Approximate description of nuclear quantum effects in nonadiabatic dynamics

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Outline

- Quantum Trajectory (QT) dynamics

- Nonadiabatic formulation; $O+H_2$

- Mixed quantum/quasi-classical dynamics

- Trajectory-guided exact dynamics

Nuclear quantum effects (NQE)

o Wavefunction localization: ZPE, dipole moments, moderate tunneling (10^{-4})
o Deep tunneling, interference
o Electronically nonadiabatic effects or **light/heavy particle dynamics**
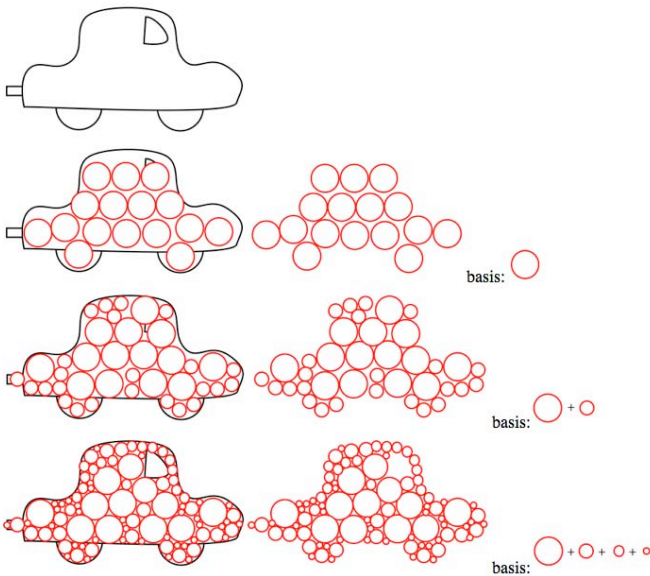
Example: NQE in Poly-(3-hexylthiophene)
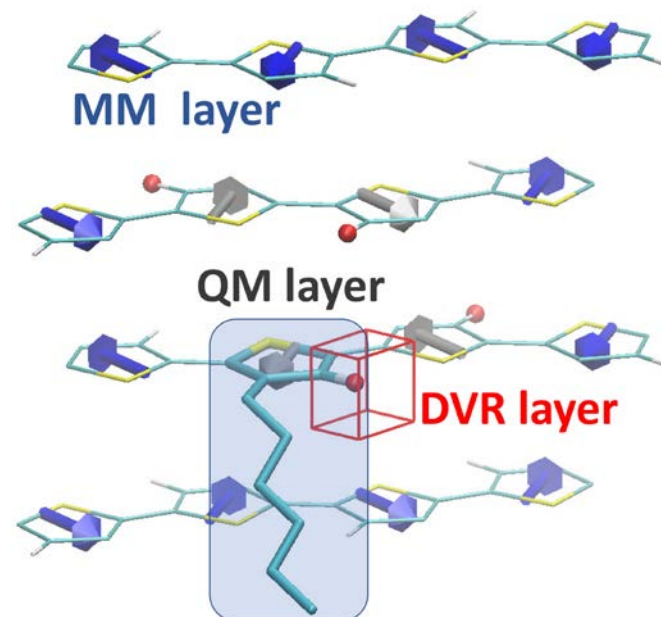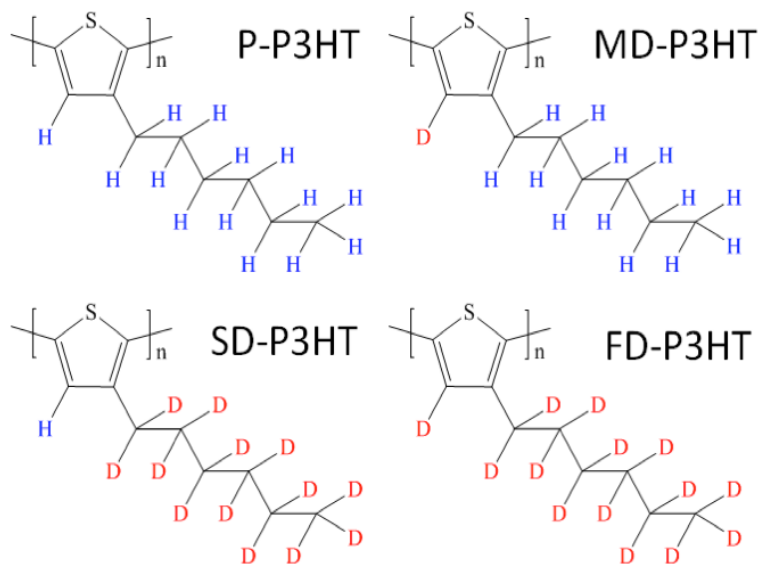
Reduced crystallinity is observed if D is
on the ring but not on the side-chains

quantum dynamics:= quantum nuclei

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

- The complexity and size of wavefunctions scale **exponentially** with dimensionality

- time-dependent adaptable to WF bases, representations, trajectories

- take advantage of mass, energy and time-scale separation

- Wavefunction factorization

Beyond the BO approximation

- exact nuclear-electronic separation

- TD-PES (Cederbaum, Gross)

- conditional WF (...Tavernelli, Kelly)

space-fixed bases are inefficient for large-amplitude motion

Why (quantum) trajectories?

o Nuclei are nearly classical; CM scales linearly

o Trajectory framework is convenient for mixed representations

o The QT formulation has classical and quantum mechanics as its limits

o Include **dominant QM effects** approximately (estimates)

o QTs define ideal 'grid' in coordinate space

o Conditional WF 'exact factorization' are based on QTs
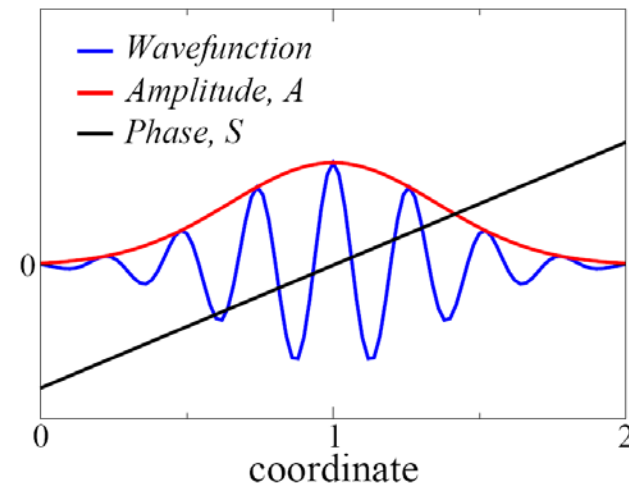
Quantum trajectories: $p = \nabla S$

