Quantum dynamics with the quantum trajectory-guided adaptable Gaussian bases

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Outline

1. Time-dependent Gaussians
2. Quantum trajectory dynamics
3. QT-driven GBFs for exact dynamics
4. Examples
5. Summary

quantum dynamics ~ quantum nuclei

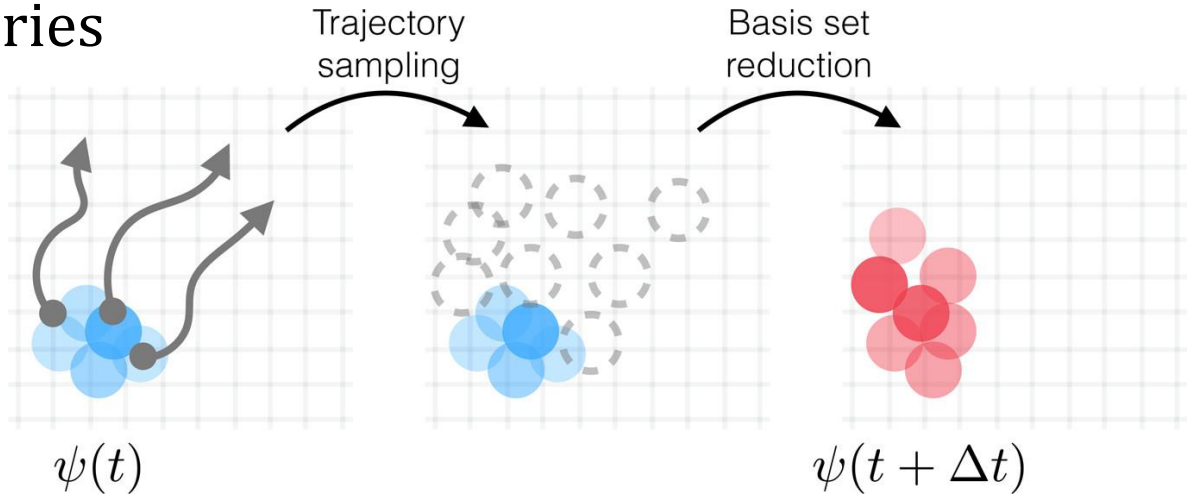
$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

- The complexity and size of WF scale **exponentially**
- Space-fixed grids/bases are inefficient for large amplitude motion
- Use time-dependent bases, representations, trajectories adaptable to WF
- Include some physics of a system, e.g. mass, energy and time-scale separation
- Factorization or layers for WFs
- Want time-dependent means to solve the TDSE

trajectory-guided (and related) basis functions

Gaussian basis functions GBFs (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
JCTC 11(1):8–16, 2015.

Why Gaussians?

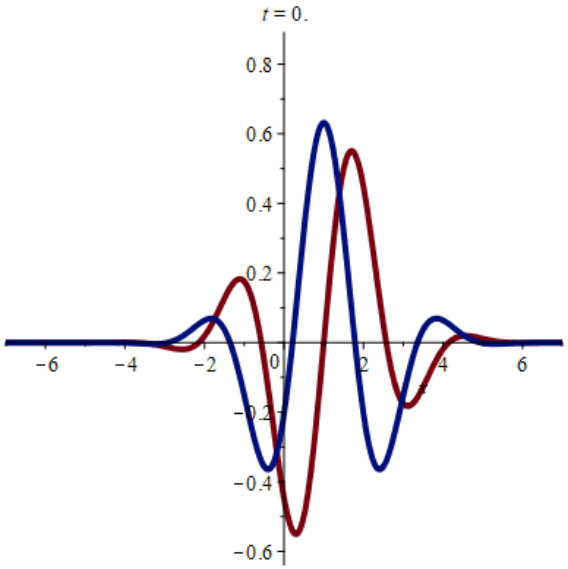
Thawed Gaussians solve TDSE for locally harmonic potentials

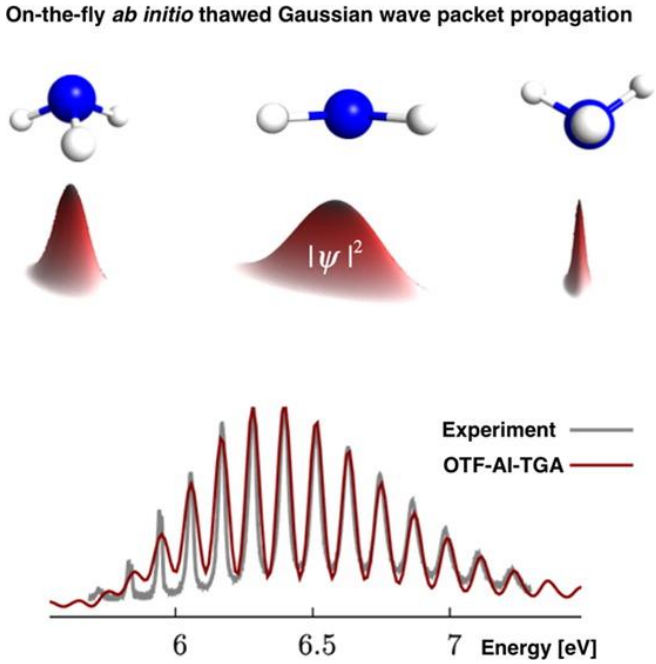
complex $\boldsymbol{A}$

$$\psi(x,t) = \mathcal{N} \exp\left(-(x-q_t)^T \boldsymbol{A}_t (x-q_t) + \imath p_t^T (x-q_t) + \imath s_t + \gamma_t\right)$$

$$\frac{dq}{dt} = \boldsymbol{M}^{-1} p, \quad \frac{dp}{dt} = -\nabla V(q) \qquad \imath \frac{d\boldsymbol{A}}{dt} = 2\boldsymbol{A}\boldsymbol{M}^{-1}\boldsymbol{A} - \frac{1}{2}\boldsymbol{V}_2, \quad \frac{d\gamma}{dt} = \mathrm{Tr}(\boldsymbol{A}_{\Im}\boldsymbol{M}^{-1})$$

$$\frac{ds}{dt} = \frac{p^T \boldsymbol{M}^{-1} p}{2} - V(q) - \mathrm{Tr}(\boldsymbol{A}_{\Re}\boldsymbol{M}^{-1})$$



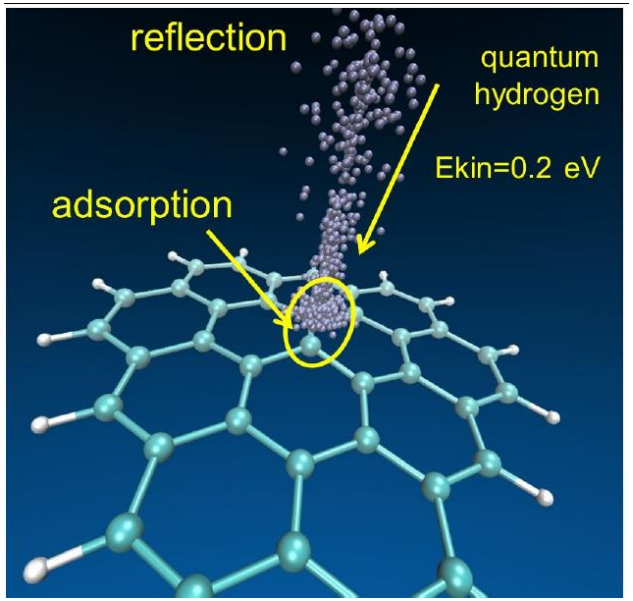


Absorption and Photoelectron Spectra of Ammonia Wherle et al
J. Phys. Chem. A, 2015, 119 (22), pp 5685–5690

Why (quantum) trajectories?

- Nuclei are nearly classical; CM scales linearly
- Trajectory framework is convenient for mixed representations
- The QT formulation has classical and quantum 'regimes'
- **Approximate** implementation gives cheap estimates of the dominant QM effects

