

Dynamics with Quantum Trajectory Guided Adaptable Gaussian bases

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Outline

① Theoretical background

Time-dependent Gaussian functions

Classical and variational Gaussian bases

Quantum trajectory dynamics

② The QTAG dynamics method

Theory and implementation

Typical chemistry models

③ Nonadiabatic dynamics in Libra

Models and implementation

Applications

④ Summary and outlook

Quantum dynamics \sim nuclear motion

TD := time-dependent

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

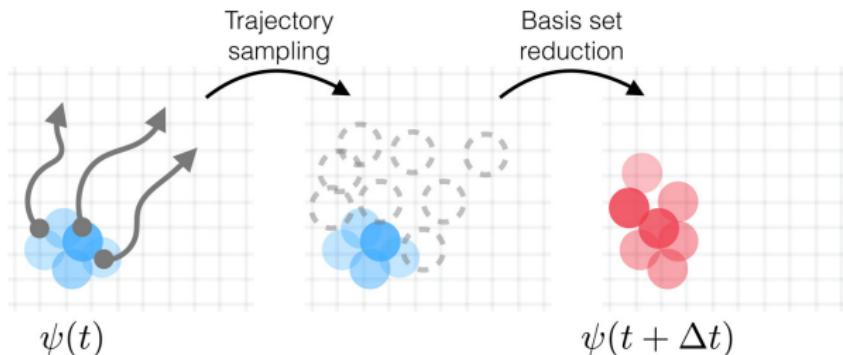
- The complexity and size of WF scale exponentially
- TD bases and representations adaptable to WF
- Physics of a system, e.g. mass, energy and time-scale separation, factorization or layers for multiscale WFs



Trajectory-guided and related Gaussian methods

GBF := Gaussian basis functions, often taken as 'frozen'

- Variational Multiconfigurational Gaussians
- Coupled Coherent Gaussians (classical trajectories)
- Full multiconfiguration spawning
- Multiconfiguration Ehrenfest, cloning
- GBF reexpansions – basis set leaping, matching pursuit, exploratory trajectories



Saller and Habershon. J. Chem. Theory Comput. 2017, 13, 7, 3085-3096

Why use Gaussians?

In atomic units: $\hbar = 1$, mass m . Local Harmonic Approximation (LHA)

- LHA Thawed Gaussian solves TDSE for the parabolic V

$$\psi(x, t) = \exp(-a_t(x - q_t)^2/2 + ip_t(x - q_t) + is_t + n_t)$$

real trajectory center q_t, p_t moves classically

$$\frac{dq_t}{dt} = \frac{p_t}{m}, \quad \frac{dp_t}{dt} = -\nabla V|_{x=q_t}$$

complex a_t (width and chirp)

$$\frac{da_t}{dt} = -\frac{a_t^2}{m} - \nabla^2 V|_{x=q_t}$$

real phase s_t and normalization factor n_t

$$\frac{ds_t}{dt} = \frac{p_t^2}{2m} - V(q_t) + \frac{\Re(a)}{m}, \quad \frac{dn_t}{dt} = \frac{\Im(a)}{m}$$

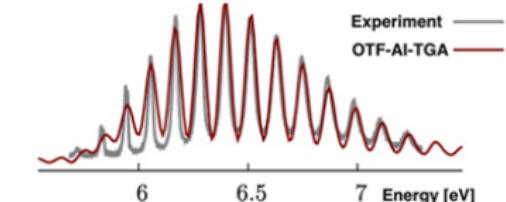
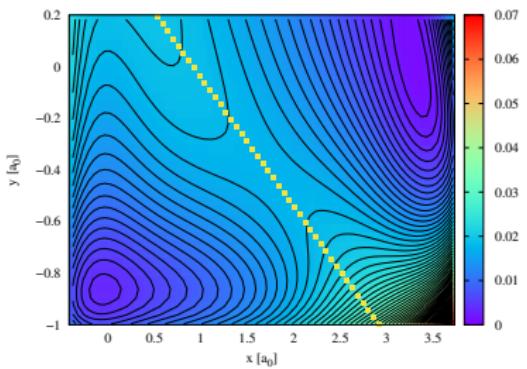
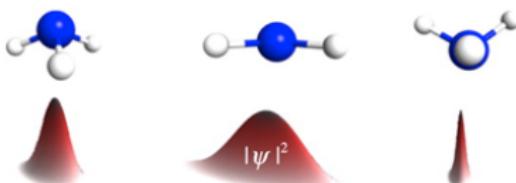
- Need the energy, gradient and hessian for a single configuration

Gaussian wavepacket dynamics

- Thawed Gaussian is exact for parabolic $V(x, t)$
- View as 'model' in any $V(x)$
- Generalization to 'excited' states
- Variational Gaussian – more rigorous and more expensive
- Reactions in condensed phase dynamics in the double well

$$C(t) = \langle \psi_0 | \psi_t \rangle \rightarrow I(E) = FT(C(t))$$

On-the-fly *ab initio* thawed Gaussian wave packet propagation



Absorption and Photoelectron Spectra of Ammonia Wherle et al J. Phys. Chem. A, 2015, 119 (22), pp 5685–5690

Wavefunction representation in terms of the GBFs

GBF := Gaussian Basis Functions

$$\psi(x, t) = \sum_j c_j(t) g_j(x, t)$$

$$g_j(x, t) = \exp\left(-\frac{a_j}{2}(x - q_j)^2 + \imath p_j(x - q_j) + \imath s_j\right)$$