Exact TDSE, operate with more classical quantities

Polar form of the wavefunction

$$\psi(\mathbf{x}, t) = A(\mathbf{x}, t) e^{\frac{i}{\hbar} S(\mathbf{x}, t)}$$

Phase is defined by the action

$$\frac{dS(\mathbf{x}, t)}{dt} = \frac{p^2}{2m} - V - U$$

Quantum potential   *<U>* is the quantum part of ZPE

$$U = -\frac{\hbar^2}{2m} \frac{\nabla^2 A(\mathbf{x}, t)}{A(\mathbf{x}, t)}$$

Trajectories define "ideal" time-dependent grid
Trajectory ensemble is important to represent QM non-locality

Practical: Approximate Quantum Potential & Force

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

$$r = \frac{grad \ A}{A}$$

- Use continuity of probability density $A^2 \delta x$ is constant

- Variationally determined quantum potential: energy is conserved; **single matrix equation per time-step**

- Mean-field like, resembles Hartree-Fock

- Infinite basis gives exact QM (like full CI)

- **Discretize WF in terms of a trajectory ensemble**
- **Evolve it in time under the time-dependent force**
- Expectation values are simple ensemble averages
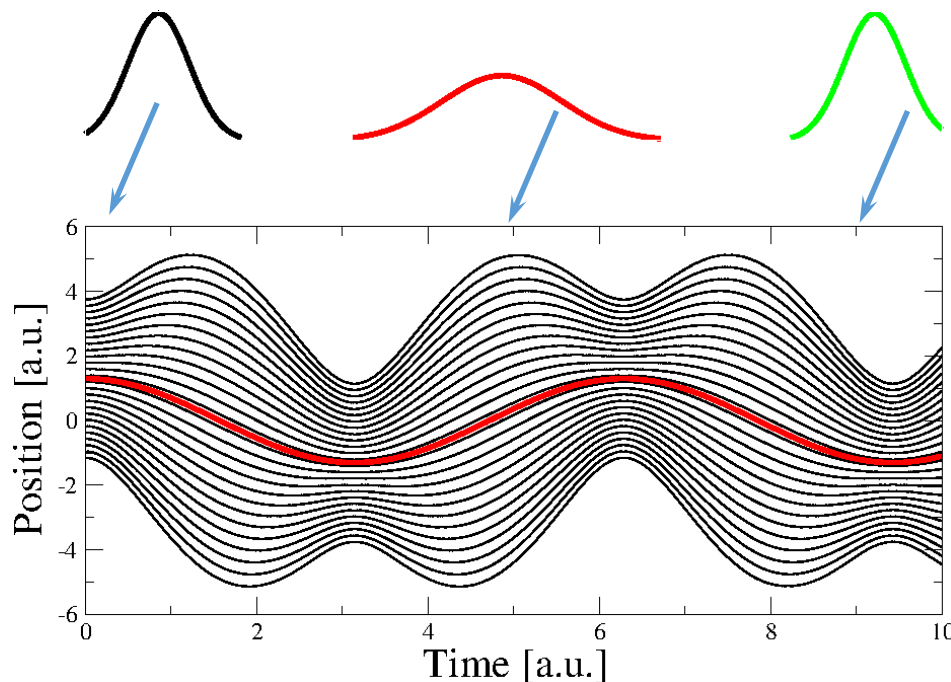
Probability density continuity

What can approximate QTs do?

- ZPE, WF bifurcation, moderate tunneling 10^{-4}
- Imaginary time/temperature, introduce friction …
- Nonadiabatic dynamics
- Interference, deep tunneling
- Use quantum correction for selected DOFs
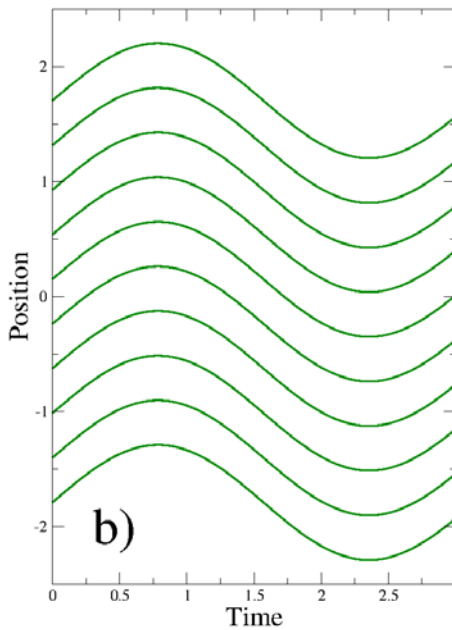- QT-inspired exact QM/(semi)classical methods

Unstable if done 'exactly'
change representation
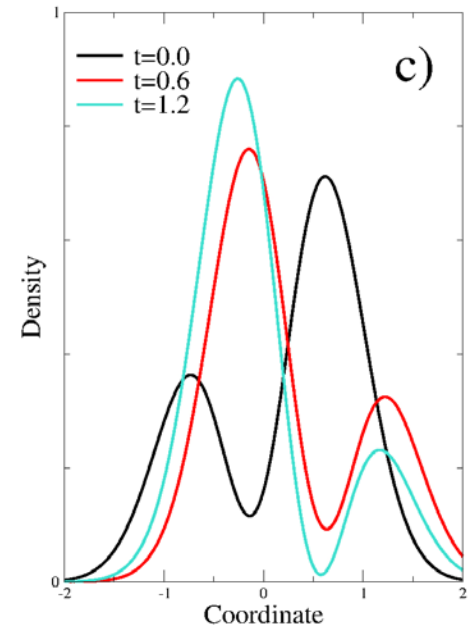
Equal trajectory footing
'Optimal' representation