- QTs define an ideal 'grid' in coordinate space

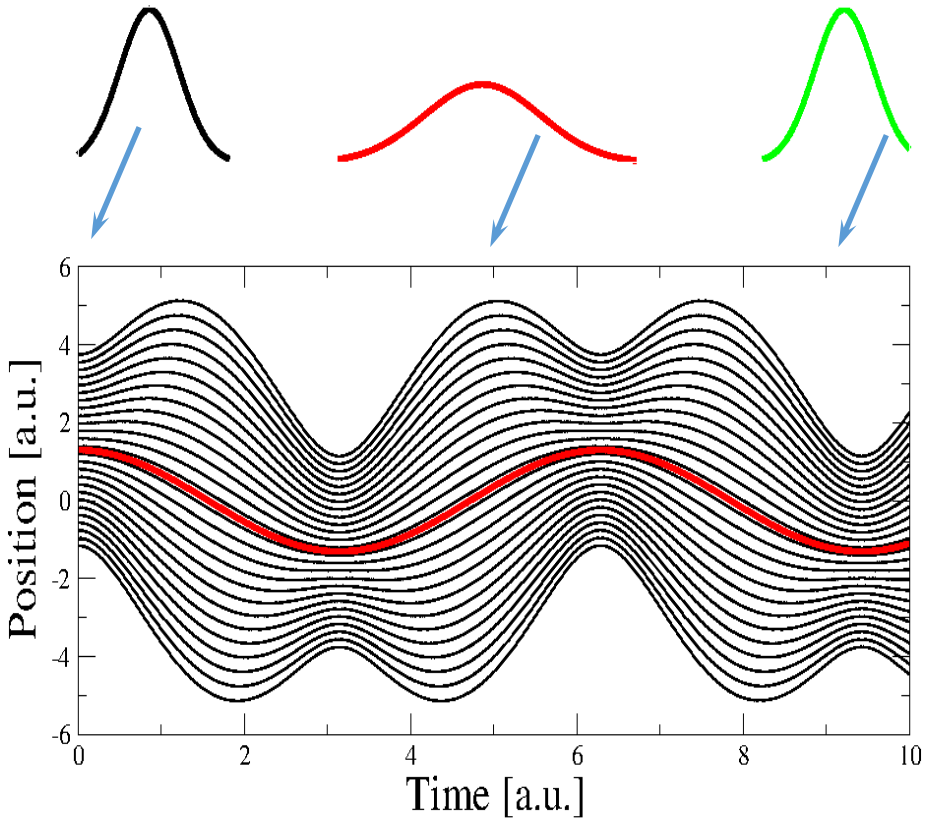


SG, Rassolov JCP **120**, 6815 (2004)
SG, J. Jakowski, L. Wang, B.G. Sumpter, JCTC 9 (2013)

WF $\psi = |\psi|\, e^{i\,s(x,t)}$

QT (q,p) $\boldsymbol{p} := \boldsymbol{\nabla}(\arg\psi)|_{\boldsymbol{x}=\boldsymbol{q}}\,, \quad \dfrac{d\boldsymbol{q}}{dt} = \dfrac{\boldsymbol{p}}{m}$

$$\frac{d\boldsymbol{p}}{dt} = -\,\boldsymbol{\nabla}(V+U)|_{\boldsymbol{x}=\boldsymbol{q}} \qquad \frac{ds}{dt} = \frac{\boldsymbol{p}\cdot\boldsymbol{p}}{2m} - (V+U)|_{\boldsymbol{x}=\boldsymbol{q}}$$



$$U = -\frac{\hbar^2}{2m}\frac{\nabla^2|\psi|}{|\psi|}$$

quantum potential

Continuity of $\rho = |\psi(x,t)|^2$

$$\frac{d\rho}{dt} = -\frac{\nabla p}{m}\rho$$

$|\psi|^2\delta x$ along a QT is constant

QT-guided adaptable Gaussian Bases (QTAG)

$$\psi(x,t) = \sum_{j=1}^{N_b} c_j(t) g_j(x,t)$$ WF expansion in GBFs

$$g_j := g_j(x;\vec{\lambda}_j(t)) = \left(\frac{a_j}{\pi}\right)^{1/4} \exp\left(-\frac{a_j}{2}(x-q_j)^2 + \imath p_j(x-q_j) + \imath s_j\right)$$

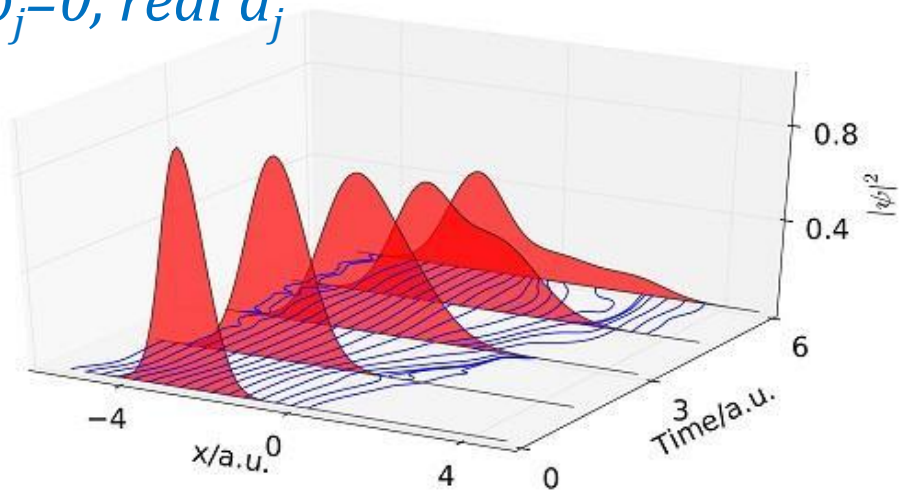
$$\mathbf{\Lambda} \equiv \langle \vec{g} \times | \left(\hat{H} - \imath\frac{\partial}{\partial t}\right) \vec{g}\rangle, \quad \mathbf{S} = \langle \vec{g} \times \vec{g}\rangle, \quad \mathbf{\Lambda}\vec{c} = \imath\mathbf{S}\frac{d\vec{c}}{dt}$$

GBF parameters $\vec{\lambda}_j(t) = (a_j, q_j, p_j, s_j)^T$

(i) use **real frozen GBFs**: *s_j=0, p_j=0, real a_j*

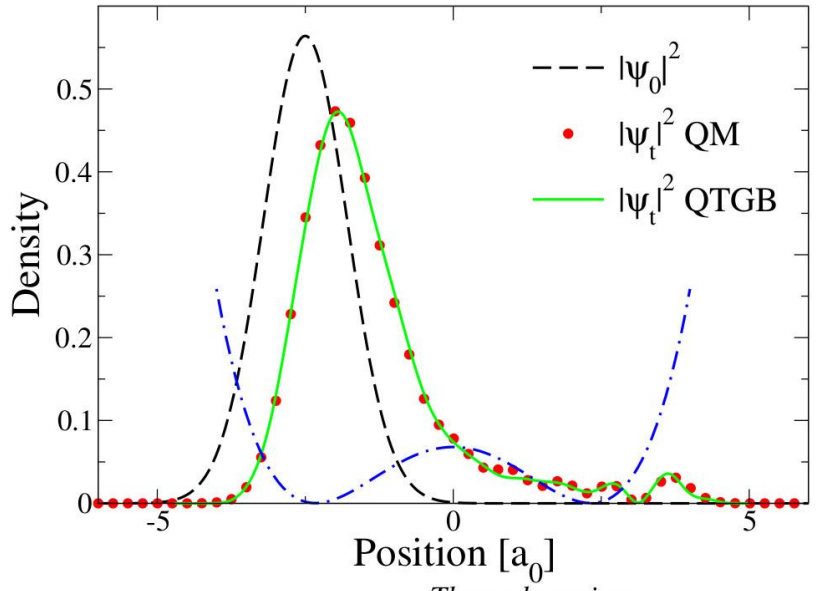
(ii) no quantum force

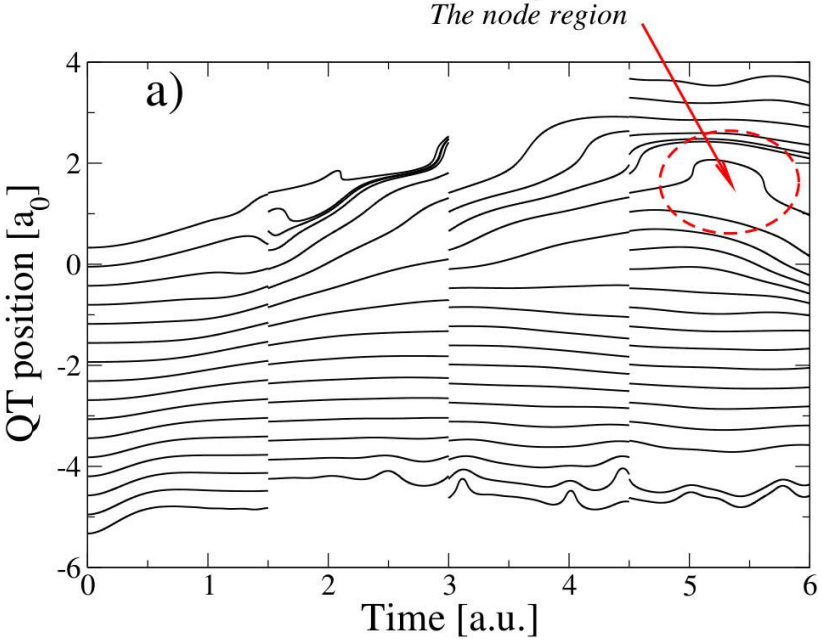
$$\frac{dq}{dt} = \frac{p}{m}, \quad p = \Im\left(\frac{\nabla\psi}{\psi}\right)$$



Gu and SG JPCA 120 (2016)

1D double well





2D V_b=0.6366 [frequency]

Basis N	10	12	16	QM
a [a.u.]	16	16	32	512 pnt
n=0	.4827	.4822	.4830	.4829
n=1	.7110	.7180	.7209	.7163

Convoluted WF for smoother ***p***

(don't need perfect QTs after all)

Re-expansion for stability and basis size adjustment

Basis degeneracy if GBFs are close

(want adaptable GBFs)

QTs 'optimize' the basis in coordinate space w/out solving the variational eqs

Relation to the fully variational basis?

