A brief overview of Coherent State based methods of quantum dynamics.

(Applications in Photochemistry and Physics)

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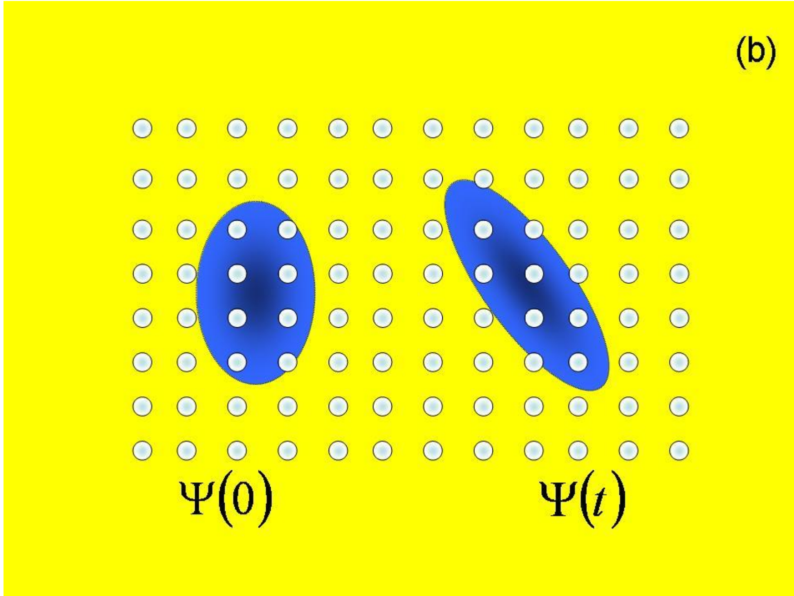
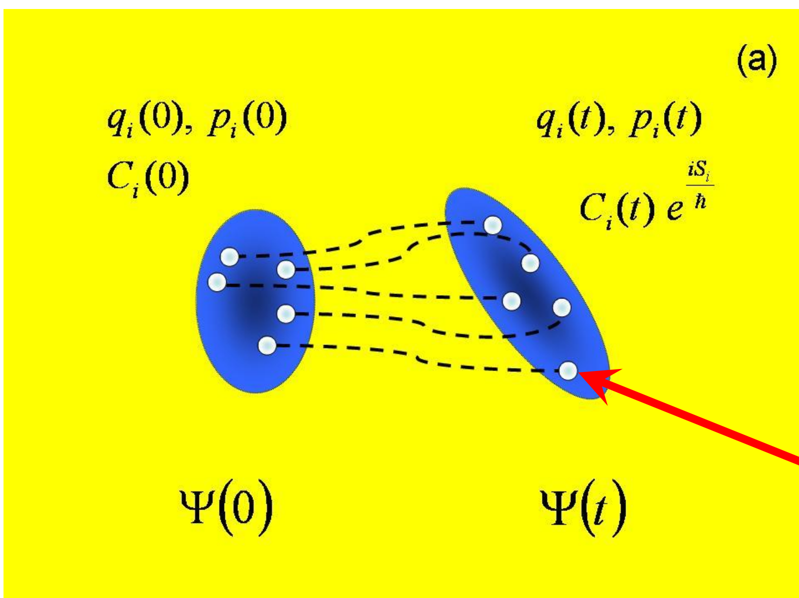


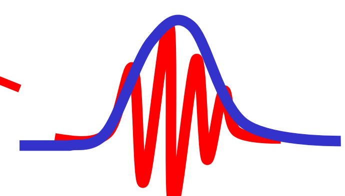
Regular
static grid

$$N = l^{M}$$



Random trajectory
guided grid

$$N \propto M^{2}$$

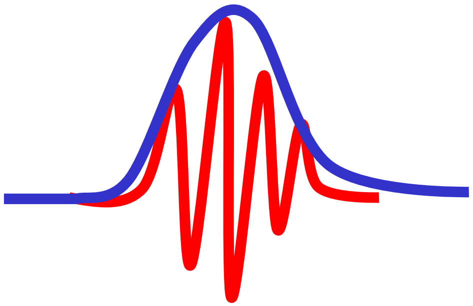


$|q, p\rangle$

Gaussian Coherent States

Coherent States are basis functions for nuclei.
In coordinate space Coherent State is a Gaussian wave packet

| q,p > is a frozen Gaussian



$$\langle x | p, q \rangle = \left(\frac{\gamma}{\pi} \right)^{\frac{1}{4}} \exp\left(-\frac{\gamma}{2}(x-q)^2 + \frac{i}{\hbar} p(x-q) + \frac{ipq}{2\hbar} \right)$$

In general multidimensional $\left| \mathbf{z} \right\rangle = \left| \mathbf{p}, \mathbf{q} \right\rangle = \left| p^{(1)}, q^{(1)} \right\rangle \ldots \left| p^{(M)}, q^{(M)} \right\rangle$