Excited states, interference
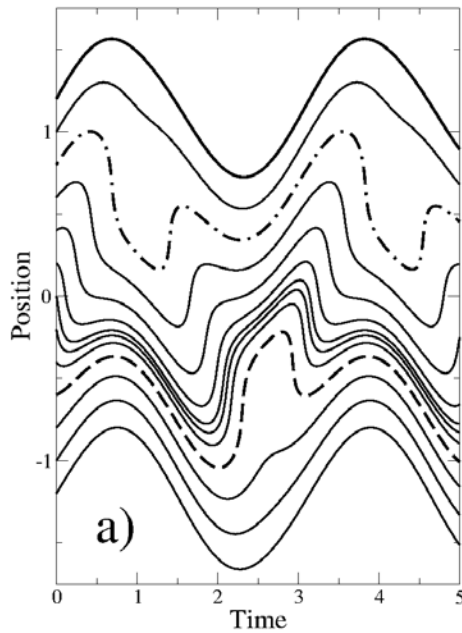
QTs   polar(x,t) $\psi(x,t)$

'mixed' representation to have smooth trajectories

$$\psi(x,t) = \text{polynomial}(x,t) * \text{polar}(x,t)$$

same for nonadiabatic dynamics

Nonadiabatic formulation with amplitudes

Mixed form of the wavefunction in the diabatic representation

$$\psi_i(x,t) = \chi_i(x,t)\phi(x,t), \quad i = 1\ldots 4$$

Wavepacket $\phi(x,t)$ is represented in terms of quantum trajectories evolving under effective classical potential

$$V_d = \sum_{ij} \langle \chi_i | \chi_j \rangle V_{ij}$$

and approximate quantum potential.

Population functions $\chi_i(x,t)$ evolve along the trajectories
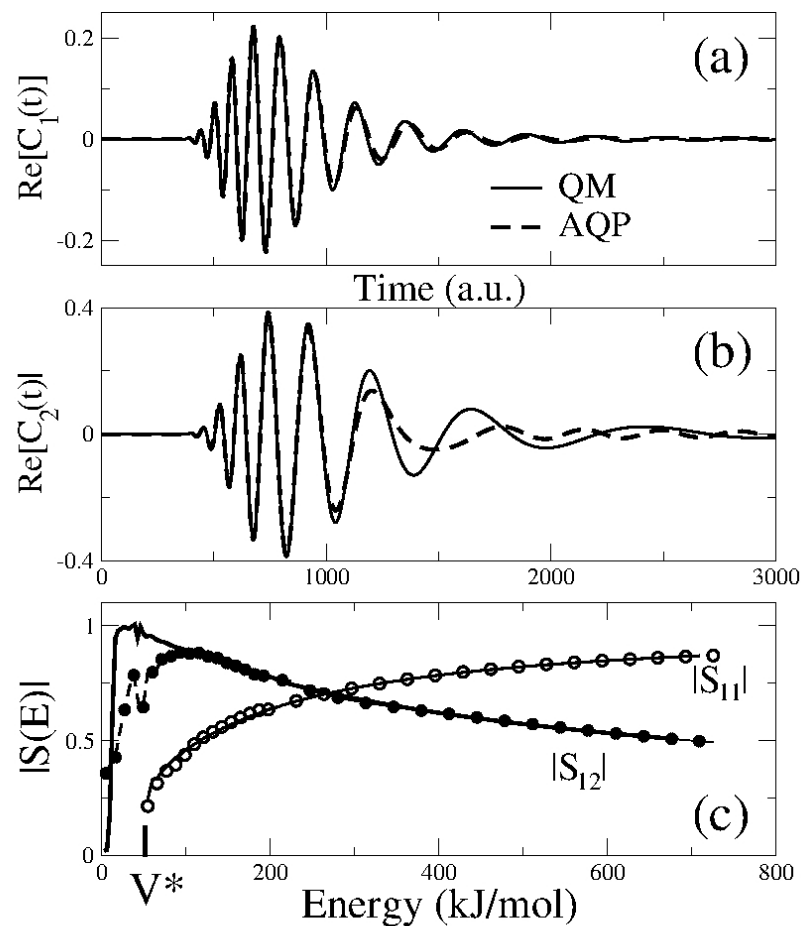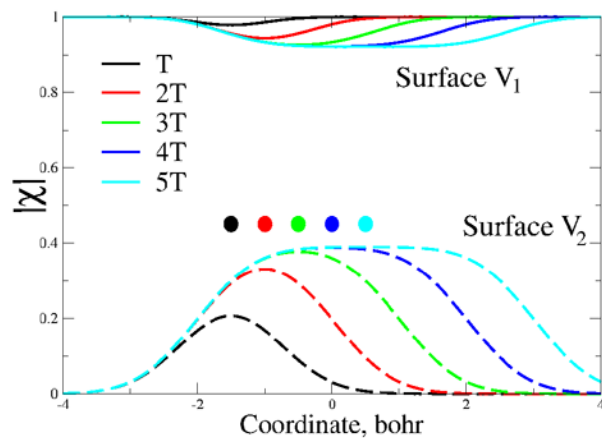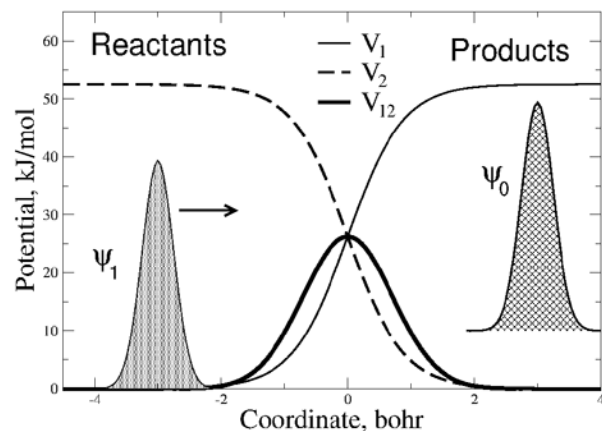
Matrix evolution equation
for the PES populations

$$i\frac{d\vec{\chi}}{dt} \approx (\mathbf{V} - V_d \mathbf{I})\vec{\chi}.$$

size DOFs× number of electronic states

– Transformation between representations is possible because we have the wavefunction

– Generalization to multiple sets of trajectories is possible

Energy-resolved probabilities for the Tully model

700 QTs: correlation functions use WF phase, **need WF 'synthesis'**

100% population transfer

(10-fold coupling)


