \boldsymbol{C}_{adi}\boldsymbol{C}_{adi}^{+}\langle\boldsymbol{\psi}_{adi}|\boldsymbol{\psi}_{adi}\rangle = \boldsymbol{I}\boldsymbol{C}_{adi}\boldsymbol{C}_{adi}^{+}\boldsymbol{I} = \boldsymbol{C}_{adi}\boldsymbol{C}_{adi}^{+}$$

$$P_{dia} = \langle\boldsymbol{\psi}_{dia}|\hat{\rho}|\boldsymbol{\psi}_{dia}\rangle = \langle\boldsymbol{\psi}_{dia}|\boldsymbol{\psi}_{dia}\rangle \boldsymbol{C}_{dia}\boldsymbol{C}_{dia}^{+}\langle\boldsymbol{\psi}_{dia}|\boldsymbol{\psi}_{dia}\rangle = \boldsymbol{S}\boldsymbol{C}_{dia}\boldsymbol{C}_{dia}^{+}\boldsymbol{S}$$

dyn_variables
- ndia, nadi, ndof, ntraj
- ampl_dia, ampl_adi
- dm_adi, dm_dia

So the conversions of the density matrices is:

$$\boldsymbol{U}\boldsymbol{P}_{dia}\boldsymbol{U}^{+} = \boldsymbol{U}^{+}\boldsymbol{S}\boldsymbol{C}_{dia}\boldsymbol{C}_{dia}^{+}\boldsymbol{S}\boldsymbol{U} = \boldsymbol{C}_{adi}\boldsymbol{C}_{adi}^{+} = \boldsymbol{P}_{adi} \rightarrow \boldsymbol{P}_{dia} = \boldsymbol{U}^{-1}\boldsymbol{P}_{adi}(\boldsymbol{U}^{-1})^{+} = \boldsymbol{U}^{+}\boldsymbol{S}\boldsymbol{P}_{adi}(\boldsymbol{U}^{+}\boldsymbol{S})^{+} = \boldsymbol{U}^{+}\boldsymbol{S}\boldsymbol{P}_{adi}\boldsymbol{S}\boldsymbol{U}$$

Coefficient transformation:

$$\boldsymbol{C}_{dia} = \boldsymbol{U}\boldsymbol{C}_{adi} \leftrightarrow \boldsymbol{C}_{adi} = \boldsymbol{U}^{-1}\boldsymbol{C}_{dia} \leftrightarrow \boldsymbol{C}_{adi} = \boldsymbol{U}^{+}\boldsymbol{S}\boldsymbol{C}_{dia}$$

$\boldsymbol{H}_{dia}\boldsymbol{U} = \boldsymbol{S}\boldsymbol{U}\boldsymbol{H}_{adi}$ and also computes derivative couplings and adiabatic gradients

computes $\boldsymbol{H}_{dia}$, $\boldsymbol{D}_{dia}$, and $\nabla\boldsymbol{H}_{dia}$ according to given methods (e.g. Python modules with Hamiltonian models)

nHamiltonian
- ampl_dia2adi
- ampl_adi2dia
- compute_adiabatic()
- compute_diabatic()

Implementation in the nHamiltonian class

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$$|\boldsymbol{\psi}\rangle = (|\psi_1\rangle, |\psi_2\rangle, \dots, |\psi_N\rangle)$$

$$\boldsymbol{H}_{dia} = \langle \boldsymbol{\psi}_{dia} | \hat{H} | \boldsymbol{\psi}_{dia} \rangle$$

Hamiltonian matrix elements

$$\boldsymbol{H}_{adi} = \langle \boldsymbol{\psi}_{adi} | \hat{H} | \boldsymbol{\psi}_{adi} \rangle$$

Unitary (similarity) transformation

$$\boldsymbol{H}_{adi} = \boldsymbol{U}^{+} \boldsymbol{H}_{dia} \boldsymbol{U} = \widetilde{\boldsymbol{H}}_{dia}$$

$$|\boldsymbol{\psi}_{adi}\rangle = |\boldsymbol{\psi}_{dia}\rangle \boldsymbol{U}$$