general variational GBF time-dependence

$$\epsilon = \int_{x\in\mathbf{R}} \left| \hat{H}\psi - \imath\partial\psi/\partial t \right|^2 dx$$

S := GBF overlaps

I := unit matrix

GBF parameters

$$\mathbf{B}\frac{d}{dt}\vec{\Lambda} = \vec{Y}$$

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

resolution of identity in a basis

$$B_{j\alpha,l\beta} = \Re\left(\rho_{jl}[\langle\partial\vec{g}_\alpha\otimes|\,\mathbf{I}-\mathbb{I}\,|\otimes\partial\vec{g}_\beta\rangle]_{jl}\right) \qquad \rho_{jl} := c_j^* c_l$$

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

$\mathbf{I} - \mathbb{I}$ subspace complementary to that covered by the basis

if the basis is good the variational equations are singular

instead consider solution when *each* GBF solves TDSE

GBF is localized on a scale of LHA and WF

$$\imath \sum_{\beta} \partial g_{l\beta} \dot{\lambda}_{l\beta} = \hat{H} g_l$$ Thawed Gaussian, *real* a_t

$$g(x,t) = \left(\frac{a_t}{\pi}\right)^{1/4} \exp\left(-\frac{a_t}{2}(x-q_t)^2 + \imath\mathcal{S}(q_t) + \imath\mathcal{S}'(q_t)(x-q_t) + \frac{\imath\mathcal{S}''(q_t)}{2}(x-q_t)^2\right)$$

TDSE gives

$$\dot{q}_j = \frac{p_j}{m}, \quad \dot{a}_j = -\frac{2a_j}{m}\nabla p_j,$$

variational

$$\dot{s}_j = \frac{p_j^2}{2m} - V(q_j) - U(q_j)$$

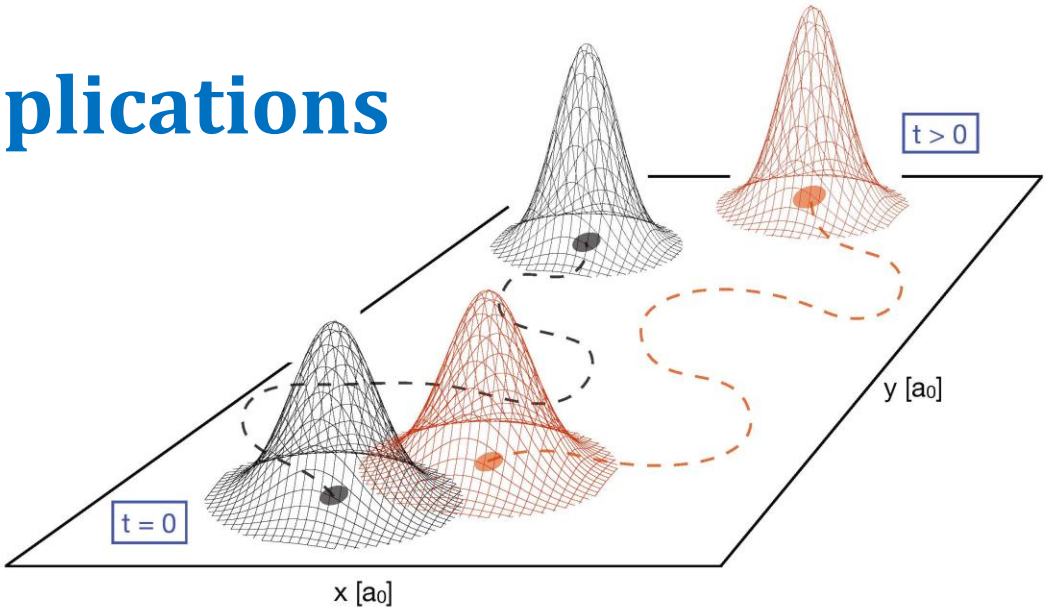
optional phase

p_j and $U(q_j)$ from

$$z_j := \left.\frac{\nabla\psi(x,t)}{\psi(x,t)}\right|_{x=q_t}$$

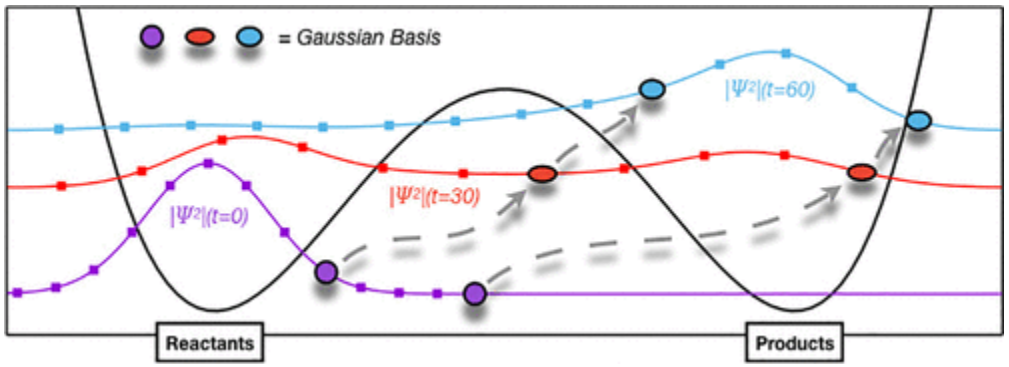
c_j from $$\mathbf{\Lambda} \equiv \langle \vec{g} \times | \left(\hat{H} - \imath\frac{\partial}{\partial t}\right) \vec{g}\rangle, \quad \mathbf{S} = \langle \vec{g} \times \vec{g}\rangle, \quad \mathbf{\Lambda}\vec{c} = \imath\mathbf{S}\frac{d\vec{c}}{dt}$$

applications



Accuracy: energy and norm conservation

Output: auto- and cross-correlations, $C(t)=\langle\psi(0)|\psi(t)\rangle$, and spectra

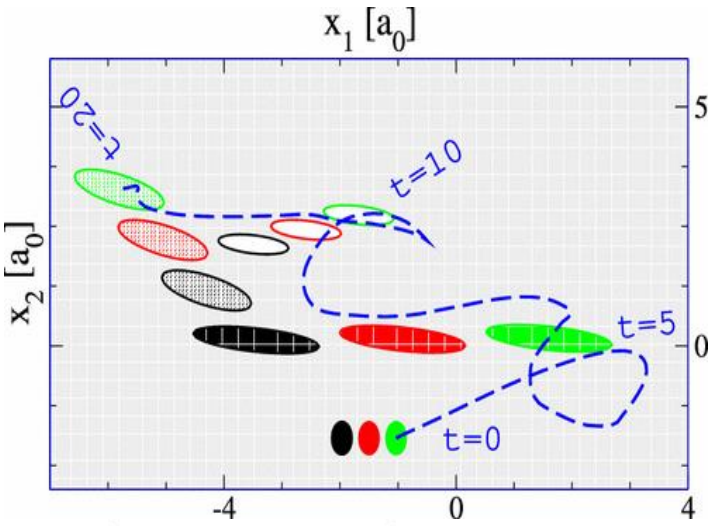


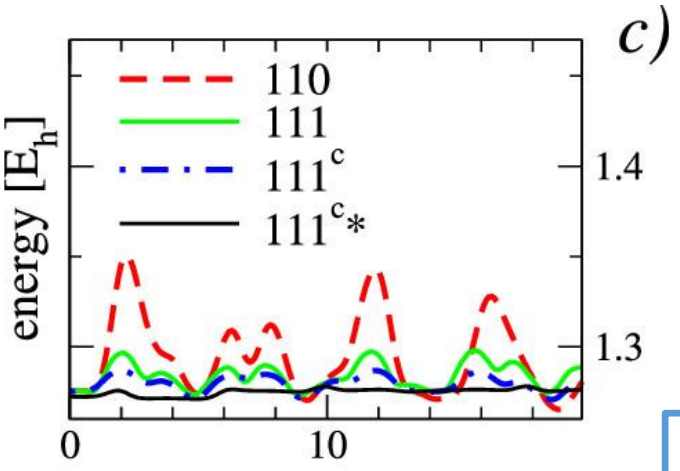
coupled HO model

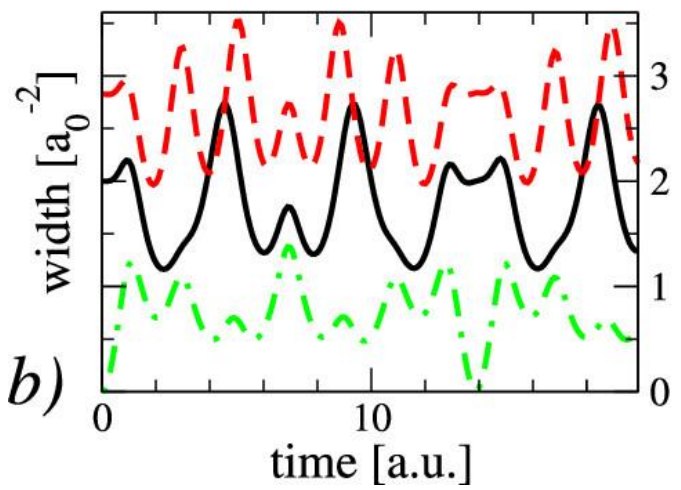
Positions of 3 GBFs : the oval size represents the GBF localization