Mixed WF representation for nonadiabatic dynamics

Semiclassical implementation:

- approximate QP and
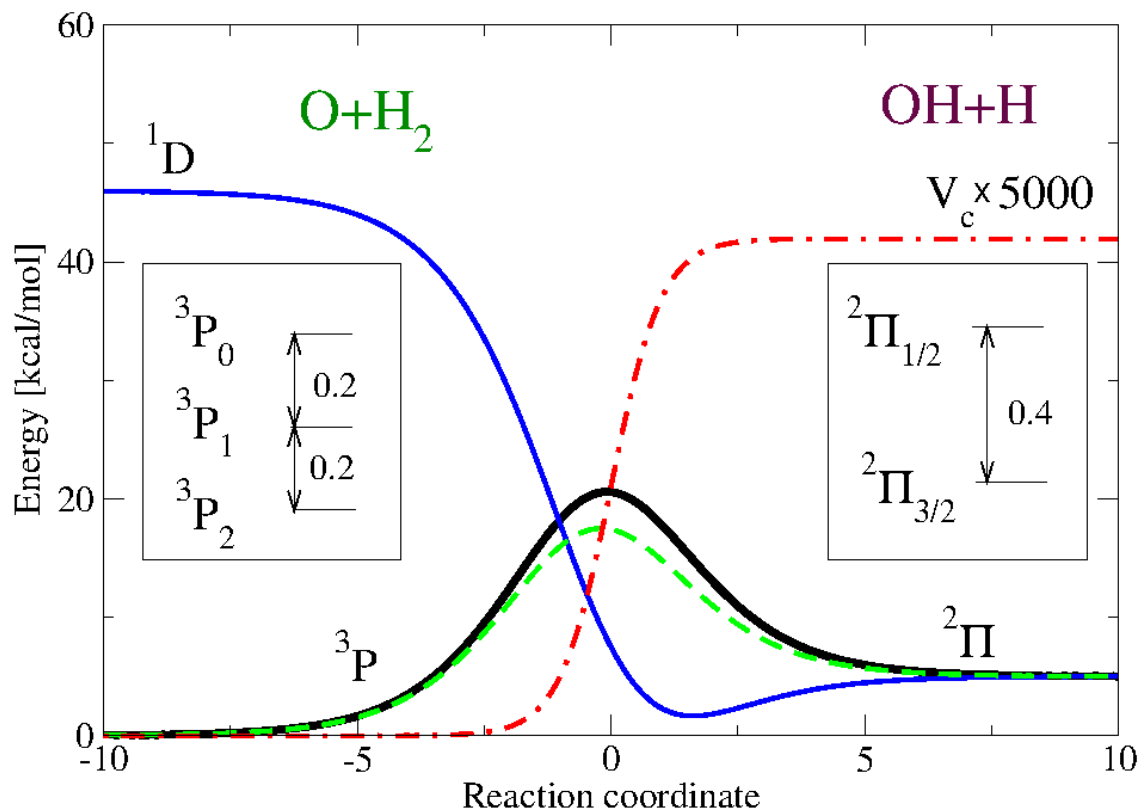- neglect of kinetic energy (h/m) in 'population' dynamics

Features to keep:

- smooth trajectory dynamics
- have trajectories in the right place, so population amplitudes are nonsingular compute

Generalization: population matrix for channel dynamics or diabatic/adiabatic switching
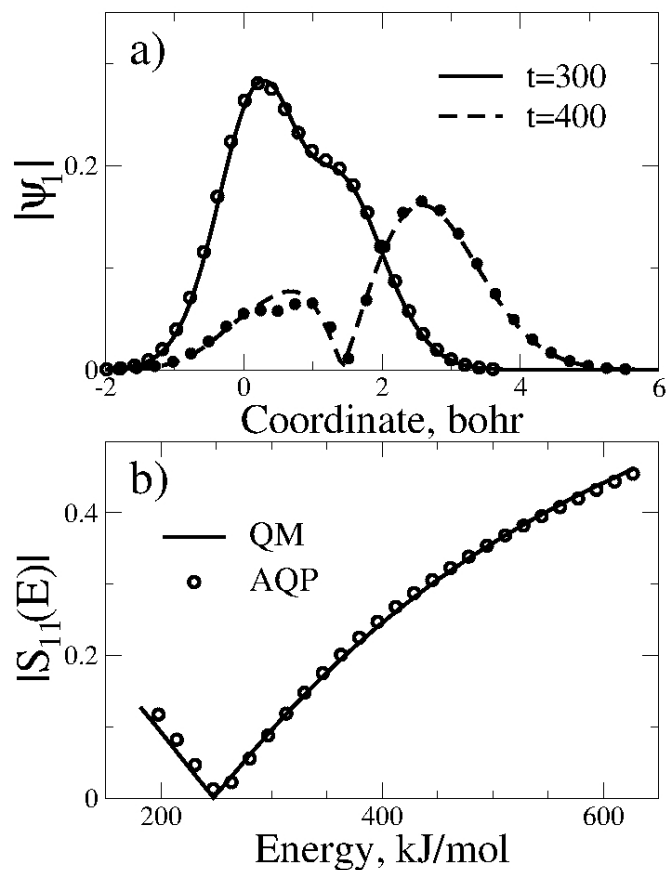
# Effect of intersystem crossing on reactivity $O+H_2$

Dynamics of non-rotating triatomic system on four electronic states

Quasiclassical trajectory/surface hopping estimate is 30% increase in reactivity

$O+H_2$ (J=0) wavepacket dynamics in Jacobi coordinates
## Ground state-to-all probability vs collision energy