- GBF parameters: $\Lambda_j = \{q_j, p_j, a_j\}$; optional x -independent phase s_j
- $(q, p, s) \in \mathbb{R}$; generally, $a = a(t) \in \mathbb{C}$, often taken as real constant
- Basis overlap and Hamiltonian matrices

$$\mathbf{S} = \langle \vec{g} | \otimes \vec{g} \rangle, \quad \mathbf{H} = \langle \vec{g} | \otimes \hat{H} \vec{g} \rangle$$

- Variational expansion coefficients $\{c_j\} \in \mathbb{C}$

$$\imath \mathbf{S} \vec{c} = (\mathbf{H} - \imath \mathbf{D}) \vec{c}, \quad \mathbf{D} = \langle \vec{g} | \otimes \frac{d}{dt} \vec{g} \rangle$$

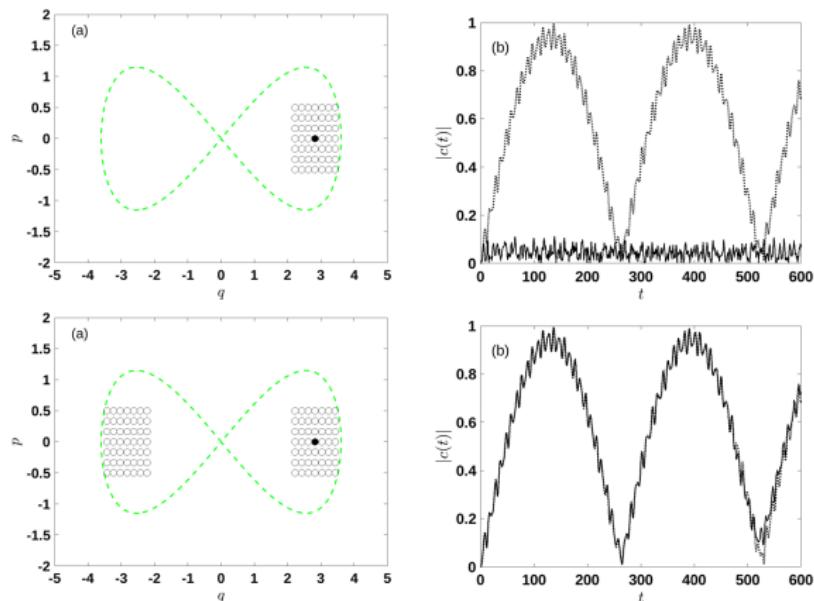
- How to evolve GBF parameters $\vec{\Lambda}$?

The classic(al) problem: the double well

Coupled coherent states (CCS) method for tunneling dynamics: an interpretative study.
F. Grossmann, IOP Conf. Ser. 2024

Classical trajectories

- useful (heavy nuclei)
- intuitive
- linear scaling
- on-the-fly force
- *do not follow QM-accessible space*
- inefficient WF representation



Left: Initial GBFs in phase space; filled circle = populated GBF (dash = separatrix)
Right: $C(t) = \langle \psi_L(0) | \psi(t) \rangle$ (dash = exact QM, solid = CCS)

GBFs from the variational principle

minimize the propagation error ϵ per McLachlan variational principle

$$\epsilon = \int |\hat{H}\psi - i\partial_t\psi|^2 dx$$

EOMs for the GBF parameters, $\vec{\Lambda}$:

$$\mathbf{B} \frac{d}{dt} \vec{\Lambda} = \vec{Y} \quad (1)$$

Using the unit matrix \mathbf{I} and the resolution of identity \mathbb{I} ,

$$\mathbb{I} := |\vec{g}\rangle \mathbf{S}^{-1} \langle \vec{g}|,$$

$$B_{j\alpha, l\beta} = \Re (\rho_{jl} [\partial \vec{g}_\alpha \otimes |(\mathbf{I} - \mathbb{I}) \partial \vec{g}_\beta]_{jl}), \quad (2)$$

$$Y_{j\alpha} = \Im \left(\sum_l \rho_{jl} \left[\partial \vec{g}_\alpha \otimes |(\mathbf{I} - \mathbb{I}) \hat{H} \vec{g}]_{jl} \right] \right). \quad (3)$$

Operator $\mathbf{I} - \mathbb{I}$ defines basis complement \rightarrow Eq. (1) is **singular at $t = 0$**

The quantum trajectory (QT) dynamics

QT descriptors = (q_t, p_t, S_t, ρ_t)

Polar form: $\psi(x, t) = |\psi(x, t)| \exp(iS(x, t))$, $\rho := |\psi(x, t)|^2$

Bohmian definition of the momentum $p_t = \nabla S(x, t)|_{x=q_t}$

Quantum potential, U , in equations of motion

$$U = -\frac{\hbar^2}{2m} \frac{\nabla^2 |\psi|}{|\psi|} \quad \frac{dp_t}{dt} = -\nabla(V + U)|_{x=q_t}$$

$$\frac{dq_t}{dt} = \frac{p_t}{m} \quad \frac{dS_t}{dt} = \frac{p_t^2}{2m} - V(q_t) - U(q_t)$$

Continuity of probability density, ρ

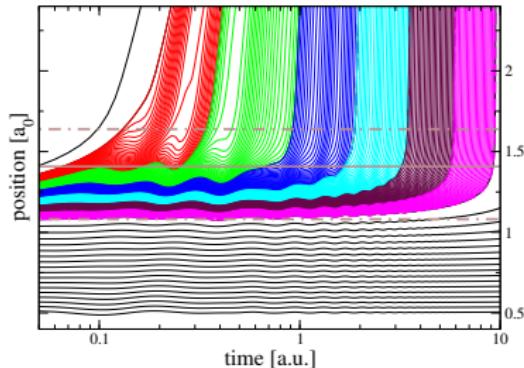
$$\frac{d\rho_t}{dt} = -\frac{\nabla p_t}{m} \rho_t \rightarrow \rho_t \delta q_t = \text{constant}$$

Dynamics of a QT ensemble

Figure: QTs for the (a) quadratic, (b) metastable well and (c) barrier potentials for $\psi(x, 0)$ taken as a Gaussian. The barrier tops are marked with brown lines.