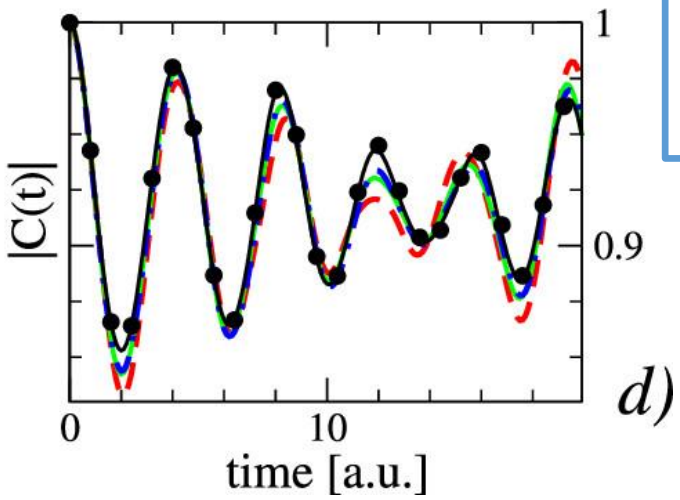
44 GBFs; * = 57 GBFs; circles = SOFT

1/0 = adapted/fixed (q,p,a)









110 frozen width

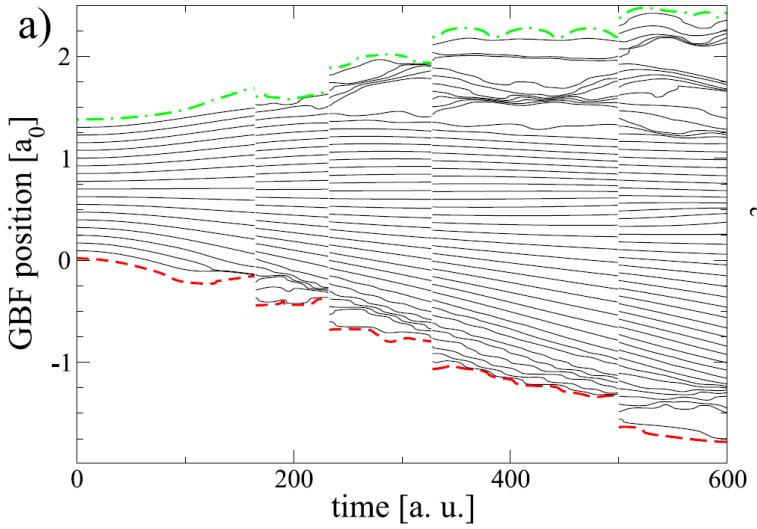
111^c adapt corr

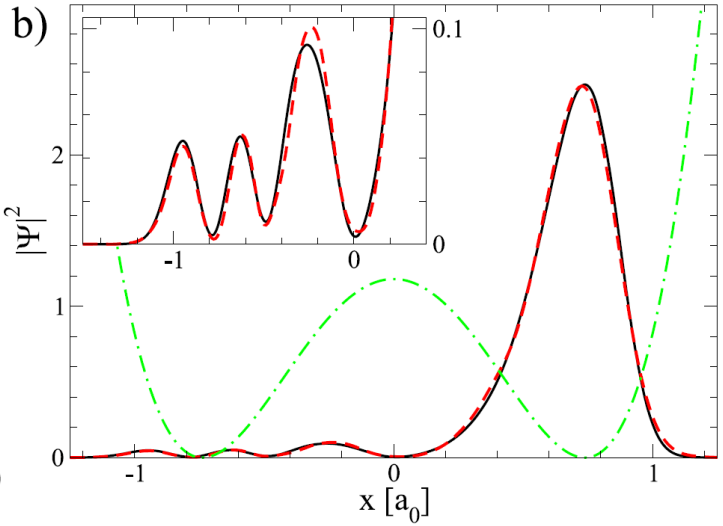
111 adapt uncor

(a_{11}, a_{12}, a_{22}) = solid, dot-dash, dash

circles = SOFT

inversion of ammonia model



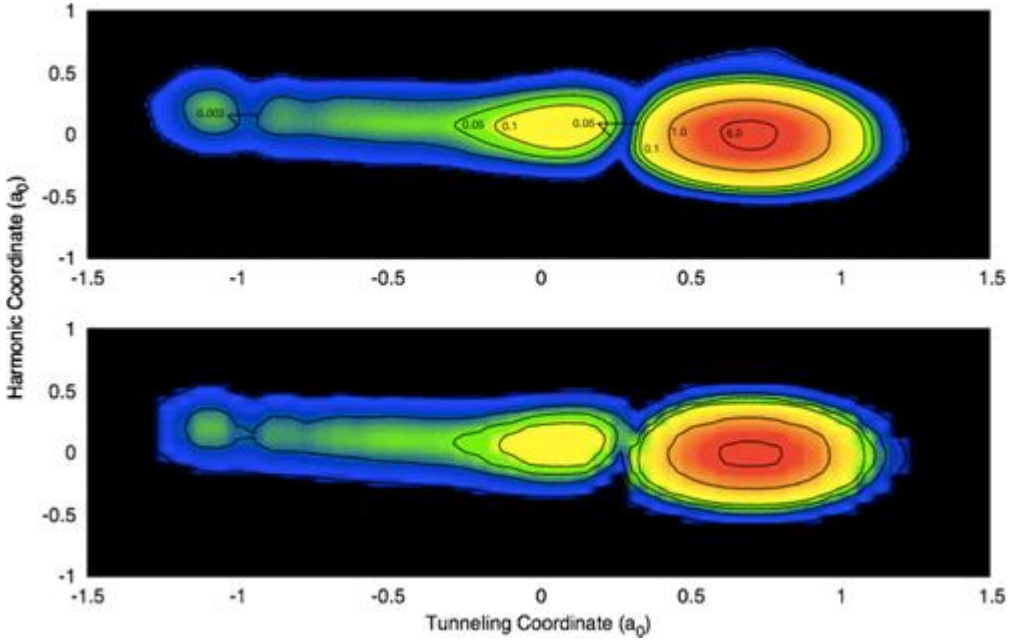


1D N_b=15-60
WF t=2000 au

V_b=22.5 kJ/mol
WF energy V_b/3

1D energy levels

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}



2D N_b= 103-269 WF at t=800 au
QTAG(top) and SOFT (bottom)

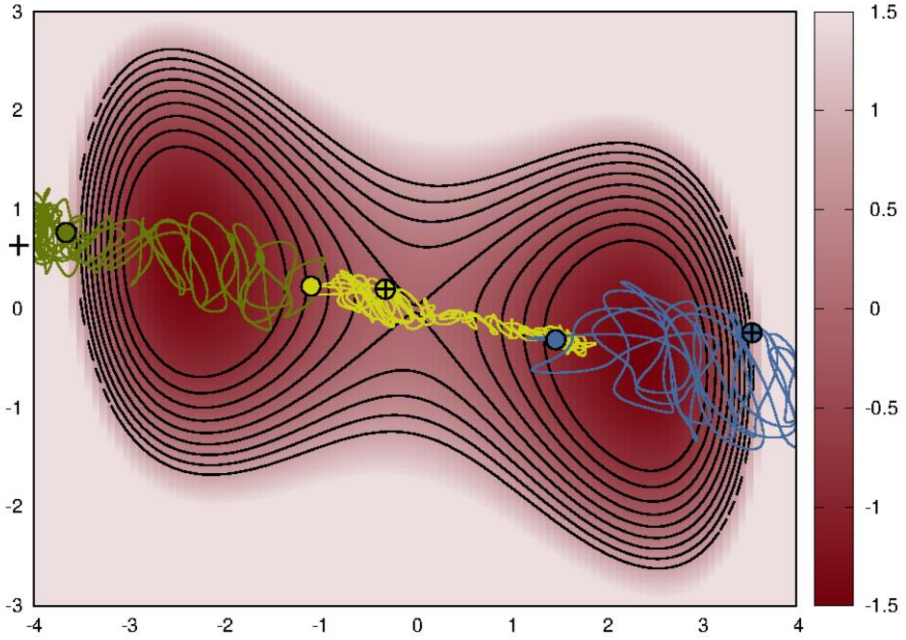
tunneling dynamics with semiclassical bath