Gaussian Coherent States

Quantum CS are the eigen states of annihilation operator.

z-notations

$$\hat{a}\ |z\rangle = z\ |z\rangle$$

$$z = \frac{\gamma^{1/2} q + i\left(\hbar/\gamma^{1/2}\right)p}{\sqrt{2}}$$

$$|z\rangle = |q, p\rangle$$

Wave function in phase space

$$\Psi(z) = \langle z|\Psi\rangle = \Psi(q, p)$$

$|z(t)\rangle = |q(t), p(t)\rangle$ can follow a trajectory in phase space

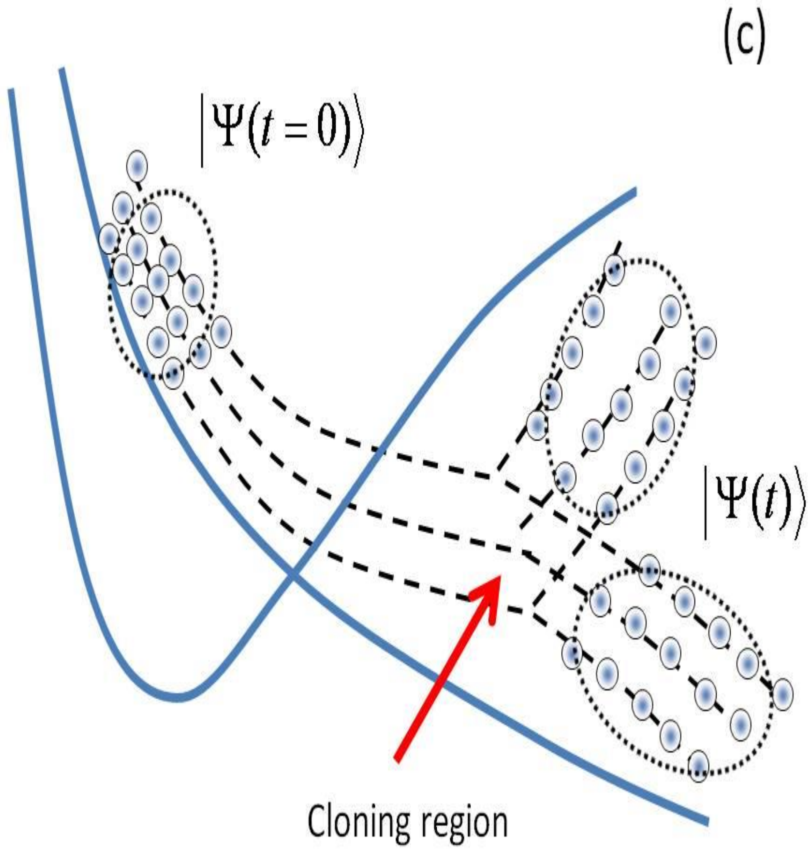
Trajectory guided Basis sets for Quantum Direct Dynamics in Photochemistry

Variational trajectories. Variational Multiconfigurational Gaussians (vMCG) (Bugrhardt, Worth)

Classical Trajectories *Ab Initio* Multiple Spawning (AIMS) (Martinez)

Ehrenfest Trajectories.
Multiconfigurational Ehrenfest (MCE),*Ab Initio* Multiple Cloning (AIMC) (Shalashilin, Makhov)

Few electronic states and complicated nuclear wave function. Can we converge?



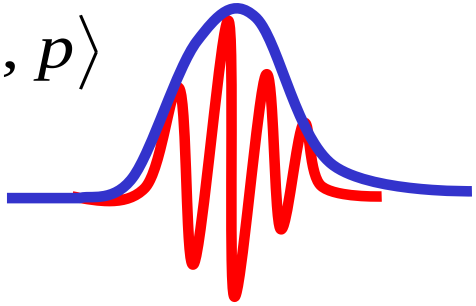
Wave function Ansatz.
Ansz 1 (Multi-set).

Electronic states

$$|\Psi\rangle = \sum_{i_e} \left(a_{1i_e}(t) \left| z_{1i_e}(t) \right\rangle + a_{2i_e}(t) \left| z_{2i_e}(t) \right\rangle + \ldots \right) |i_e\rangle$$

Nuclear basis of CSs

$$z = \frac{\gamma^{1/2} q + i\left(\hbar / \gamma^{1/2}\right) p}{\sqrt{2}} \qquad |z\rangle = |q, p\rangle$$



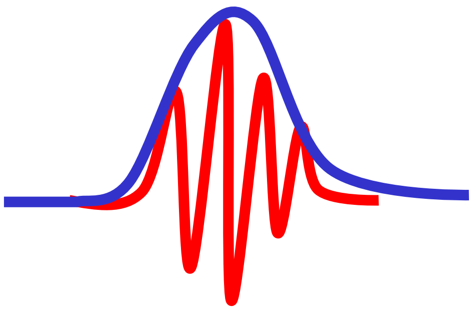
Nuclear wave packet at each electronic state (AIMS-classical trajectories, vMCG – variational trajectories)

Wave function Ansatz.
Ansz 2.1 (Single-set).