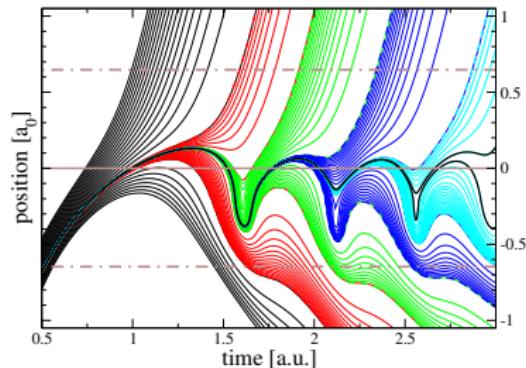
Garashchuk, Rassolov, Annual Reports in Computational Chemistry 16

(2020) Pages 41-90



(b)

(a)



(c)

QT-guided Adaptable Gaussian (QTAG) Bases

GBF expansion + QT 'inspired' dynamics of the GBFs

$$\psi(x, t) = \sum c_n(t) g_n(x; q_n(t), p_n(t), a_n(t))$$

- Variational EOMs for the coefficients, $\{c_n\}$
- QT motion of the GBF centers, $\{q_n\}$

$$\frac{dq_n}{dt} = \frac{p_n}{m} \quad p_n := \Im \left(\frac{\nabla \psi}{\psi} \right)_{x=q_n}$$

- QT evolution of *real* GBF width, $\{a_n\} \in \mathcal{R}$

$$\frac{da}{dt} = -\frac{\nabla p}{m}$$

- Want GBF in the right place at the right time, not perfect QTs
- 'Smooth' definition of $\{p_n\}$, i.e. convoluted ψ , linearized p , ...

Implementation

Time-propagation algorithm: Basis Orthogonalization/Transformation (BOT)

Table: Definitions: $\psi(x, t) = \sum_{i=1}^{N_b} c_i(t)g_i(x)$, $\vec{b} = \langle \vec{g} | \psi \rangle$, $\vec{c} = \mathbf{S}^{-1}\vec{b}$, $\mathbf{S} = \langle \vec{g} \otimes \vec{g} \rangle$.
The basis transformation matrix $\mathbf{T} = \langle \vec{g}_{new} \otimes \vec{g}_{old} \rangle$. Increment τ does not need to be small, as long as \vec{g} adequately represents ψ .

	operation	input	output
0	solve $\mathbf{H}\mathbf{Z} = \mathbf{S}\mathbf{Z}\mathcal{E}$	$\mathbf{H}, \mathbf{S}, t$	diagonal $\mathcal{E}, \mathbf{Z}, \mathbf{S}^{-1} = \mathbf{Z} \cdot \mathbf{Z}^\dagger$
1	propagate by τ	\vec{b}, \vec{c}	$\vec{c}(t+\tau) = \mathbf{Z}e^{-i\mathcal{E}\tau}\mathbf{Z}^\dagger \vec{b}(t)$
2	define new basis	\vec{g}_{old}	$\vec{g}_{new}, \mathbf{H}_{new}, \mathbf{S}_{new}$
3	solve $\mathbf{H}\mathbf{Z} = \mathbf{S}\mathbf{Z}\mathcal{E}$	$\mathbf{H}_{new}, \mathbf{S}_{new}$	new $\mathcal{E}, \mathbf{Z}, \mathbf{S}^{-1}$
4	transform to \vec{g}_{new}	$\vec{b} \vec{c} \vec{g}_{new} \vec{g}_{old}$	$\vec{b}_{new} = \mathbf{T}\vec{c}_{old}, \vec{c}_{new} = \mathbf{S}_{new}^{-1}\vec{b}_{new}$
5	"observables"	$\vec{c} \vec{g} \mathbf{H} \mathbf{S}$	$\psi(x, t), \langle \psi \hat{H} \psi \rangle = \vec{c}^\dagger \mathbf{H} \vec{c} \dots$
6	relabel <i>new</i> as <i>old</i> and $t + \tau$ as t		continue to (6) or stop