Dynamics of the wavepacket initialized on $^3P_1$ (QM — solid lines, classical — dash, AQP— symbols): a) Diabatic probabilities; b) Adiabatic probabilities; c-d) Populations.
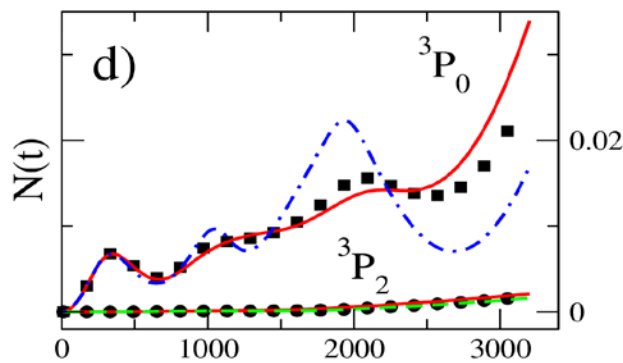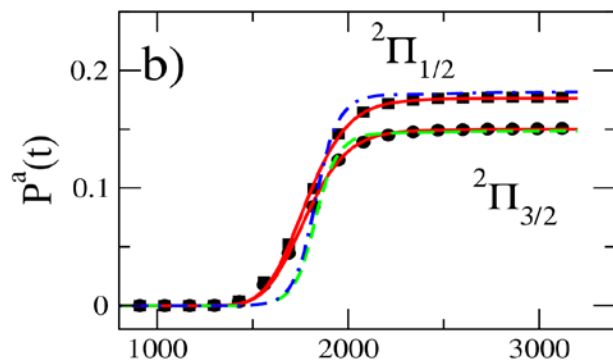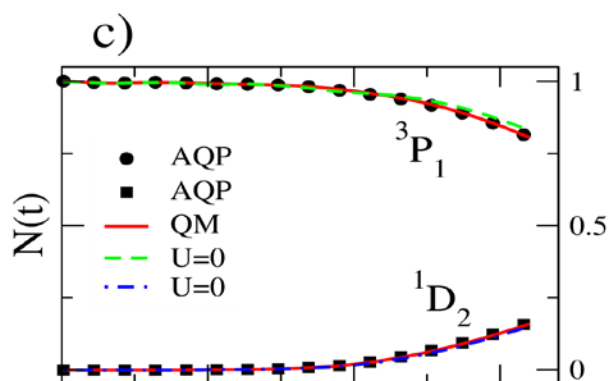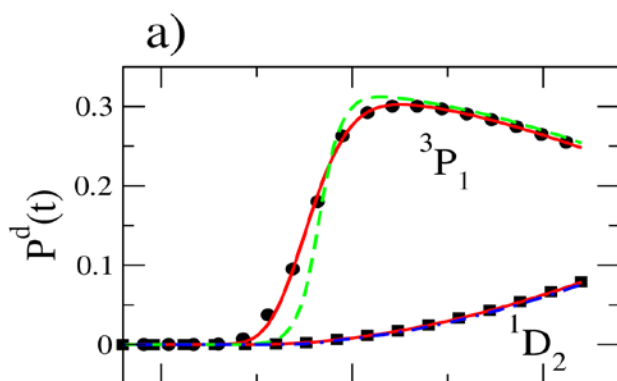
Generalization to arbitrary coordinates

Nonlinear AQP basis to describe H2 anharmonicity

O+H$_2$ conclusion: spin-orbit interaction has negligible effect on reactivity

Probabilities for the wavepacket initialized on (a) $^3P_2$, (b) $^3P_1$ and (c) $^3P_0$ as functions of energy. Probabilities to $^2\Pi_{3/2}$ are shown with dash (QM) and filled circles (AQP). Probabilities to $^2\Pi_{1/2}$ are shown with dot-dash (QM) and triangles (AQP). Their sum is shown with the solid line (QM) and open circles. Stars indicate the single surface AQP results.
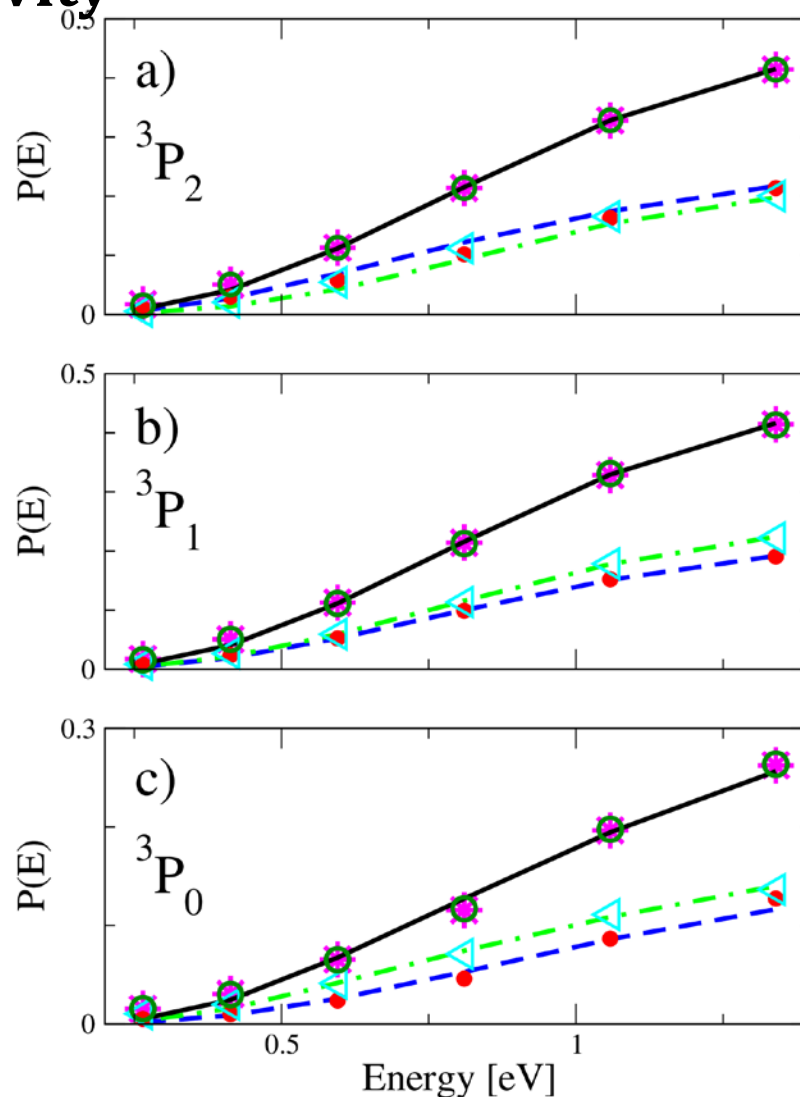
The energy conserving hybrid Q/C dynamics

sub-ensembles or   quasiclassical = include ZPE for classical DOF

$$\psi(x, y, t) = \psi_1(x, t; y)\psi_2(y, t)$$
$$= A_1(x, t; y)e^{\imath S_1(x,t;y)} A_2(y, t)e^{\imath S_2(y,t)}$$

$$\frac{dy_t}{dt} = \frac{p_{yt}}{M}, \quad \frac{dp_{yt}}{dt} = -\int |\psi_1(x, t; y_t)|^2 \frac{\partial V}{\partial y}\Big|_{x, \ y=y_t} dx$$

$$\frac{dx_t}{dt} = \frac{p_{xt}}{m}, \quad \frac{dp_{xt}}{dt} = -\frac{\partial}{\partial x}(V(x; y_t) + U_1(x, t; y_t))\Big|_{x=x_t}$$