Electronic states

$$\left|\Psi\right\rangle = \sum_{l=1,N} \left(a_{l1}(t)\left|1\right\rangle + a_{l2}(t)\left|2\right\rangle + \ldots \right)\left|z_l(t)\right\rangle$$

Nuclear basis of CSs



MCEv1 – Ehrenfest trajectories, coupled with each other

Wave function Ansatz.
Ansz 2.2 (Sindle-set).

$$\left|\Psi\right\rangle = \sum_{l=1,N} A_l \left(a_{l1}(t)\left|1\right\rangle + a_{l2}(t)\left|2\right\rangle + \ldots \right)\left|z_l(t)\right\rangle$$

Amplitude

Ehrenfest configuration
can be normalised

Sum of normalised Ehrenfest configurations
(MCEv2 – Ehrenfest trajectories, vMCG –variational trajectories)

Variational trajectories are complicated, expensive and unstable

The vector of parameters $\boldsymbol{\alpha} = \{ a_1, \ldots, a_N, \mathbf{z}_1, \ldots, \mathbf{z}_N \}$

alltogether N+N×M parameters

The Lagrangian $$L(\boldsymbol{\alpha}) = \left\langle \Psi(\boldsymbol{\alpha}) \right| i \frac{\hat{\partial}}{\partial t} - \hat{H} \left| \Psi(\boldsymbol{\alpha}) \right\rangle$$

$$L = \sum_{i,j} \left\{ \frac{i}{2}\left[a_i^* \dot{a}_j - a_j \dot{a}_i^* \right] \langle z_i | z_j \rangle + \frac{i}{2}\left[\left((z_i^* - z_j^*) \dot{z}_j + \frac{\dot{z}_j z_j^*}{2} - \frac{z_j \dot{z}_j^*}{2} \right) - \left((z_j - z_i) \dot{z}_i^* + \frac{z_i \dot{z}_i^*}{2} - \frac{\dot{z}_i z_i^*}{2} \right) \right] + a_i^* a_j \langle z_i | z_j \rangle - a_i^* a_j \langle z_i | z_j \rangle H_{ord}(z_i^*, z_j) \right\}$$

Ω is big and bad

(N+N×M) **×** (N+N×M) matrix

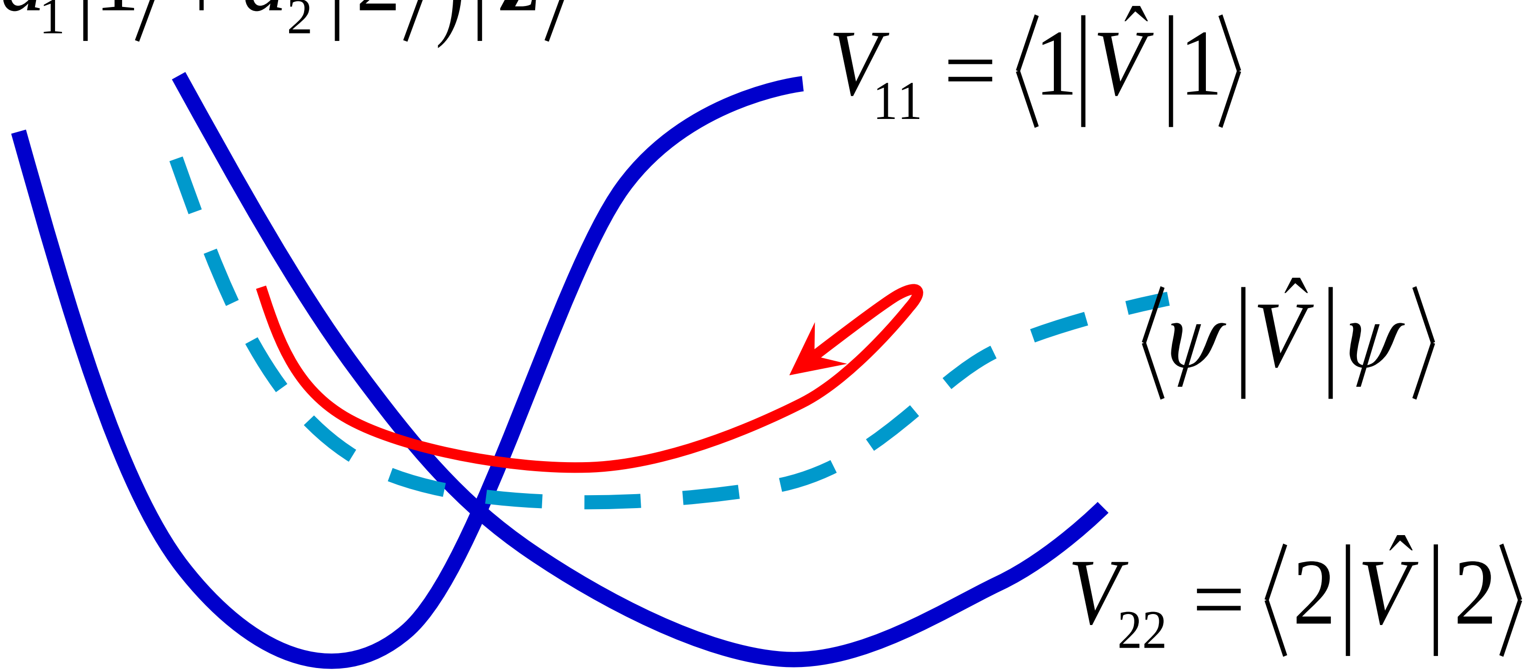
$$\boldsymbol{\Omega}\ \dot{\boldsymbol{\alpha}} = \frac{\partial \langle \Psi | H | \Psi \rangle}{\partial \boldsymbol{\alpha}}$$