Implementation

BOT + wavefunction reexpansion

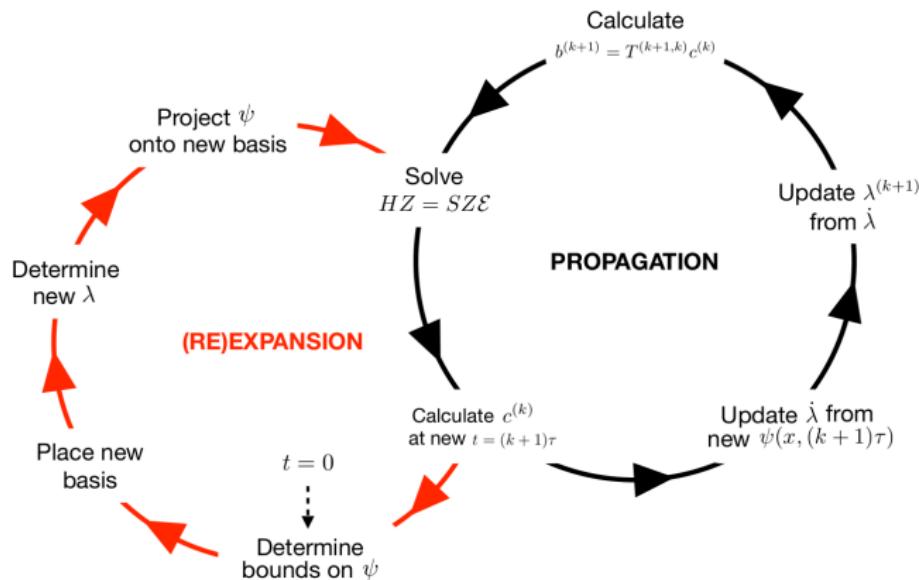
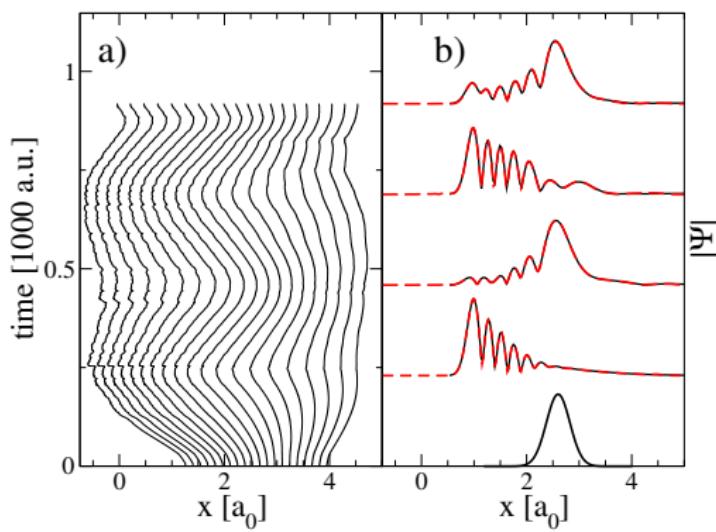


Figure: (left) (Re)expansion of $\psi(x, t)$ in a basis; (right) BOT propagation. Start at $t = 0$ label, complete the left loop, and propagate along the right loop; if a reexpansion criterion is met, then run the left loop.

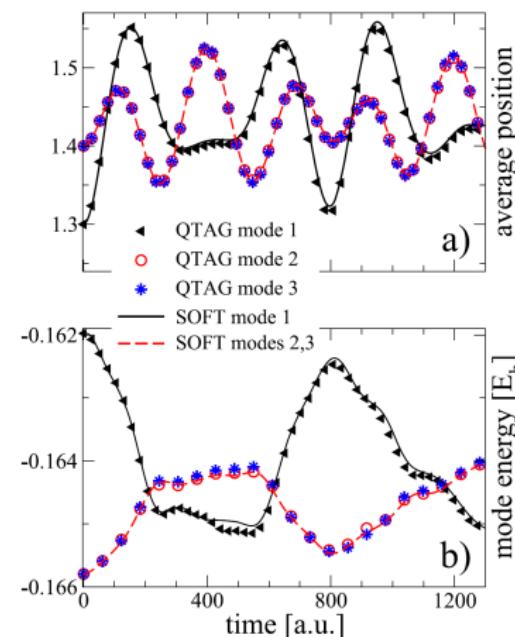
Examples

Anharmonic oscillator

H₂ Morse: interference
39 GBFs (dash=exact)



coupled 3D bath
843 GBFs (SOFT=exact)



Examples

The double well dynamics: the inversion mode of ammonia

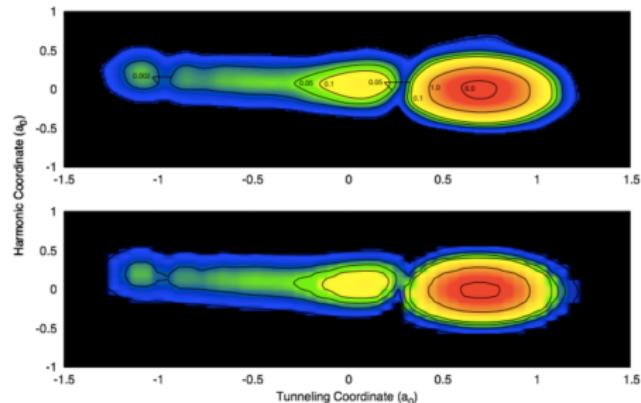
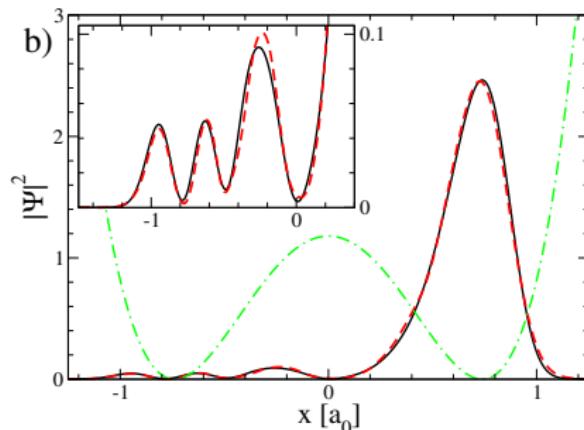


Figure: Tunneling $|\psi|^2$ (left) in 1D (19 GBFs, dash = exact) and (right) in 2D.