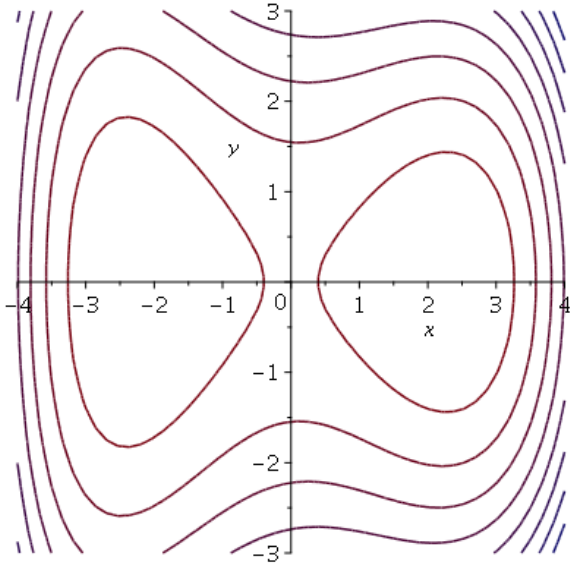
model I

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

model II

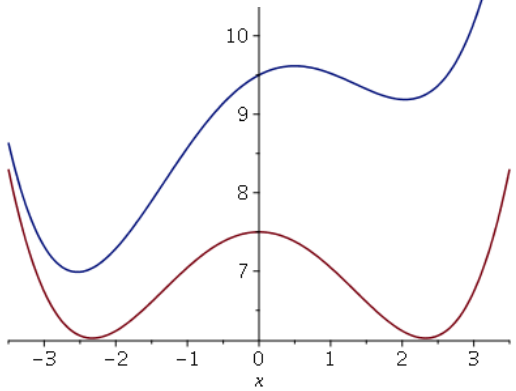
$$V^{\mathrm{II}} = \frac{x_1^4}{16\eta} - \frac{x_1^2}{2} + \frac{c}{2}\sum_{\nu=2}^{N_d} x_1 x_\nu^2 + \sum_{\nu=2}^{N_d}\frac{x_\nu^2}{2}$$