Variational trajectories are complicated expensive and unstable

Classical trajectories are simple but not quantum enough. Multi-set (Ansz.1) is hard to converge.

Ehrenfest Trajectories are simple and quantum. The convergence of ET basis sets has been tested.

$$|\psi\rangle = \left(a_1|1\rangle + a_2|2\rangle\right)|\mathbf{z}\rangle$$



$$\langle\psi|\hat{V}|\psi\rangle =$$

$$= \frac{\langle\mathbf{z}|\hat{V}_{11}|\mathbf{z}\rangle a_1{*}a_1 + \langle\mathbf{z}|\hat{V}_{22}|\mathbf{z}\rangle\, a_2{*}a_2 + \langle\mathbf{z}|\hat{V}_{12}|\mathbf{z}\rangle\, a_1{*}a_2 + \langle\mathbf{z}|\hat{V}_{21}|\mathbf{z}\rangle\, a_2{*}a_1}{a_1{*}a_1 + a_2{*}a_2}$$

Ehrenfest Trajectories are simple and quantum. The convergence of ET basis sets has been tested.

Individual Ehrenfest trajectories usually do not describe QD very well, but they are very efficient if used as basis functions

Ehrenfest trajectories are simple and quantum. Their convergence has been tested.

3 tricks which make Gaussian CS based methods work.

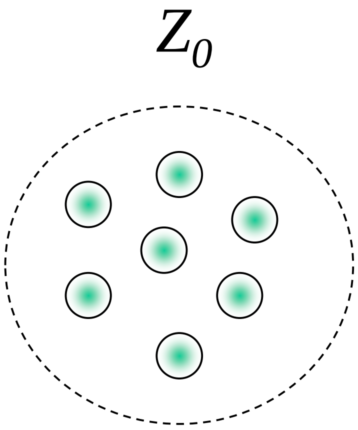
Sampling

Sampling

Sampling

Coherent State Samplings:

Swarms

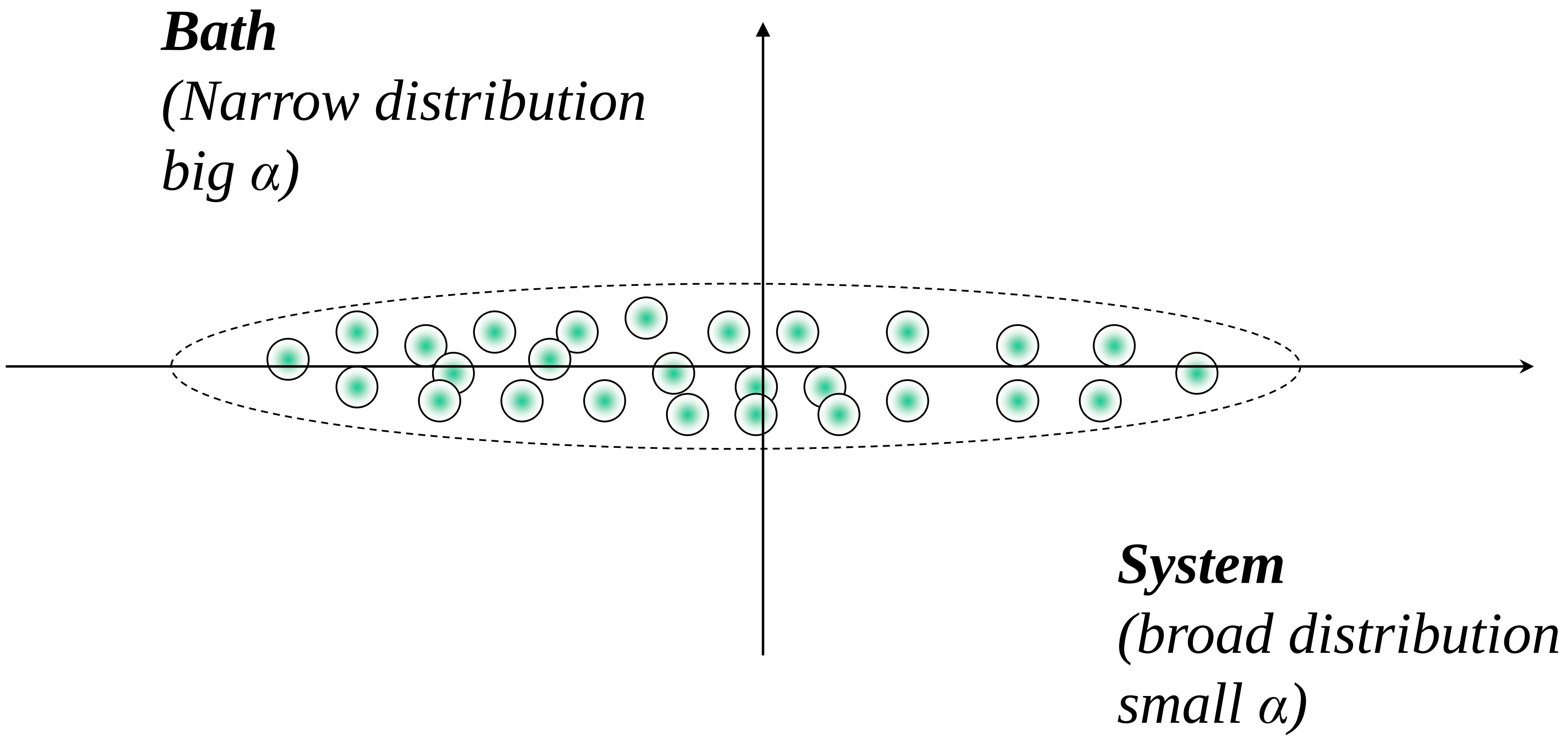


Compression parameter

$$F \propto \exp\left(-\left(\alpha\left[\mathbf{Z}_i - \mathbf{Z}_0\right]\right)^2\right)$$

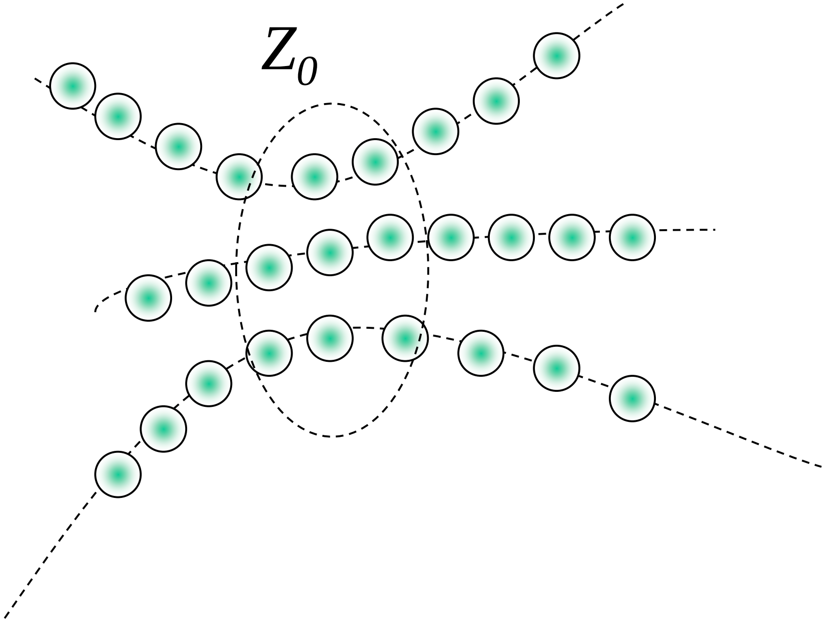
Coherent State Samplings:

Pancakes



Coherent State Samplings:

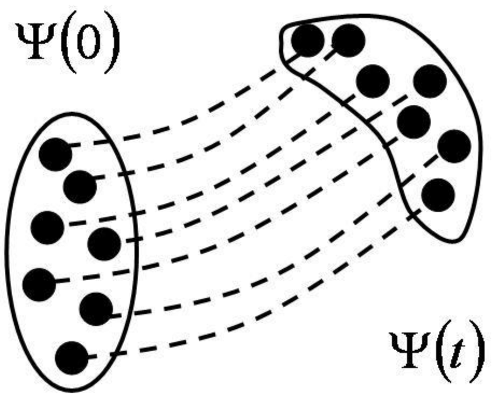
Trains

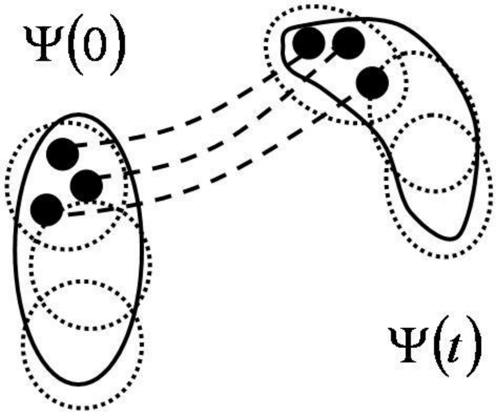


Swarms and pancakes of trains

Coherent State Samplings:

Bit by bit propagation





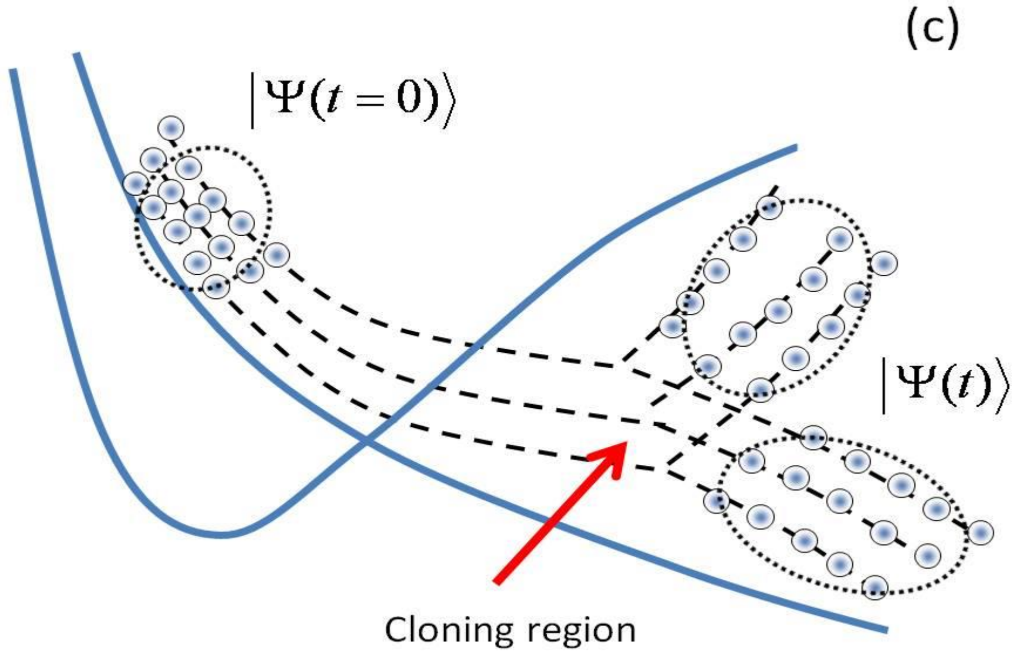
Split wave function into "bits". Propagate each "bit" separately using small basis.

$$\left|\Psi(t)\right\rangle = e^{-i\hat{H}t}\left|\Psi(0)\right\rangle \qquad \left|\Psi(t)\right\rangle = \int e^{-i\hat{H}t}\left|z\right\rangle\left\langle z\right|\frac{dpdq}{2\pi}\left|\Psi(0)\right\rangle$$

$\hat{I}$

Coherent State Samplings:

Cloning



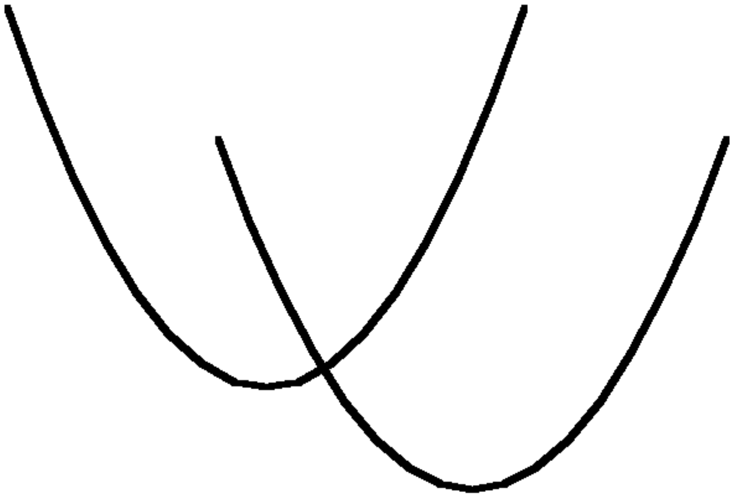
$$|\psi(t)\rangle = \left(a_1(t)|1\rangle + a_2(t)|2\rangle\right)|\mathbf{z}(t)\rangle$$

Cloning is a straightforward way to do spawning (Martinez)