First-order derivative coupling vectors

$$\boldsymbol{D}_{adi} \equiv \langle \boldsymbol{\psi}_{adi} | \boldsymbol{\nabla} \boldsymbol{\psi}_{adi} \rangle$$

$$\boldsymbol{D}_{dia} \equiv \langle \boldsymbol{\psi}_{dia} | \boldsymbol{\nabla} \boldsymbol{\psi}_{dia} \rangle$$

nHamiltonian

- CMATRIX* ham_dia, nac_dia, hvib_dia
- CMATRIX* ham_adi, nac_adi, hvib_adi
- CMATRIX* ovlp_dia, time_overlap_dia
- CMATRIX* ovlp_adi, time_overlap_adi
- CMATRIX* basis_transform
- vector<CMATRIX*> dc1_adi, dc1_dia
- vector<CMATRIX*> d1ham_adi, d1ham_dia
- compute_adiabatic()

$$\boldsymbol{D}_{dia} = \left\langle \boldsymbol{\psi}_{dia} \middle| \frac{\partial}{\partial t} \middle| \boldsymbol{\psi}_{dia} \right\rangle$$

Scalar NACs

$$\boldsymbol{D}_{adi} = \left\langle \boldsymbol{\psi}_{adi} \middle| \frac{\partial}{\partial t} \middle| \boldsymbol{\psi}_{adi} \right\rangle$$

"Vibronic" Hamiltonian

$$H_{vib,dia} = H_{dia} - i\hbar D_{dia}$$

$$H_{vib,adi} = H_{adi} - i\hbar D_{adi}$$

Time-overlaps (transition density matrices)

$$\langle \boldsymbol{\psi}_{dia}(t - \Delta t) | \boldsymbol{\psi}_{dia}(t) \rangle = \boldsymbol{St}_{dia}(t - \Delta t, t) \approx I$$

$$\langle \boldsymbol{\psi}_{adi}(t - \Delta t) | \boldsymbol{\psi}_{adi}(t) \rangle = \boldsymbol{St}_{adi}(t - \Delta t, t)$$

$$\langle \boldsymbol{\psi}_{dia} | \boldsymbol{\psi}_{dia} \rangle = \boldsymbol{S}$$

$$\langle \boldsymbol{\psi}_{adi} | \boldsymbol{\psi}_{adi} \rangle = \boldsymbol{I}$$

The diabatic basis is not necessarily orthonormal

How to compute NACs?

$$\begin{cases} \boldsymbol{U}^{+} \nabla \boldsymbol{H}_{dia} \boldsymbol{U} - \left(\widetilde{\boldsymbol{D}}_{dia}^{+} \boldsymbol{H}_{adi} + \boldsymbol{H}_{adi} \widetilde{\boldsymbol{D}}_{dia} \right) = \nabla \boldsymbol{H}_{adi} - \left(\boldsymbol{D}_{adi}^{+} \boldsymbol{H}_{adi} + \boldsymbol{H}_{adi} \boldsymbol{D}_{adi} \right) \\ \widetilde{\nabla \boldsymbol{H}_{dia}} - \left(\widetilde{\boldsymbol{D}}_{dia}^{+} \widetilde{\boldsymbol{H}}_{dia} + \widetilde{\boldsymbol{H}}_{dia} \widetilde{\boldsymbol{D}}_{dia} \right) = \nabla \boldsymbol{H}_{adi} - \left(\boldsymbol{D}_{adi}^{+} \boldsymbol{H}_{adi} + \boldsymbol{H}_{adi} \boldsymbol{D}_{adi} \right) \end{cases}$$

Then use special structure of the matrix

Nonadiabatic Couplings

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Properties of the NACs

$$\bar{\boldsymbol{D}}_{dia}^{+} + \bar{\boldsymbol{D}}_{dia} = \boldsymbol{\nabla S}$$

$$\bar{\boldsymbol{D}}_{adi} + \bar{\boldsymbol{D}}_{adi}^{+} = \boldsymbol{\nabla} S_{adi} = 0 \rightarrow (D_{adi}^{\alpha})^{+} = -D_{adi}$$

This is a well-known property!