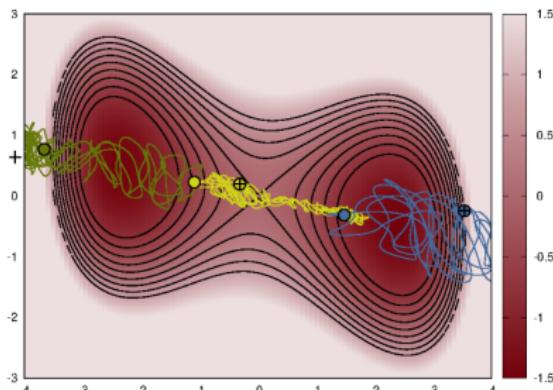
Level	Fixed-grid [E_h]	QTAG [E_h]
0 ⁺	2.295×10^{-3}	2.295×10^{-3}
0 ⁻	2.298×10^{-3}	2.297×10^{-3}
1 ⁺	6.348×10^{-3}	6.348×10^{-3}
1 ⁻	6.504×10^{-3}	6.503×10^{-3}

Table: The energy levels in 1D

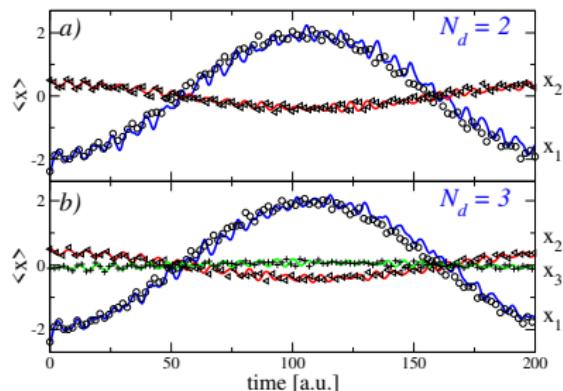
Examples

Double well with high-dimensional bath I: linear coupling

$$V^l = \frac{x_1^4}{16\eta} - \frac{x_1^2}{2} + c \sum_{\nu=2}^{N_d} x_{\nu-1}x_{\nu} + \sum_{\nu=2}^{N_d} \frac{x_{\nu}^2}{2}$$



GBF positions in 2D. QTAG basis: 25 GBFs for 1-20 bath modes using single 'bath' GBF.

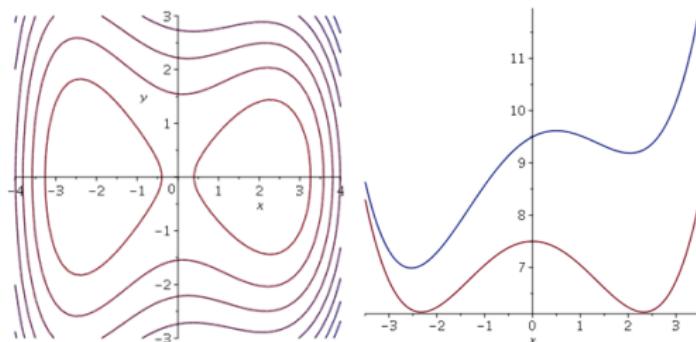


$\langle x_{\nu} \rangle$: QTAG = lines; SOFT = symbols

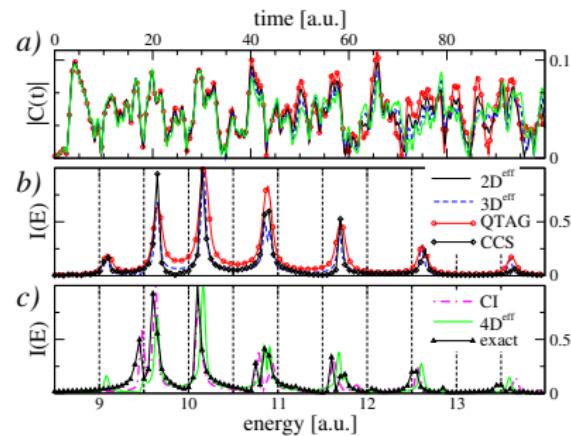
Examples

Double well II: non-linear coupling; 40 GBFs \otimes single 'bath' GBF

$$V^{\text{II}} = \frac{x_1^4}{16\eta} - \frac{x_1^2}{2} + \frac{c}{2} \sum_{\nu=2}^{N_d} x_1 x_\nu^2 + \sum_{\nu=2}^{N_d} \frac{x_\nu^2}{2}$$



Non-linear coupling; effect of bath DOFs on the reaction path



Auto-correlation function and the power spectrum for 20 DOFs

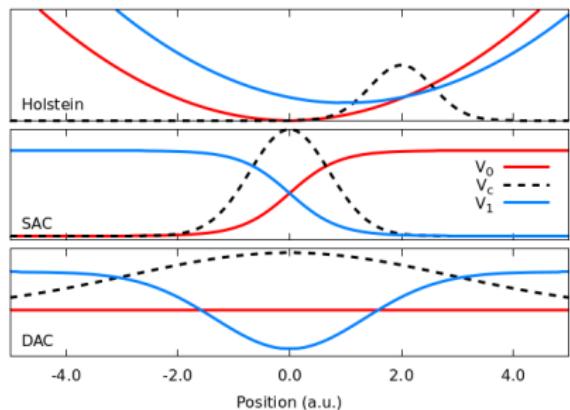
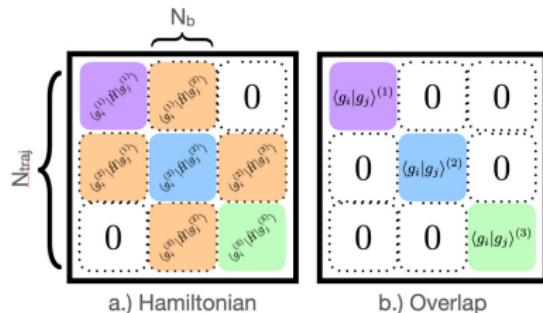
Nonadiabatic dynamics