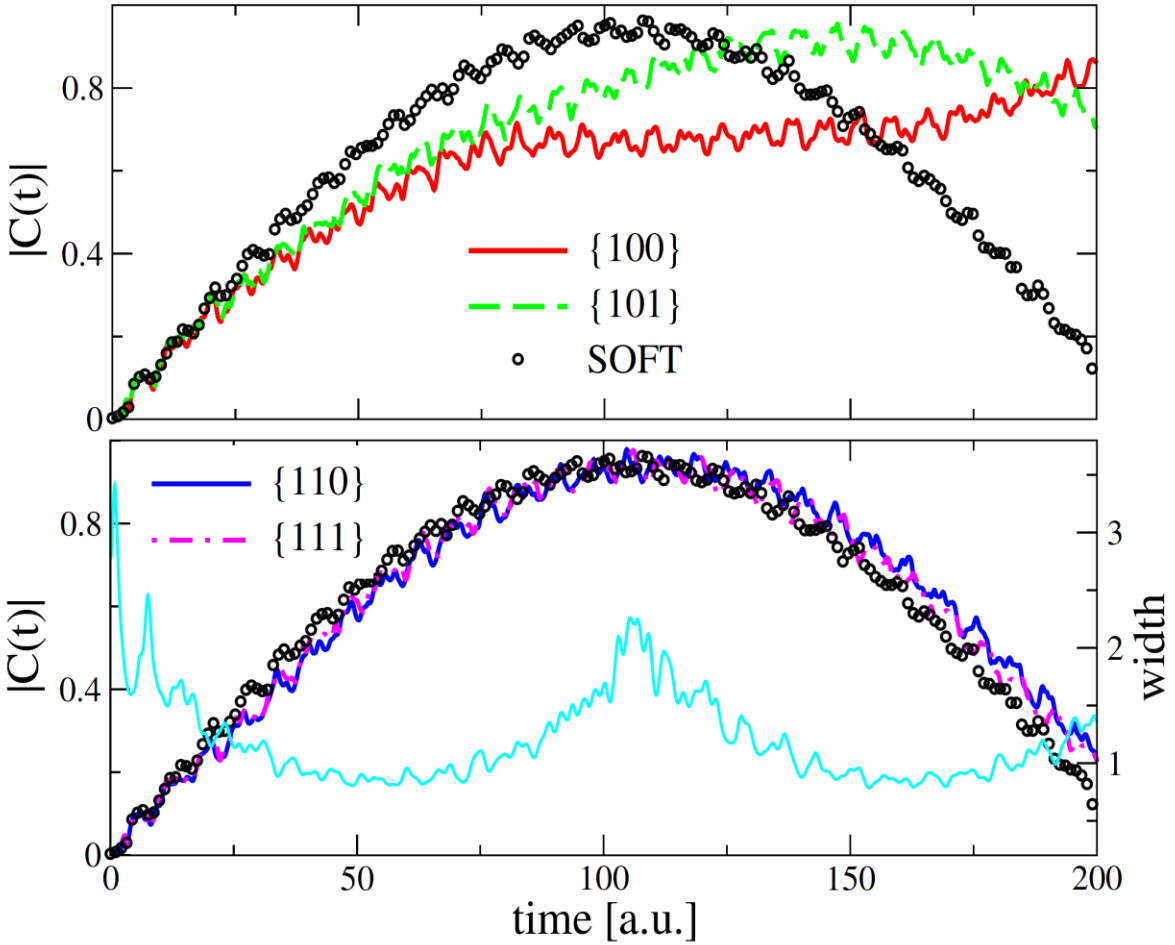
Bath modes increase the barrier ~ 15%

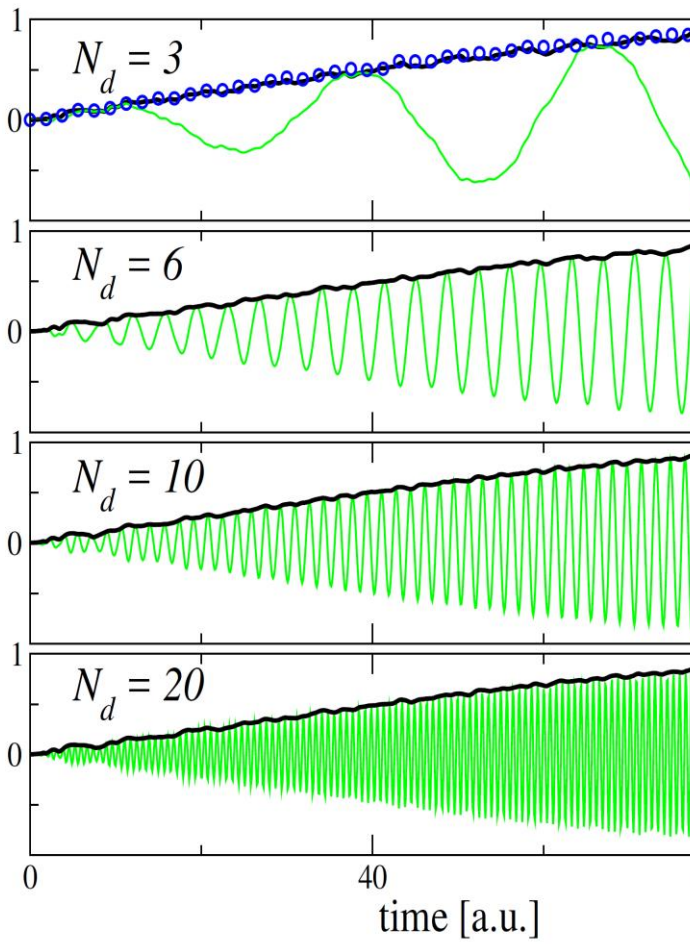
Nd=1, 20



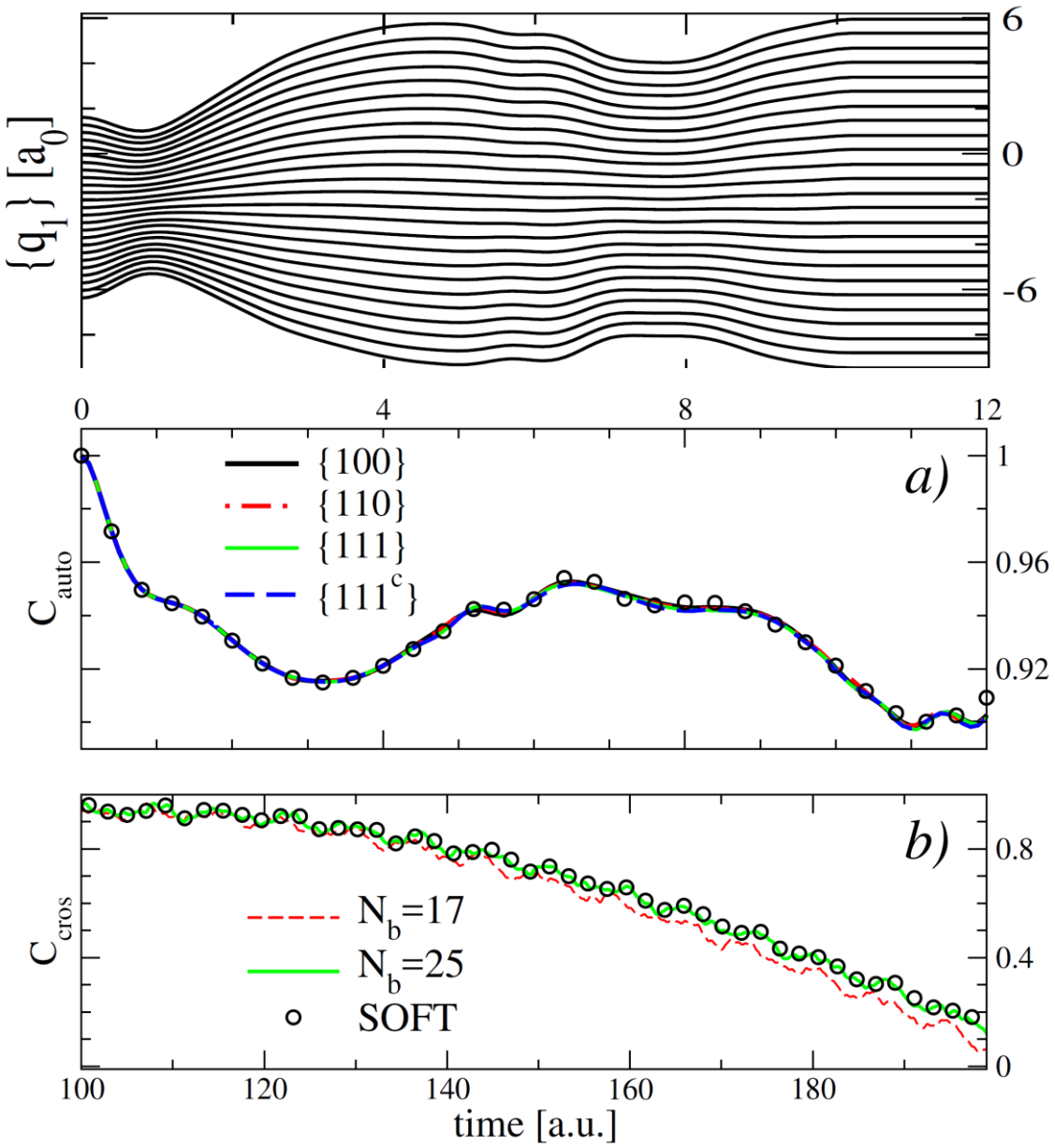
model I: cross-correlation functions

single function per bath DOFs





(left) N_d = 2: 25 GBFs with four types {q,p,a} of basis adaptability. The GBF width $a_1(t)$ for {111} basis is on the bottom panel; vertical axis is on rhs. (right) {110} basis is used



model I in 2D

correlated QTAG

(i) more flexible GBFs improve accuracy

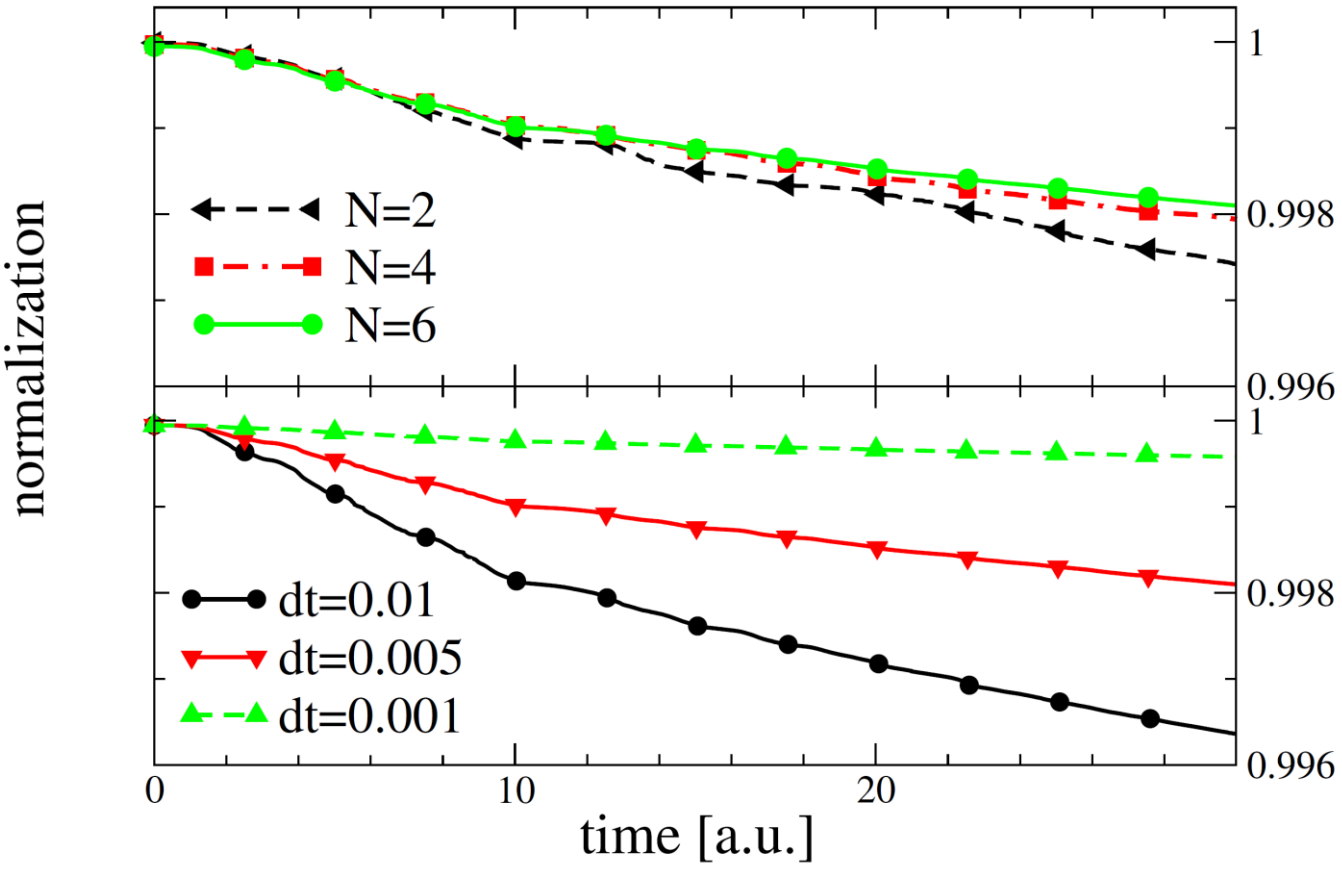
(ii) and they can be stopped

thawed GBFs for bath DOFs?

(a) C_{auto} with four basis types of 25 GBFs (b) C_{cros} with fully adaptable $\{111^c\}$

model I

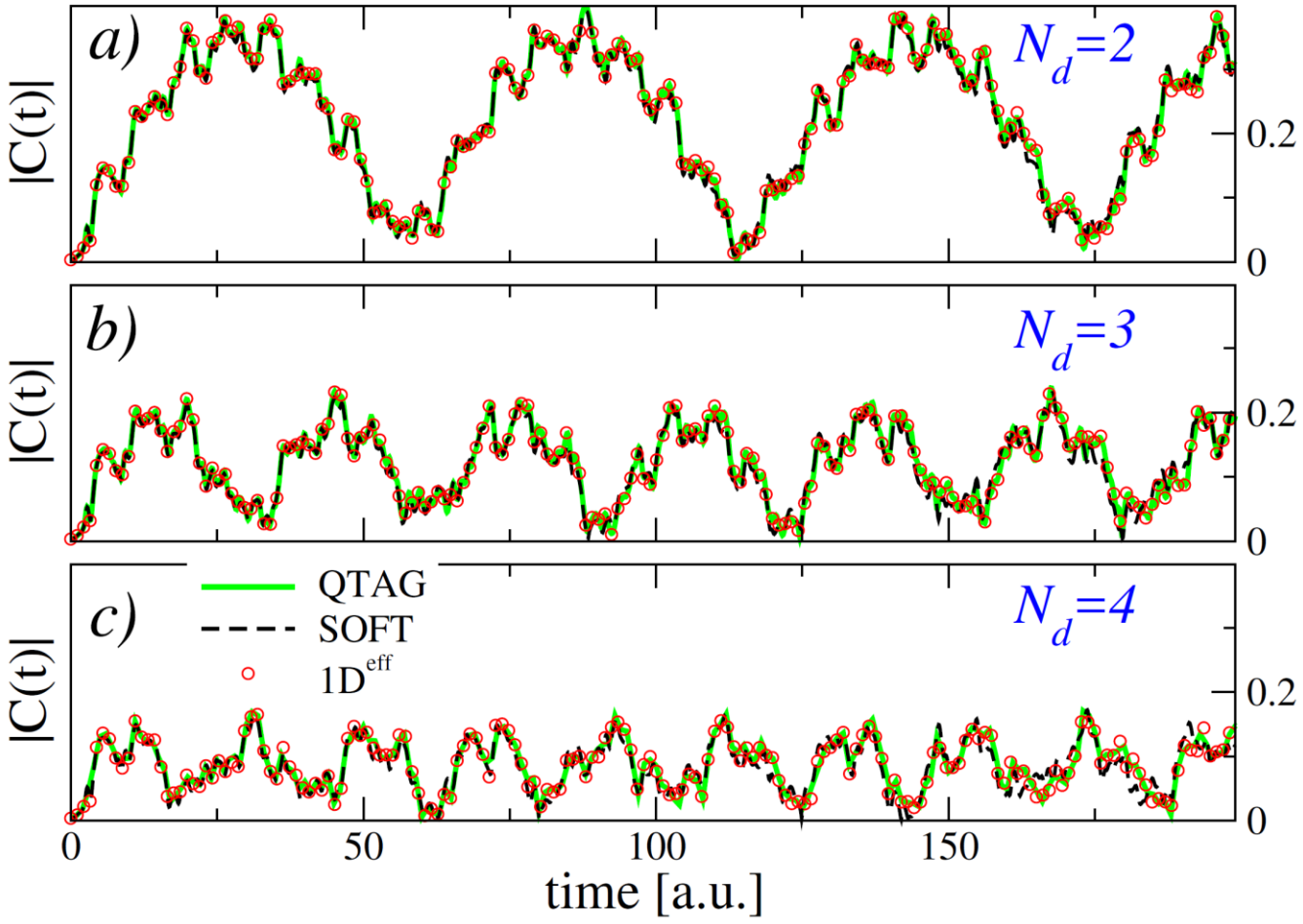
normalization conservation for 2,4,6 dimensions(top) and as a function of timestep for N_d=6 (bottom) with 'diagonalize/project' scheme



better propagators?