$$D_{adi}^{\alpha} = \widetilde{D}_{dia}^{\alpha} + U^{+} S \nabla_{\alpha} U$$

$D_{rep,ij}^{\alpha} \equiv \langle \psi_{rep,i} | \nabla_{\alpha} \psi_{rep,j} \rangle$ is a scalar

$\boldsymbol{D}_{rep,ij} \equiv \langle \psi_{rep,i} | \nabla \psi_{rep,j} \rangle$ understood as a column-vector

$\bar{\boldsymbol{D}}_{rep} \equiv \langle \boldsymbol{\psi}_{rep} | \boldsymbol{\nabla} \boldsymbol{\psi}_{rep} \rangle$ understood as a vector of matrices $D_{rep}^{\alpha} = \langle \boldsymbol{\psi}_{rep} | \nabla_{\alpha} \boldsymbol{\psi}_{rep} \rangle$

Important observations

the equation becomes an identity when $U = I$

$$\underbrace{\widetilde{\nabla_{\alpha} H_{dia}} - \left((D_{adi}^{\alpha})^{+} \widetilde{H}_{dia} + \widetilde{H}_{dia} \widetilde{D}_{dia}^{\alpha} \right)}_{U^{+} \langle \boldsymbol{\psi}_{dia} | \nabla_{\alpha} H | \boldsymbol{\psi}_{dia} \rangle U} = \underbrace{\nabla_{\alpha} H_{adi} - \left((D_{adi}^{\alpha})^{+} H_{adi} + H_{adi} D_{adi}^{\alpha} \right)}_{\langle \boldsymbol{\psi}_{adi} | \nabla_{\alpha} H | \boldsymbol{\psi}_{adi} \rangle}$$

Quantum-Classical Hamiltonian and Ehrenfest forces

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$$H^{MF}(\boldsymbol{R},\boldsymbol{P};\Psi) = \frac{\langle\Psi|H^{qc}(\boldsymbol{R},\boldsymbol{P})|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{2}\boldsymbol{P}^T M^{-1}\boldsymbol{P} + \frac{C_{adi}^{+}H_{adi}C_{adi}}{C_{adi}^{+}C_{adi}} = \frac{1}{2}\boldsymbol{P}^T M^{-1}\boldsymbol{P} + \frac{C_{dia}^{+}H_{dia}C_{dia}}{C_{dia}^{+}SC_{dia}}$$

nHamiltonian

- Ehrenfest_energy_adi
- Ehrenfest_energy_dia

TD-SE for the amplitudes

$$i\hbar S\frac{dC_{rep}}{dt} = \left(H_{rep} - i\hbar d_{rep}\right)C_{rep}$$

$$\frac{dH^{MF}}{dt} = 0$$

Energy conservation

$$\dot{\boldsymbol{R}} = M^{-1}\boldsymbol{P}$$

Enforcing the "classical" form of equations of motion for nuclear DOFs $\dot{\boldsymbol{P}} = f^{MF}(\boldsymbol{R},\Psi_{\mathrm{rep}})$

$$f_n^{MF} \equiv f_{n,adi}^{MF} = \frac{1}{C_{adi}^{+}C_{adi}}C_{adi}^{+}F_{adi,n}^{HF}C_{adi} = f_{n,dia}^{\mathrm{MF}} = \frac{1}{C_{dia}^{+}SC_{dia}}C_{dia}^{+}F_{dia,n}^{HF}C_{dia}$$

nHamiltonian

- Ehrenfest_forces_adi
- Ehrenfest_forces_dia
- Ehrenfest_forces_tens_adi
- Ehrenfest_forces_tens_dia