Perticularly useful for nonadiabatic dynamics

Numerical test (Spin-Boson Model)

$$\hat{H} = \begin{vmatrix} \hat{H}_B + \hat{H}_C + \varepsilon & \Delta \\ \Delta & \hat{H}_B - \hat{H}_C - \varepsilon \end{vmatrix}$$



$$\hat{H}_B = \sum_m \omega^{(m)} \left(\hat{a}^{(m)+} \hat{a}^{(m)} + \frac{1}{2} \right)$$

$$\hat{H}_C = \sum_m \frac{C^{(m)}}{\sqrt{2\omega^{(m)}}} \left(\hat{a}^{(m)+} + \hat{a}^{(m)} \right)$$

$$\left\langle \tilde{\mathbf{z}}_k \middle| \hat{H}_B \middle| \tilde{\mathbf{z}}_j \right\rangle = \left\langle \tilde{\mathbf{z}}_k \middle| \tilde{\mathbf{z}}_j \right\rangle \sum_m \omega^{(m)} \left(\tilde{z}_k^{(m)} * \ \tilde{z}_j^{(m)} + \frac{1}{2} \right)$$

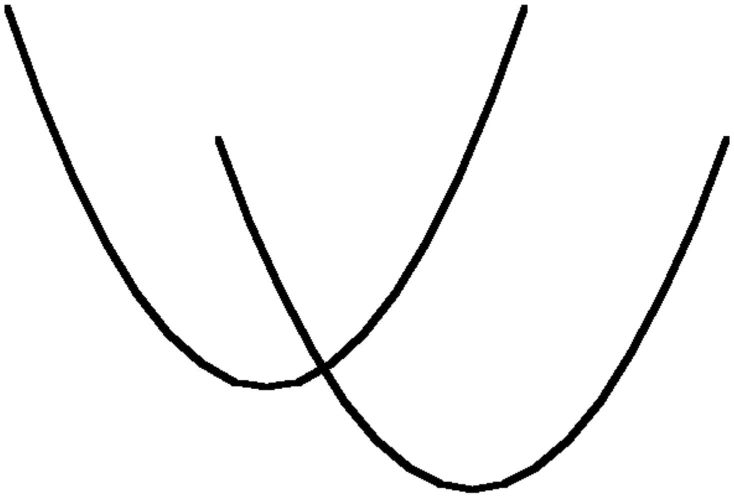
$$\left\langle \tilde{\mathbf{z}}_k \middle| \hat{H}_C \middle| \tilde{\mathbf{z}}_j \right\rangle = \left\langle \tilde{\mathbf{z}}_k \middle| \tilde{\mathbf{z}}_j \right\rangle \sum_m \frac{C^{(m)}}{\sqrt{2\omega^{(m)}}} \left(\tilde{z}_k^{(m)} * + \tilde{z}_j^{(m)} \right)$$

Calculate Thermal averaged populations.

Vibrational bath is discretised $10^1 - 10^2$ vibrations.

Numerical test (Spin-Boson Model)

$$\hat{H} = \begin{vmatrix} \hat{H}_B + \hat{H}_C + \varepsilon & \Delta \\ \Delta & \hat{H}_B - \hat{H}_C - \varepsilon \end{vmatrix}$$



The effect of sampling techniques used in the multiconfigurational Ehrenfest method

JCP **148**, 184113 (2018)

Comparison of MCEv1 and MCEv2

Multi-Configurational Ehrenfest Method (MCEv1)

$$MCEv1\ ,\quad Anz2.1$$

$$\Psi = +\left(a_1^{(1)}\left|1\right\rangle + a_0^{(1)}\left|0\right\rangle\right)\left|\mathbf{z}^{(1)}(t)\right\rangle$$
$$\left(a_1^{(2)}\left|1\right\rangle + a_0^{(2)}\left|0\right\rangle\right)\left|\mathbf{z}^{(2)}(t)\right\rangle$$

In MCEv1 Ehrenfest trajectories push each other.
Converges very well for systems with 100s of DOF

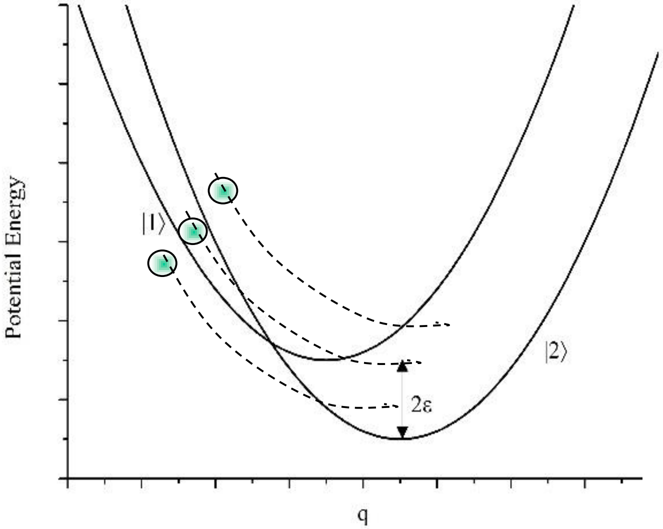
Multi-Configurational Ehrenfest Method (MCEv2)