LIBRA: model potentials; diagonal kinetic energy; nonadiabatic coupling in V

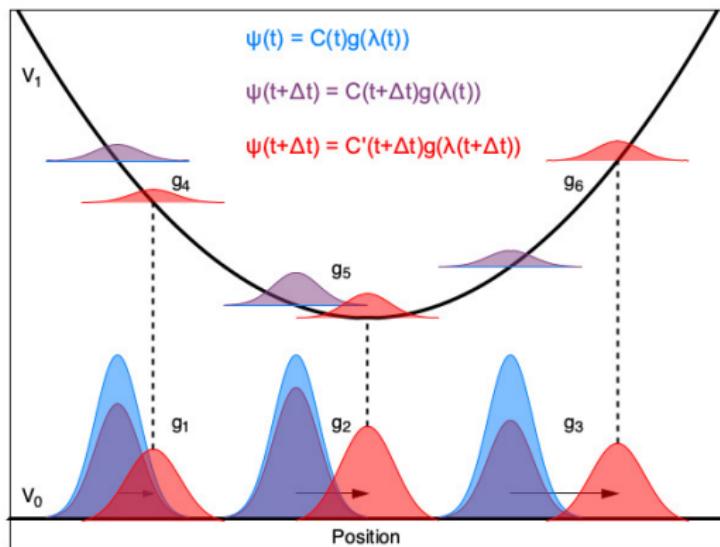
- Multiple electronic states, Bohn-Huang expansion of the electron-nuclear wavefunction:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_n \underbrace{\psi_n(\mathbf{R}, t)}_{\text{nuclear}} \underbrace{\chi_n(\mathbf{r}; \mathbf{R})}_{\text{electronic}}$$

- Each ψ_n is expressed in its GBF set; *linearized* (for each surface) QT momentum
- 1st (BAT) or 2nd (LHA) order expansion of V : Tully models SAC/DAC = single/dual avoided crossing; Holstein = quadratic PES with Gaussian coupling
- GBFs of an underpopulated state are synced to those of populated PES



Nonadiabatic BOT propagation



-
1. Propagate $C(t + \Delta t)$ in orthonormal basis stored in \mathbf{Z} .
 2. Update $P(t + \Delta t)$ according to Ψ defined by $C(t + \Delta t)$ and $\lambda(t)$.
 3. Update $Q(t + \Delta t)$ and $a(t + \Delta t)$ via $P(t + \Delta t)$ and $\nabla P(t + \Delta t)$.
 4. Reexpand $C(t + \Delta t) \rightarrow C'(t + \Delta t)$ with bases defined by $\lambda(t + \Delta t)$.
-

$$\mathbf{S}(t + \Delta t)\mathbf{C}'(t + \Delta t) = \mathbf{S}(t + \Delta t, t)\mathbf{C}(t + \Delta t)$$

QTAG workflow

Python: `libra_py.dynamics.qtag`

initialize	compute	save	plot
<ul style="list-style-type: none">• initialize• grid• gaussian• coeffs	<ul style="list-style-type: none">• time_overlap• qtag_momentum• propagate_basis• qtag_pops, qtag_energy• wf_calc_nD, psi• run_qtag	<ul style="list-style-type: none">• init_qtag_data• init_qtag_savers• save_qtag_hdf5_1D• save_qtag_hdf5_2D• save_qtag_hdf5_3D• save_qtag_data	<ul style="list-style-type: none">• plot_wf_1D• plot_wf_2D• wf_plot• energy_and_pops• trajectories

C++/Python: dyn/electronic (`libelectronic`): `propagate_electronic`

C++/Python: dyn/gwp (`libgwp`)

`gwp_overlap_matrix`



`qtag_overlap_elementary`

`gwp_kinetic_matrix`



`qtag_kinetic_elementary`

C++/Python: dyn/qtag (`libqtag`)