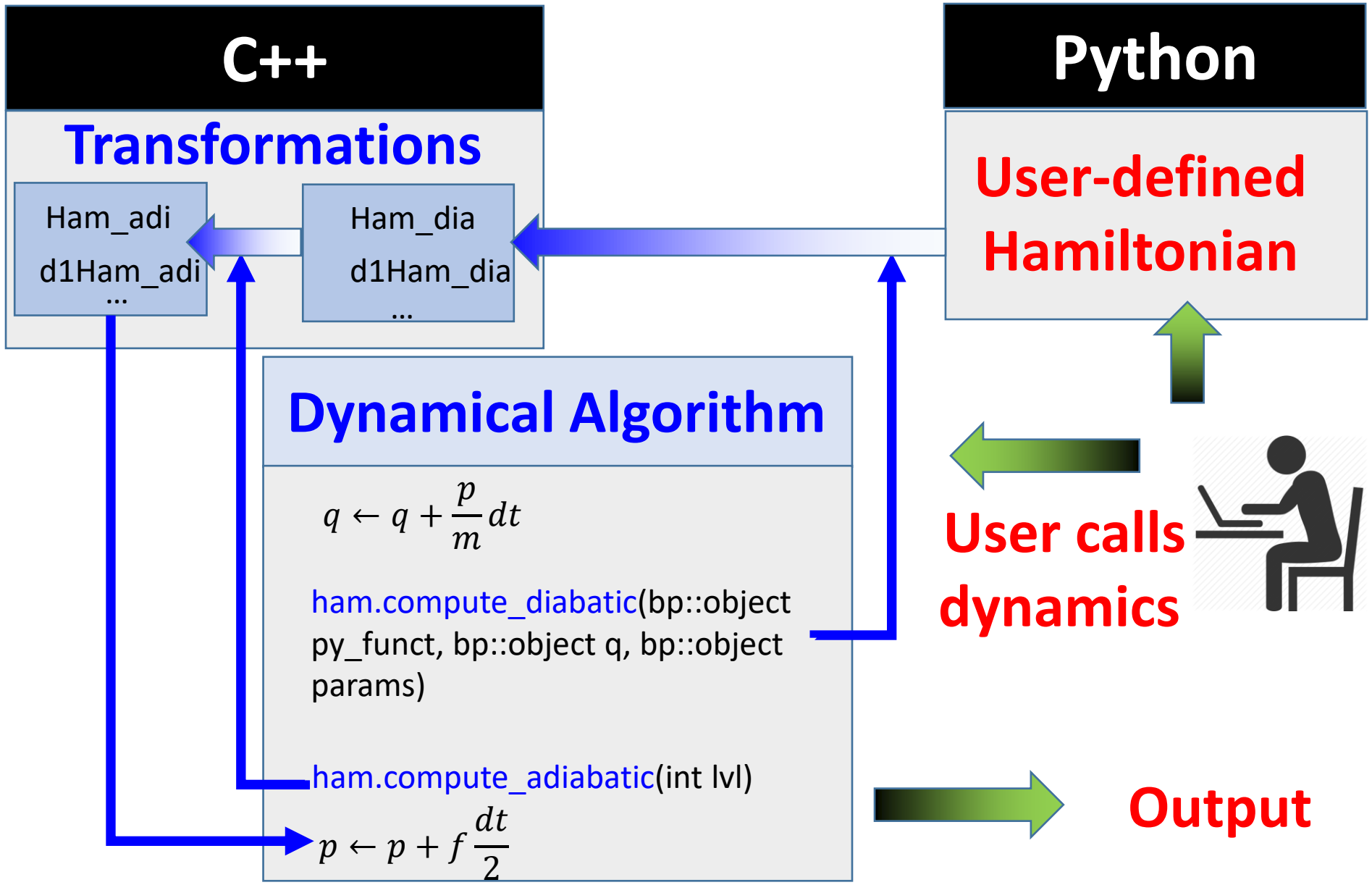
$$F_{adi,n}^{HF} = -\langle\boldsymbol{\psi}_{adi}|\nabla_n H|\boldsymbol{\psi}_{adi}\rangle = \left[-\nabla_n H_{adi} + D_{adi,n}^{+}H_{adi} + H_{adi}D_{adi,n}\right]$$

$$F_{dia,n}^{MF} = -\langle\boldsymbol{\psi}_{dia}|\nabla_{\mathrm{n}} H|\boldsymbol{\psi}_{dia}\rangle = \left[-\nabla_n H_{dia} + D_{dia,n}^{+}S^{-1}H_{dia} + H_{dia}S^{-1}D_{dia,n}\right]$$

More on the nHamiltonian class.