model II (nonlinear coupling, trajectories 'do not go' across the barrier)

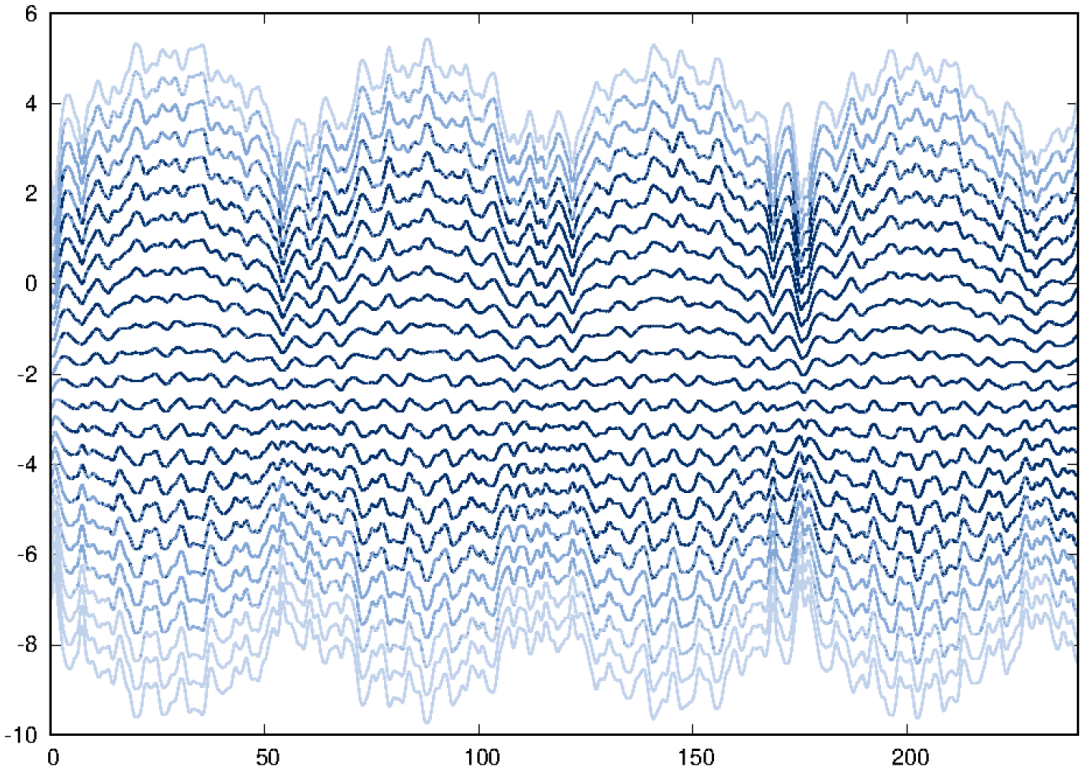
effective potential $\widetilde{V}_{N_d} = \frac{x_1^4}{16\eta} - \frac{x_1^2}{2} + \tilde{c}x_1 + V_0, \quad \tilde{c} = c\frac{N_d - 1}{2}, \quad V_0 = \frac{N_d - 1}{2}$

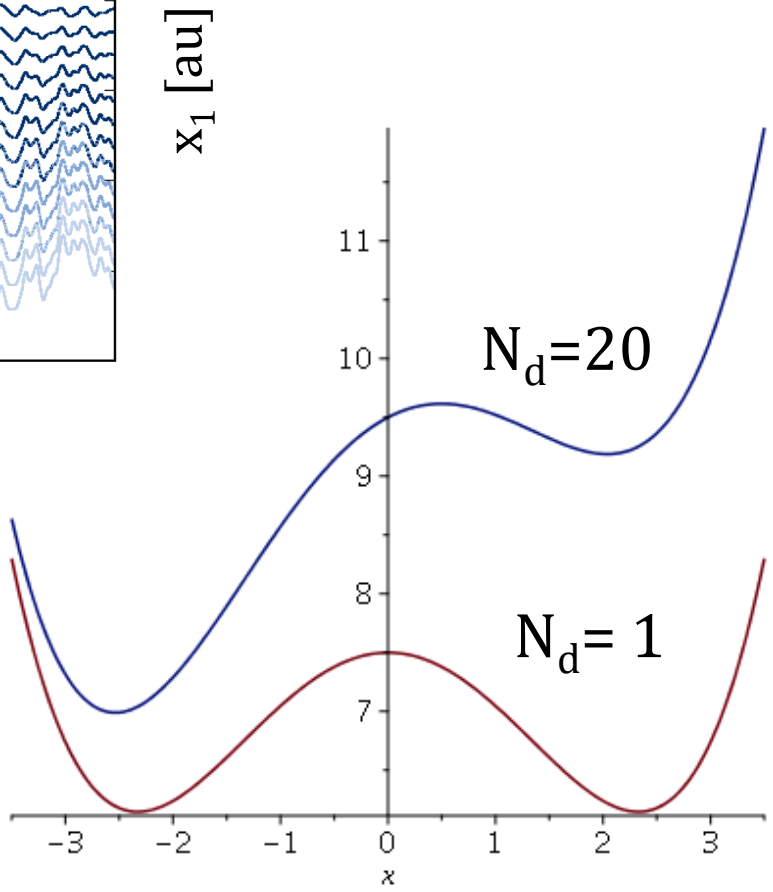


C_{cros} from QTAG (25 GBFs), SOFT in full D, and in 1D with effective potential

model II

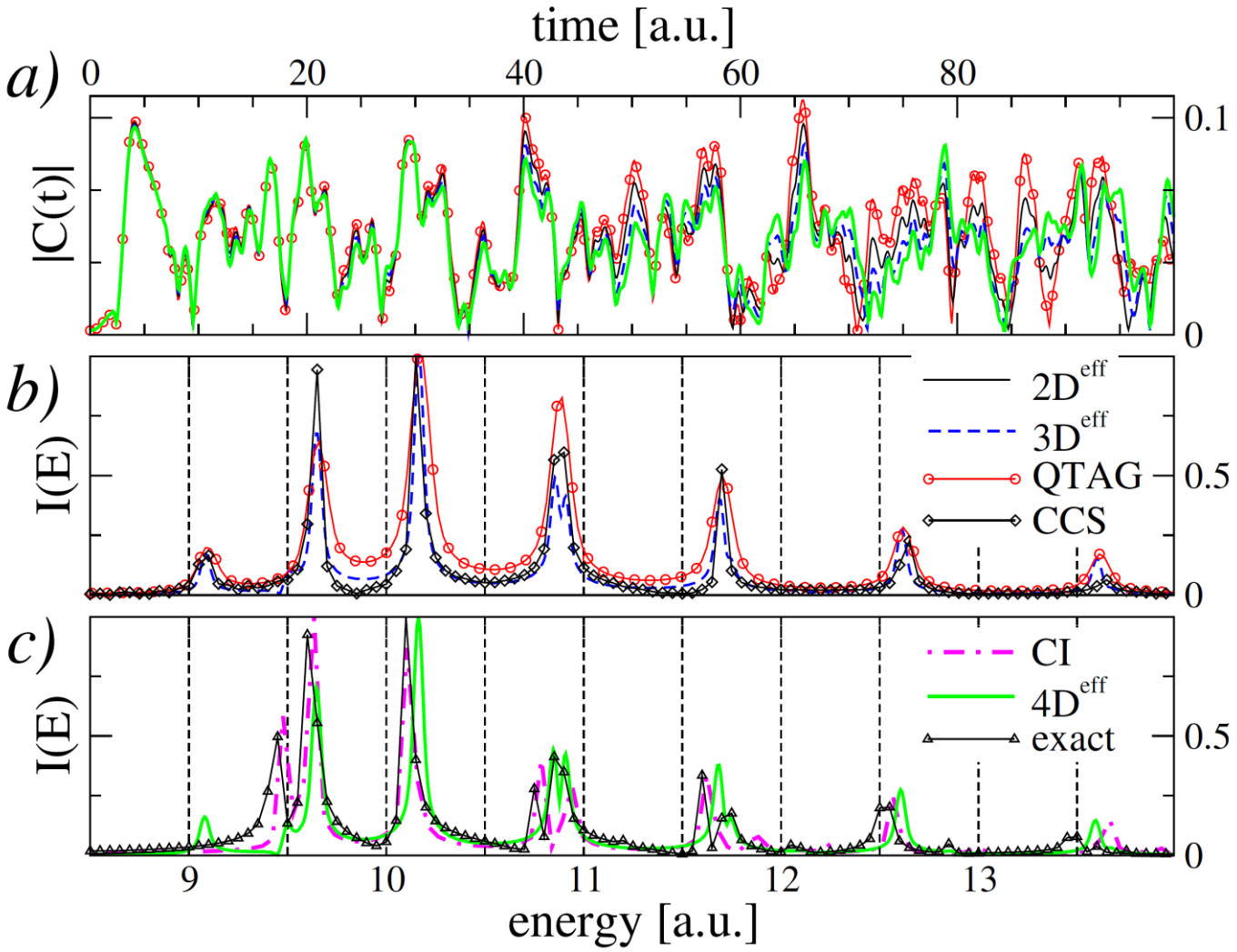
the color intensity correlates with the amplitudes of the respective GBFs





well-to-well dynamics disappears with N_d

model II single function per bath DOFs $N_d = 20, N_b = 40$



peaks split due to bath DOFs

(a) C_{cros} from QTAG, SOFT and effective potentials

(b,c) The spectra compared to CCS, trajectory-guided CI and full basis.