`qtag_overlap`



`qtag_hamiltonian_and_overlap`

BAT, BATe

LHA, LHAE

`qtag_potential`



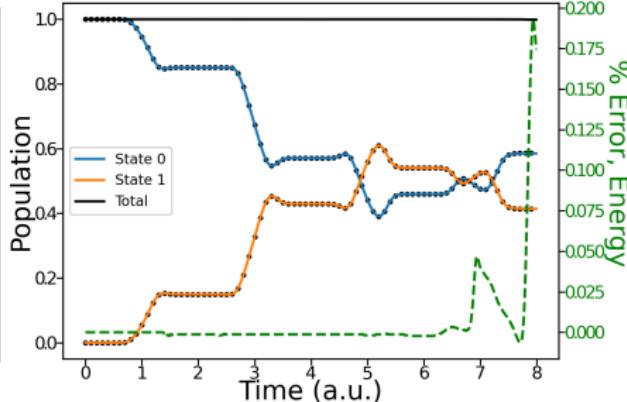
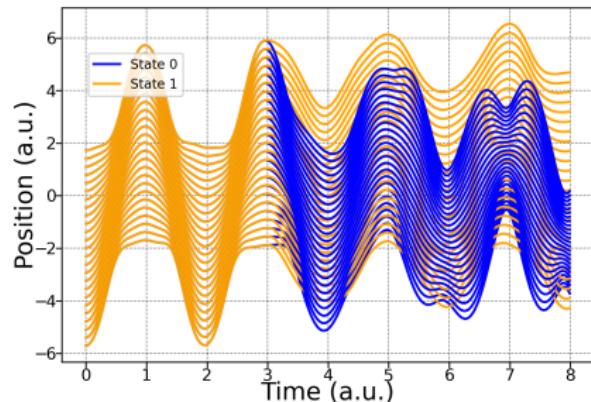
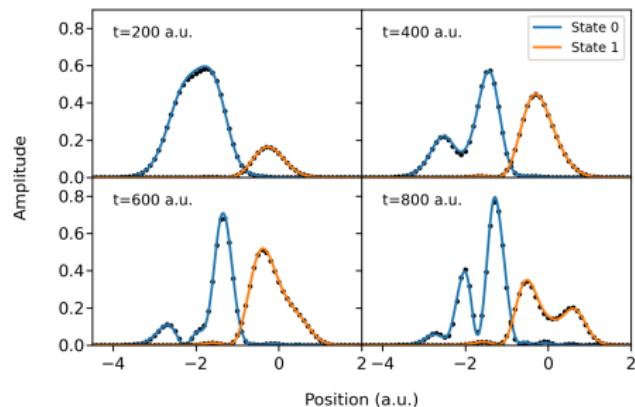
`qtag_momentum`

`qtag_psi`

Structure of the QTAG components of Libra in the Python (top) and C++ (bottom) layers. Arrows in the C++ layer indicate dependencies relating certain functions

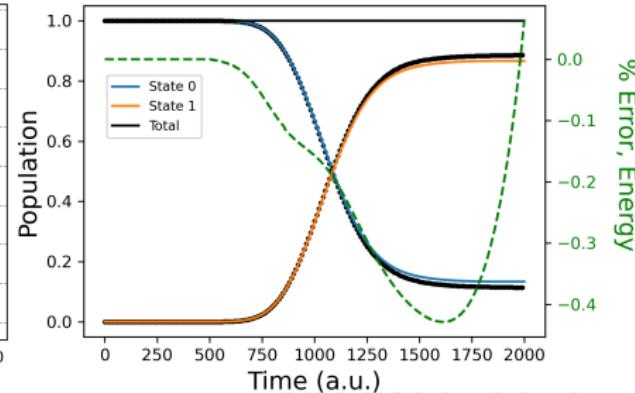
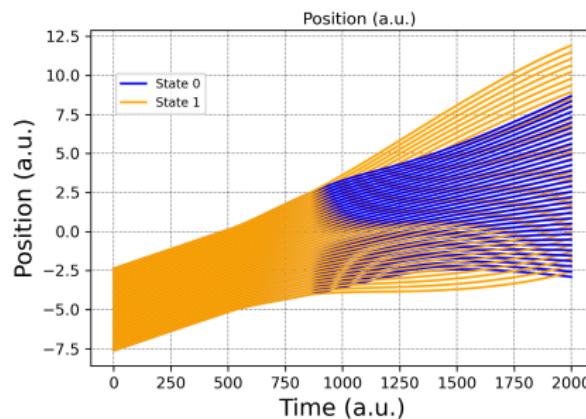
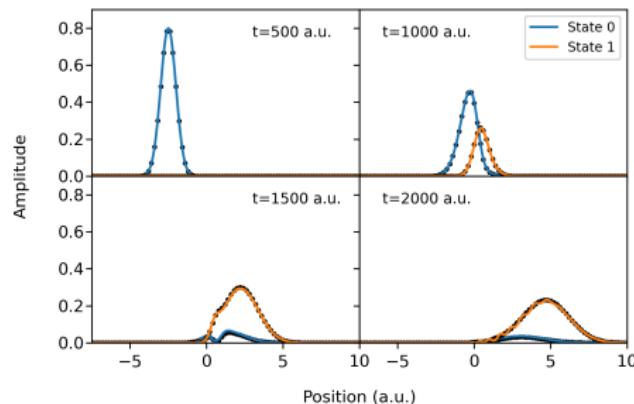
Applications: Holstein