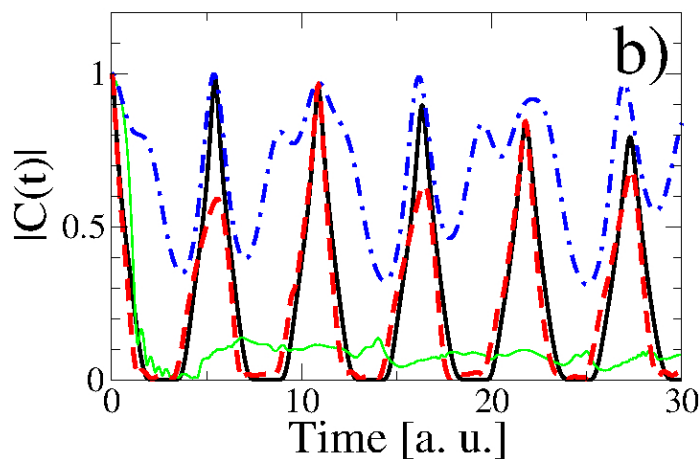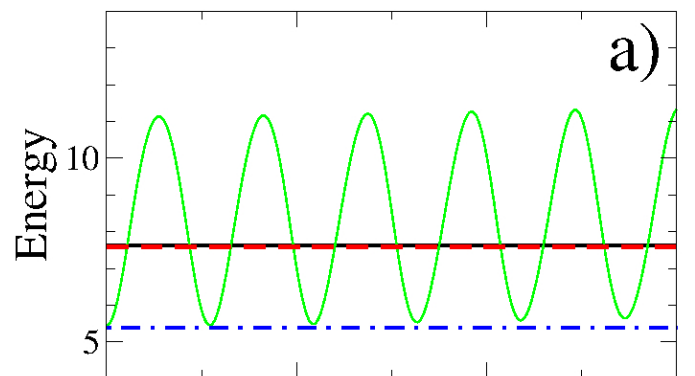$$U_1(x, t; y) = -\frac{(2m)^{-1}}{A_1(x, t; y)}\frac{\partial^2 A_1(x, t; y)}{\partial x^2}$$

$$S\ (x_t, y_t) = S(x_0, y_0) \tag{27}$$
$$+ \int_0^t \left(\frac{p_{x\tau}^2}{2m} - V(x_\tau, y_\tau) - U_1(x_\tau; y_\tau) + \frac{p_{y\tau}^2}{2M}\right) d\tau.$$
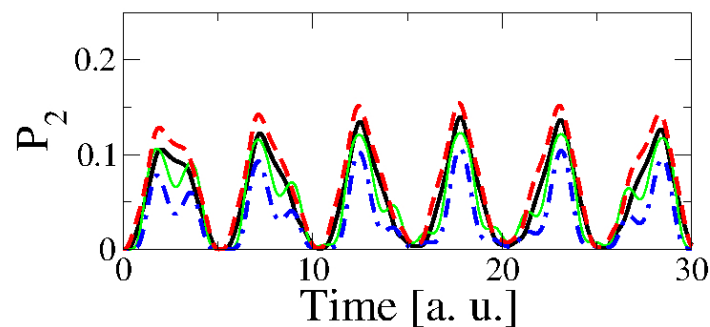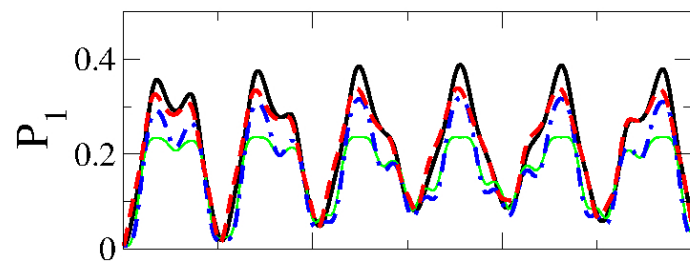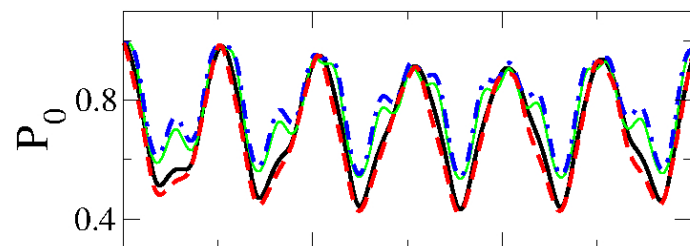
Vibrationally nonadiabatic system