Making Interfaces

How `compute_dynamics` works



Different ways of computing matrix elements. Example of H_{dia}^{vib}

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Blue = Required Input
Green = Output
Green with D = Can be set up directly via Python function call

Function	Q	P	H_{dia}	D_{dia}	d_{dia}	H_{dia}^{vib}
nHamiltonian::**compute_diabatic**(bp::object py_funct …)			D	D	D	D
nHamiltonian::**compute_nac_dia**(…)						
nHamiltonian::**compute_hvib_dia**(…)						

Different ways of computing matrix elements. Example of H_{adi}^{vib}

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Function	Q	P	S	H_{dia}	∇H_{dia}	D_{dia}	U	H_{adi}	∇H_{adi}	D_{adi}	d_{adi}	H_{adi}^{vib}
nHamiltonian::**compute_diabatic**(bp::object py_funct …)			D	D	D	D						
nHamiltonian::**compute_adiabatic**(…)												
nHamiltonian::**compute_adiabatic**(bp::object py_funct …)							D	D	D	D	D	D
nHamiltonian::**compute_nac_adi**(…)												
nHamiltonian::**compute_hvib_adi**(…)												

nHamiltonian class as a hierarchical data type to handle multiple trajectories

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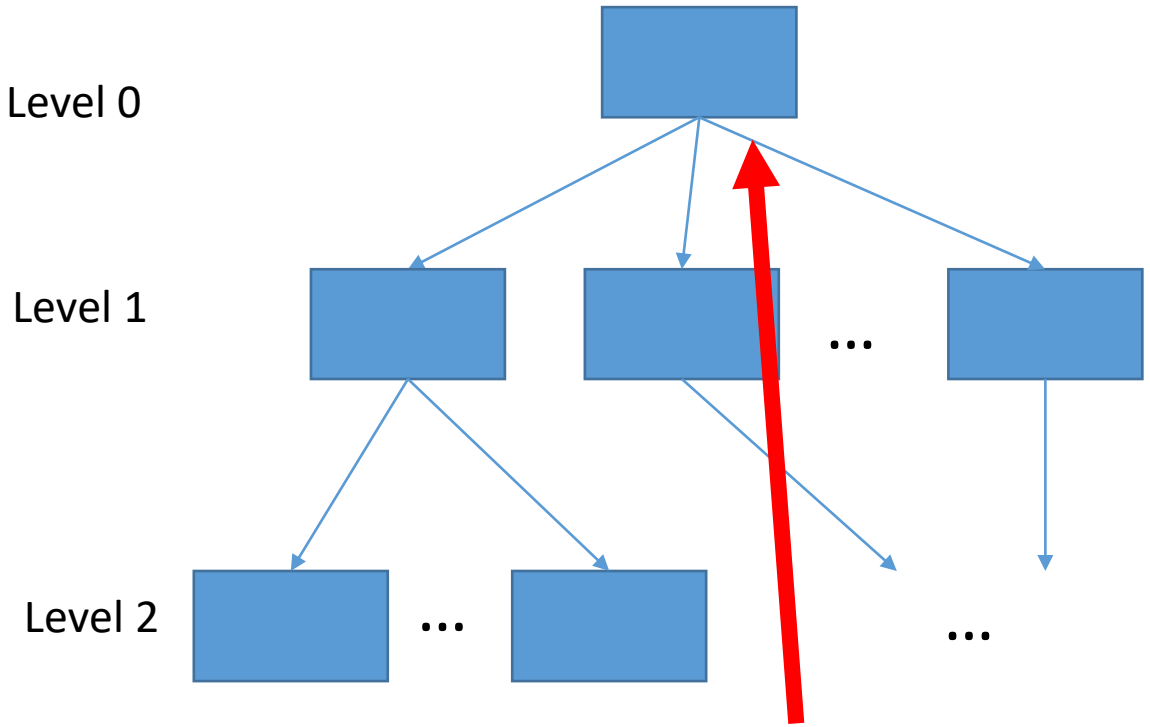
nHamiltonian