LHA. Multiple passes through the coupling region



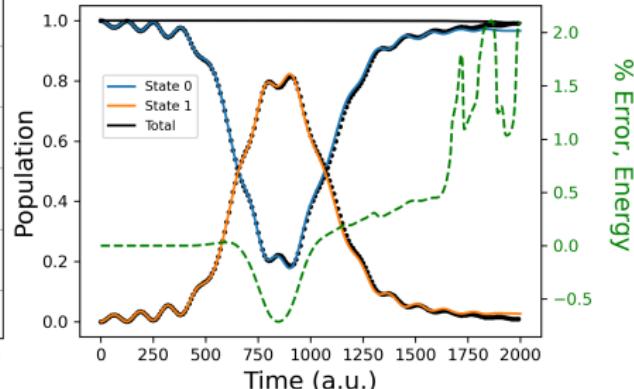
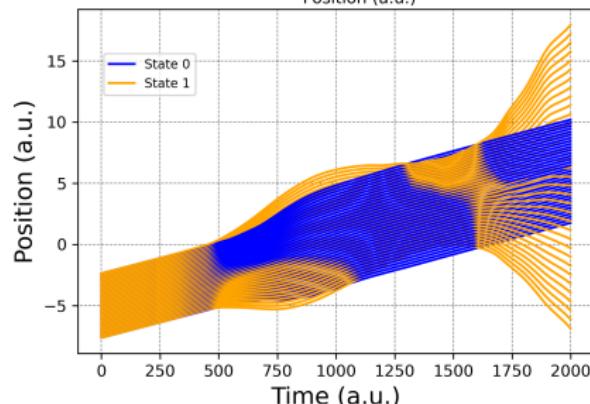
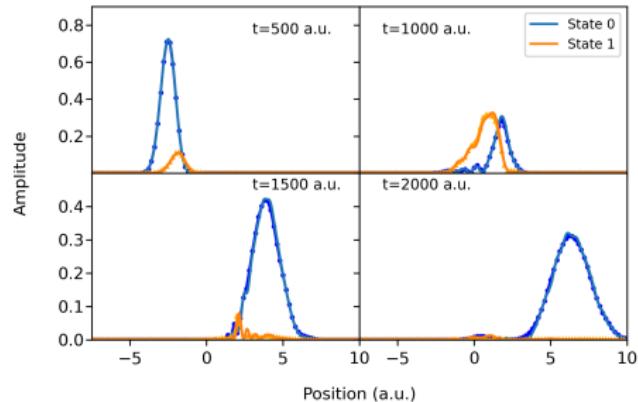
Applications: single avoided crossing

BAT. Wavepacket spreading



Applications: dual avoided crossing

BAT. State 0 = 'free' propagation, State 1 = scattering on a ramp



Development

Semi-local definition of the GBF momentum

Using a Gaussian window,

$$w_n(x; \beta, q_n) = \sqrt{\beta/\pi} \exp(-\beta(x - q_n)^2).$$

Least Squares Fit to $\mathbf{z} = \nabla\psi/\psi$:

$$\min ||\mathbf{z}_n - \tilde{\mathbf{z}}|| = \int |z_n - d_1 - d_2(x - x_n)|^2 |\psi|^2 w_n dx$$

The optimal \vec{d} from the matrix eq.

$$\mathbf{M}\vec{d} = \vec{b}, M_{ij} = \int (x - q_n)^{i+j-2} w_n |\psi|^2 dx, \quad b_i = \int w_n (x - q_n)^{i-1} \psi^* \nabla \psi dx$$

d_1 and d_2 yield p_n and ∇p_n :

$$\frac{dq_n}{dt} \sim \Im(d_1), \quad \frac{da_n}{dt} \sim \Im(d_2)$$

- (i) no division by ψ
- (ii) single 'locality' parameter β – constant or linked to GBF width
- (ii) **linear fit is exact** for Gaussian ψ for any window

Development

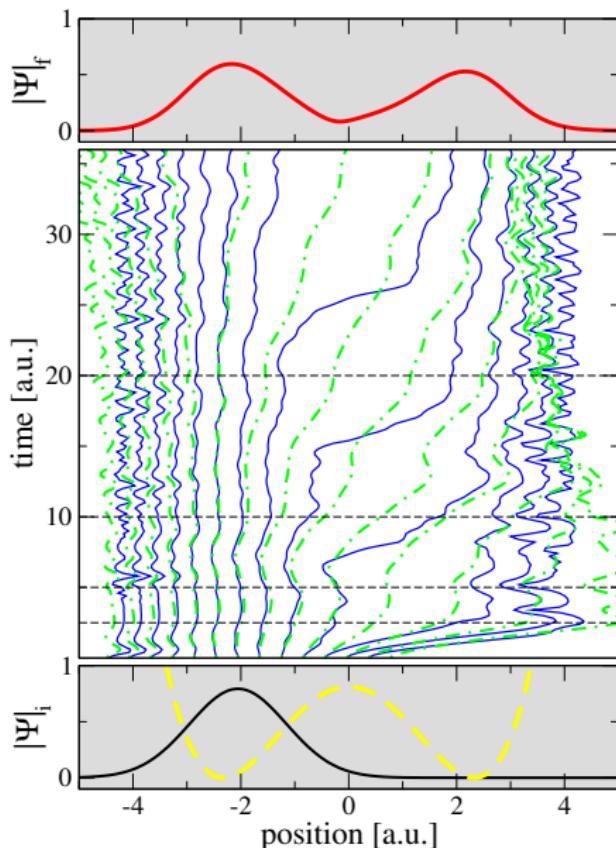


Figure: Dynamics in the double-well potential (yellow dash). Center: Selected GBF centers (green dot-dash) updated by the semi-local momentum, and exact QTs (blue lines). Bottom and top: $|\psi$ at $t_i = 0$ and $t_f = 36$ a.u.

Garashchuk, Grossmann (in revision)

Development

Note on energy conservation

For time-independent V , $\langle \psi | \hat{H} | \psi \rangle = \text{constant}$ if the basis is

- ① stationary
- ② complete (for a given ψ) time-dependent
- ③ defined by the Dirac-Frenkel or Largange Variational principle

The basis quality measure ϵ defined by the hamiltonian variance matrix

$$\Delta_H := \mathbf{H}^2 - \mathbf{H}^\dagger \mathbf{S}^{-1} \mathbf{H}, \quad \epsilon = \mathbf{c}^\dagger \Delta_H \mathbf{c}$$

- time-step 'optimization'
 - switch to a stationary basis
 - new basis re-expansion
-
- Correlated Thawed Gaussians for all bath DOFs
 - Nonadiabatic QTAD dynamics in high dimensions

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The End

Questions? Comments?