Habershon JCTC 13 (2017), Shalashilin Chem. Phys. 322 (2006) & CPL 641 (2015)

summary

- QTs define compact WF representations for exact, approximate, mixed quantum dynamics

- QT-guided adaptable Gaussians are efficient and compatible with semiclassical representation of bath modes

- linear-in-x phase is important, GBF width adaptation is limited by LHA (V_{ij} evaluations); issues of stability and (re)expansions

- Need a general criterion to balance stationary and time-dependent representations based on broad features of WF

Thank you!

Bing Gu (UC Irvine)
Matt Dutra
Sachith Wickramasinghe

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Propagation using energy eigenstates

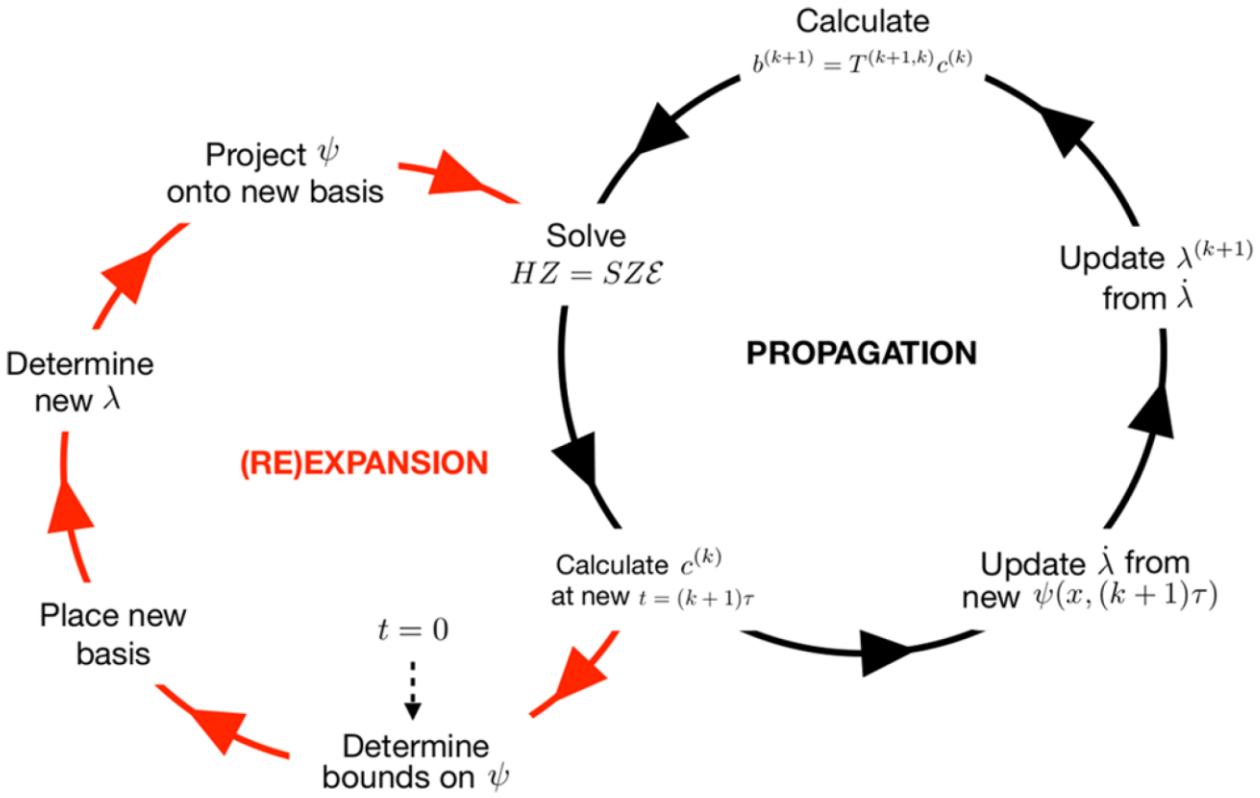
$$\psi(x,t_K)=\prod_{k=0}^{K-1}\vec{g}_{K-1}\mathbf{Z}_{K-1}e^{-\imath\mathbf{\Lambda_K}(\mathbf{t_K}-\mathbf{t_{K-1}})}\mathbf{Z}^{\dagger}_{K-1}\mathbf{T}_{K-1,K-2}\ldots\mathbf{T}_{1,0}\mathbf{Z}_0e^{-\imath\mathbf{\Lambda_0}(\mathbf{t_1}-\mathbf{t_0})}\mathbf{Z}^{\dagger}_0\vec{b}_0(t_0)$$

start	solve $\mathbf{HZ}=\mathbf{SZ\Lambda}$	$\mathbf{H},\mathbf{S},t$	diagonal $\mathbf{\Lambda}$, $\mathbf{Z}$, $\mathbf{S^{-1}}=\mathbf{Z}\cdot\mathbf{Z}^{\dagger}$, $\mathbf{Z}^{\dagger}\mathbf{SZ}=\mathbf{I}$
(i)	propagate by τ	$\vec{b},\ \vec{c}$	$\vec{c}(t+\tau)=\mathbf{Z}\exp(-\imath\mathbf{\Lambda}\tau)\mathbf{Z}^{\dagger}\vec{b}(t), \vec{b}(t)=\mathbf{S}\vec{c}(t)$
(ii)	define new basis	$\vec{g}_{old}$	$\vec{g}_{new}$, $\mathbf{H}_{new}$, $\mathbf{S}_{new}$
(iii)	solve $\mathbf{HZ}=\mathbf{SZ\Lambda}$	$\mathbf{H}_{new}$,$\mathbf{S}_{new}$	new $\mathbf{\Lambda},\mathbf{Z},\ \mathbf{S}^{-1}$
(iv)	transform ψ to $\vec{g}_{new}$	$\vec{b},\ \vec{c},\ \vec{g}_{new},\ \vec{g}_{old}$	$\vec{b}_{new}=\langle\vec{g}_{new}\otimes\vec{g}_{old}\rangle\vec{c}_{old}$, $\vec{c}_{new}=\mathbf{S}^{-1}_{new}\vec{b}_{new}$
(v)	"observables"	$\vec{c},\vec{g},\ \mathbf{H},\ \mathbf{S}$	$\psi(x,t)=\vec{g}^{T}(x)\cdot\vec{c}(t)$, $\langle\psi\hat{H}\psi\rangle=\vec{c}^{\dagger}\mathbf{H}\vec{c}$
(vi)	relabel *new* as *old* and $t+\tau$ as t		continue to (i) or stop

Conservation of the norm and energy depends on the basis completeness

$$\langle\psi|\hat{H}|\psi\rangle=\vec{c}^{\dagger}_1\mathbf{H}_1\vec{c}_1=\vec{c}^{\dagger}_0\langle\vec{g}_0|\mathbb{I}_1\hat{H}\mathbb{I}_1|\vec{g}^{T}_0\rangle\vec{c}_0\approx\vec{c}^{\dagger}_0\mathbf{H}_0\vec{c}_0\qquad\mathbb{I}_1=|\vec{g}_1\rangle\mathbf{S}^{-1}_1\langle\vec{g}_1|$$

Time evolution algorithm: (left) steps of the expansion, or reexpansion, of a wave function in a basis; (right) time propagation with basis orthogonalization and transformations (BOT). A simulation begins at the t = 0 label, completes the left (red) loop, and propagates along the right (black) loop until a reexpansion criterion is met at which point the (re)expansion branch is again taken or the simulation completes. See text for the reexpansion criteria.



Approximate Quantum Potential & Force

- Use a **small basis *(x,y,…1)*** to approximate the **nonclassical** momentum

$$r := \frac{\nabla A(x,t)}{A(x,t)} \qquad \text{where} \qquad A=|\psi|$$

- Variationally determined quantum potential: the WF energy is conserved
- Linear in x basis is exact for a Gaussian wavepacket
- Mean-field like, resembles Hartree-Fock
- Infinite basis gives exact QM (like full CI)

- Discretize WF in terms of a trajectory ensemble
- Evolve QTs under the sum of classical and quantum forces
- Expectation values are simple ensemble averages