- level
- id
- nHamiltonian* parent
- vector<nHamiltonian*> children

- nnucl, nadi, ndia

- CMATRIX* ham_dia, nac_dia, hvib_dia
- CMATRIX* ham_adi, nac_adi, hvib_adi
- CMATRIX* ovlp_dia, time_overlap_dia
- CMATRIX* ovlp_adi, time_overlap_adi
- CMATRIX* basis_transform
- vector<CMATRIX*> dc1_adi, dc1_dia
- vector<CMATRIX*> d1ham_adi, d1ham_dia

- ampl_dia2adi
- ampl_adi2dia



int entanglement_opt

A selector of a method to couple the trajectories in this ensemble.
- 0: no coupling [default]
- 1: ETHD
- 2: ETHD3 (experimental)
- 22: another flavor of ETHD3 (experimental)

Packing variables for multiple trajectories

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Individual trajectory

Swarm of uncoupled trajectories

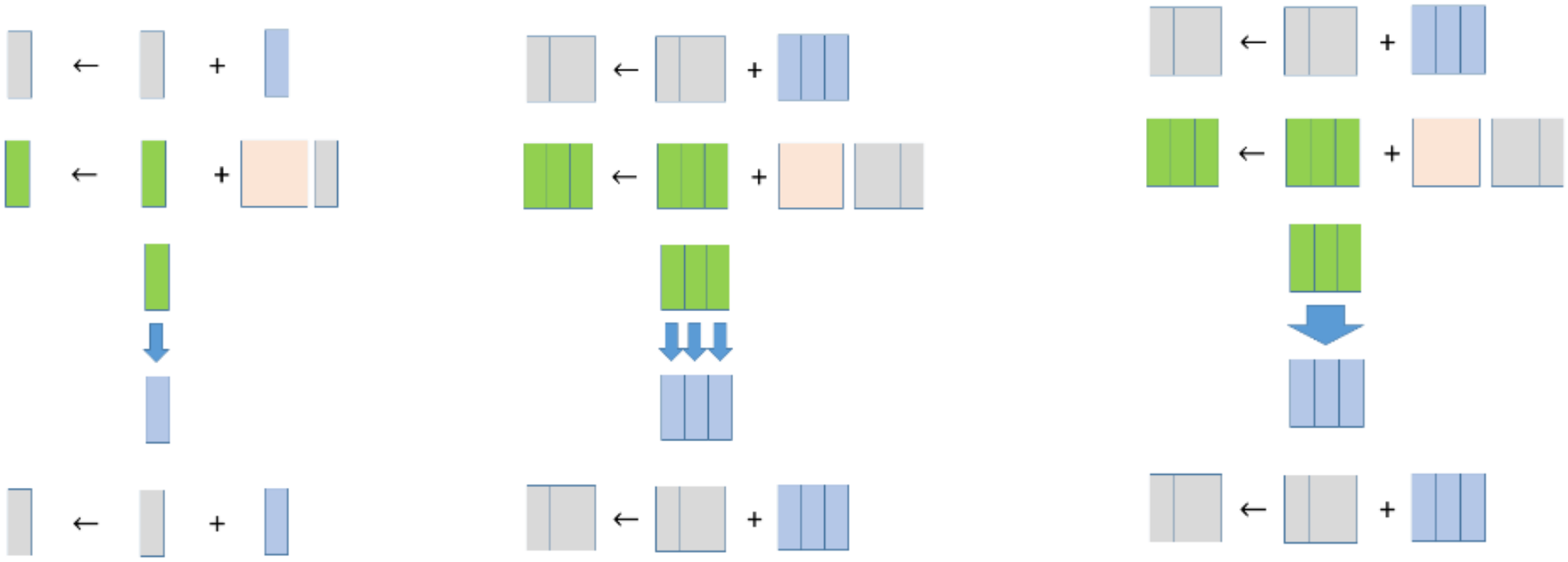
Swarm of coupled trajectories

$$p \leftarrow p + f\frac{dt}{2}$$

$$q \leftarrow q + M^{-1}pdt$$

Forces update

$$p \leftarrow p + f\frac{dt}{2}$$



Keep the Dynamical Workflow Fixed

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User defines how to run the dynamical simulation

```
for i in range(500):
    propagate_el(Cdia, Cadi, Hvib, Sdia, 0.5*dt, rep)
    p = p + 0.5*f*dt
    q = q + dt*p/m
    compute_model(model, Hdia, Sdia, d1ham_dia, dc1_dia, q, params)
    ham.compute_adiabatic(1);
    f = compute_frc(ham, Cdia, Cadi, rep)
    p = p + 0.5*f*dt
    Hvib = compute_Hvib(Hdia, Hadi, dc1_dia, dc1_adi, p, m, rep)
    propagate_el(Cdia, Cadi, Hvib, Sdia, 0.5*dt, rep)
Etot = compute_etot(ham, p, Cdia, Cadi, m, rep)
```

User defines what function to use to compute entries in the Hamiltonian object (diabatic/adiabatic Ham, overlap matrix, derivatives, etc.) - NEXT

Example: Model Calculations

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```
def model2(q, params):

    obj = tmp()
    obj.ham_dia = CMATRIX(2,2);   obj.ovlp_dia = CMATRIX(2,2);
    obj.d1ham_dia = CMATRIXList();  obj.d1ham_dia.append( CMATRIX(2,2))
    obj.dc1_dia = CMATRIXList();  obj.dc1_dia.append( CMATRIX(2,2))