$$V=k(x-Y)^2/2+Ky^2/2 \qquad M/m=10$$

exact QM dynamics (black), mixed w/out E_y (green), mixed w/out (blue) and with (red) quasiclassical momentum adjustment
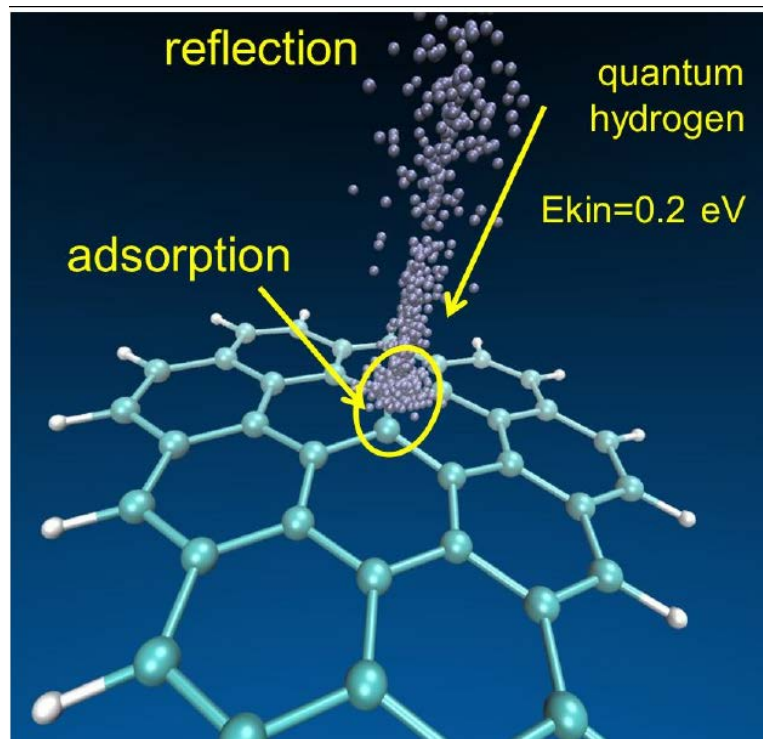

WF correlation

populations

QTES (QTs with on-the-fly electronic structure)

- The QT **code is merged with ES** Density Functional Tight Binding DFTB (Jakowski, ORNL)

- **Electronic energy evaluation is parallelized (open MP)**

- **Quantum correction is included for selected DoFs**

- **Multiple independent "sub"-ensembles** represent nearly classical DOFs


"A Hybrid Quantum Trajectory-Electronic Structure Approach for Exploring Nuclear Effects in the Dynamics of Nanomaterials"

SG, J. Jakowski, L. Wang, B.G. Sumpter, JCTC 2013

$H + C_{37}H_{15}$ 4320 trajectories propagated for 1000 timesteps on 360 cores of CRAY XT5 About 1 min per step/per trajectory

C$_{37}$H$_{15}$ + hydrogen (a) or deuterium (b)

the main QM effect is due to delocalization of the proton wavefunction, which changes geometry of C$_{37}$H$_{15}$
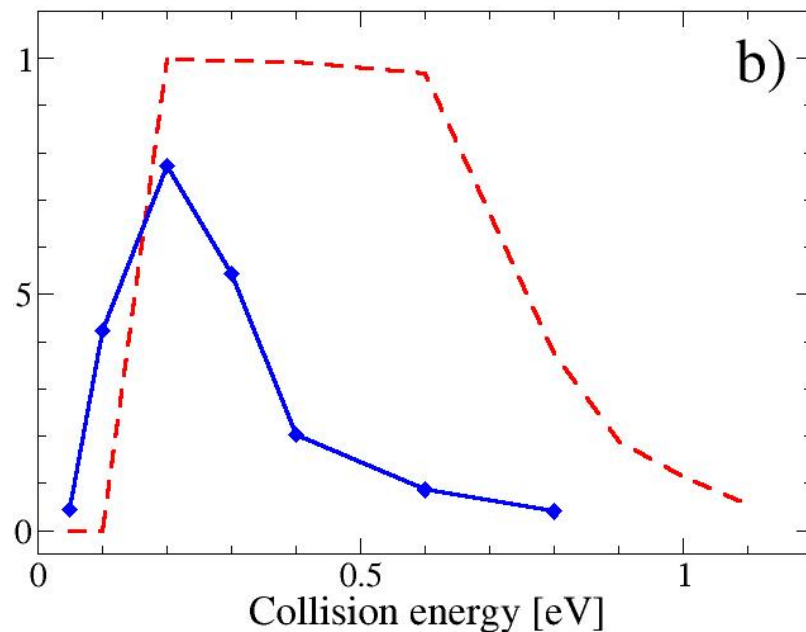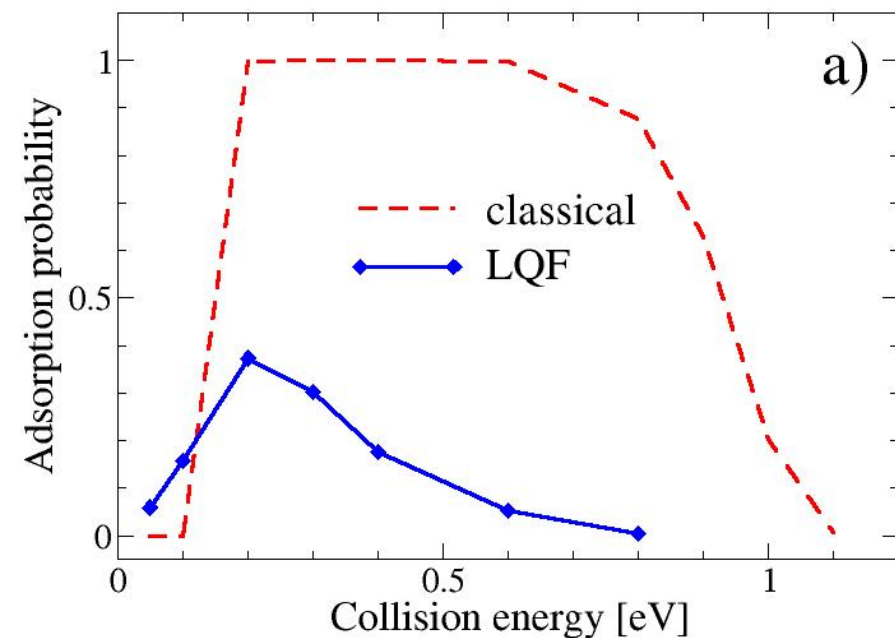
- **<u>Minimize ES evaluations</u>**

(5K QTs* 1000 time steps * 15 sub-ensembles)

- **<u>"multiscale" ES evaluations; MD-like adjustable time-step</u>**

In the works to nonadiabatic with multiple PES

Exact QM with QT-guided Gaussian Bases
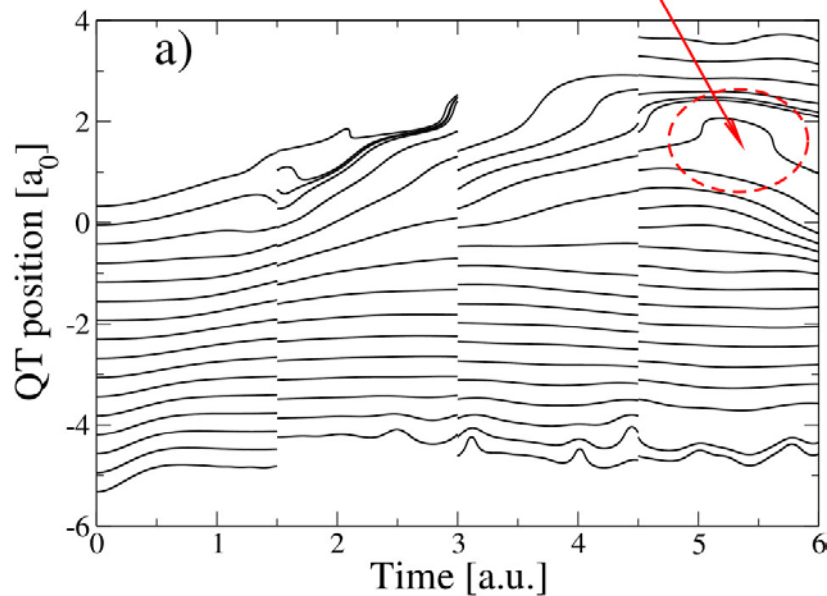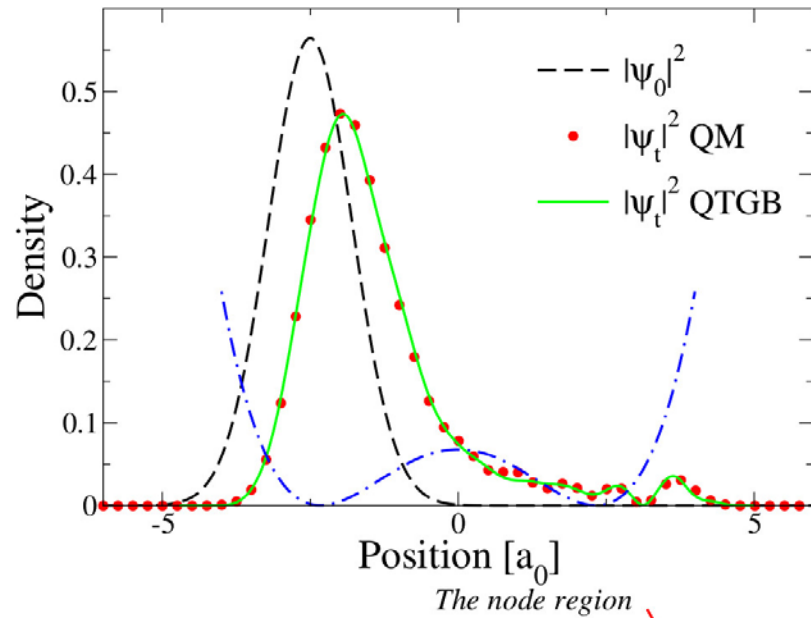
real frozen Gaussians, positions from QTs

$$\psi = \Sigma\, g_k(x)c_k \qquad g_k(x)=\exp(-a(x-q_t)^2)$$

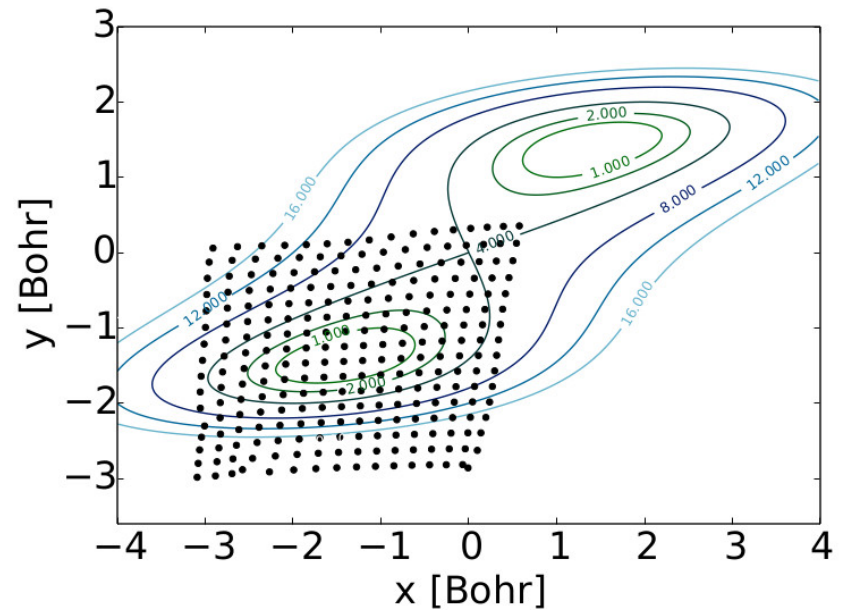$$dq_t/dt=p/m \quad \text{p is defined by } \Psi$$

sparse set of QTs (variational?)

- **Local quadratic expansion of V in matrix elements**

- **Re-expansion for stability and basis size adjustment**

- **Solve $\widetilde{H}c=i\,S\,\dot{c}$** $\qquad \widetilde{H}$ non-hermitian; $S_{jk}=<g_j|g_k>$ degenerate

1d double well

The node region

2d double well

V_b=0.6366 [frequency]

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

Summary

- NQEs are important (recent experiments with isotope substitutions)
- Approximate QTs are useful for assessment of NQEs within the mixed description of light/heavy particles
- QTs are useful to define compact WF representations for the 'BO-and-beyond' exact (approximate, mixed) quantum dynamics
- Related to new exact factorization (TD-PES) and conditional WF

Reusable modules/methods

- Initialization of trajectories (random, pseudo-random)
- Interpolation, convolution etc to synthesize WF if needed
- Stable dynamics; minimization of ES evaluations

  - Adaptable propagators for trajectories with time-dependent potentials

  - Time-dependent matrix eqs with complex matrices and degenerate bases

    - Re-expansions of WF in a non-degenerate basis

    - Evaluation of potential energy matrix elements

- Choice of electronic structure codes; dynamics/ES integration

Thank you!

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