    x = q.get(0)
    x0,k,D,V = params["x0"], params["k"], params["D"], params["V"]

    obj.ovlp_dia.set(0,0, 1.0+0.0j);  obj.ovlp_dia.set(0,1, 0.0+0.0j);
    obj.ovlp_dia.set(1,0, 0.0+0.0j);  obj.ovlp_dia.set(1,1, 1.0+0.0j);

    obj.ham_dia.set(0,0, k*x*x*(1.0+0.0j) );   obj.ham_dia.set(0,1, V*(1.0+0.0j));
    obj.ham_dia.set(1,0, V*(1.0+0.0j));          obj.ham_dia.set(1,1, (k*(x-x0)**2 + D)*(1.0

    for i in [0]:
        obj.d1ham_dia[i].set(0,0, 2.0*k*x*(1.0+0.0j) );   obj.d1ham_dia[i].set(0,1, 0.0+0.0j);
        obj.d1ham_dia[i].set(1,0, 0.0+0.0j);                obj.d1ham_dia[i].set(1,1,2.0*k*(x-x0)*(1.0+0.0j));

        obj.dc1_dia[i].set(0,0, 0.0+0.0j);   obj.dc1_dia[i].set(0,1,-0.1+0.0j);
        obj.dc1_dia[i].set(1,0, 0.1+0.0j);   obj.dc1_dia[i].set(1,1, 0.0+0.0j);

    return obj
```

Initialize Python objects

Set matrix elements according to your model

Example: Atomistic Calculations

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```
def model_atomistic(q, params, indx):

    natoms = params["natoms"];  ndof = q.num_of_rows;  ndia = params[ "ndia" ]
    params[ "output_filename" ] = "detailed.out“

    obj = tmp()
    obj.ham_dia = CMATRIX(1,1);
    obj.ovlp_dia = CMATRIX(1,1);          obj.ovlp_dia.set(0,0, 1.0+0.0j)
    obj.d1ham_dia = CMATRIXList();
    for i in xrange(ndof):
        obj.d1ham_dia.append( CMATRIX(1,1) )

    os.system("mkdir wd/job_"+str(indx))
    os.system("cp dftb_in.hsd wd/job_"+str(indx)) #+"/dftb_in.hsd")
    os.chdir("wd/job_"+str(indx))

    create_input.update_coordinates(q, params)
    os.system("srun %s < dftb_in.hsd > out" % (exe_name) )  # DFTB calculations are run here!
    dftb_forces = parse_output.get_forces(params)
    os.chdir("../../")

    for i in xrange(ndof):
        obj.d1ham_dia[i].set(0,0, dftb_forces[i]*(-1.0+0.0j) )
        obj.dc1_dia[i].set(0, 0, 0.0+0.0j)

return obj
```

Initialize Python objects

Prepare and Run external program

Set matrix elements according to your model