$$MCEv2 \quad , \quad Anz2.2$$

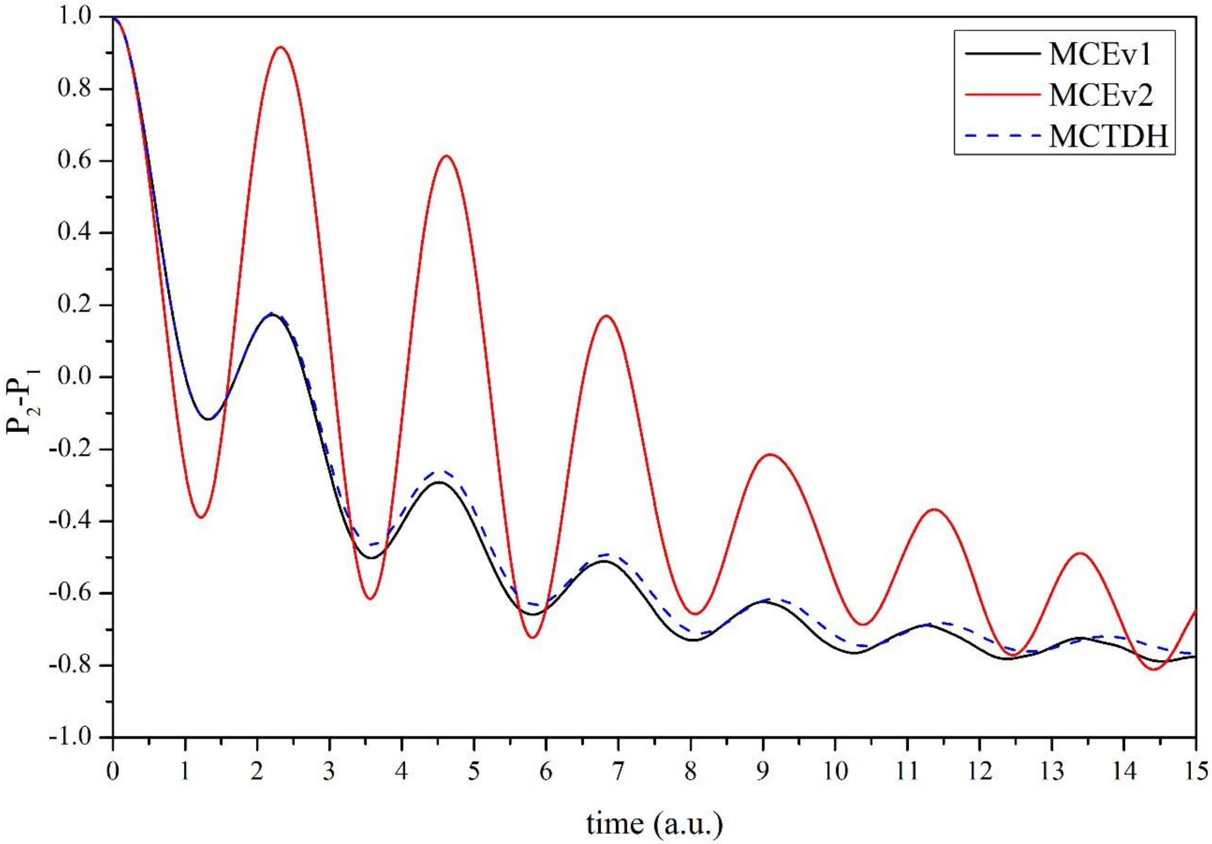
$$\Psi = A^{(1)}\left(a_1^{(1)}\left|1\right\rangle + a_0^{(1)}\left|0\right\rangle\right)\left|\mathbf{z}^{(1)}(t)\right\rangle + A^{(2)}\left(a_1^{(2)}\left|1\right\rangle + a_0^{(2)}\left|0\right\rangle\right)\left|\mathbf{z}^{(2)}(t)\right\rangle$$

In MCEv2 Ehrenfest trajectories are independent.

Numerical test (Spin-Boson Model)

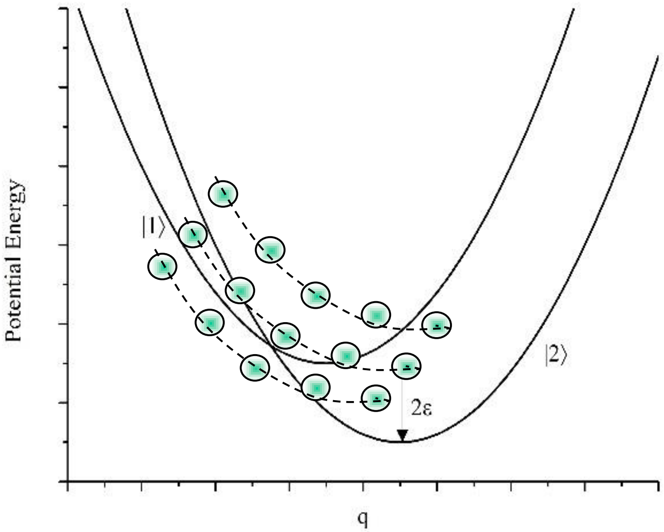


MCEv1 and MCEv2. Simple swarm.

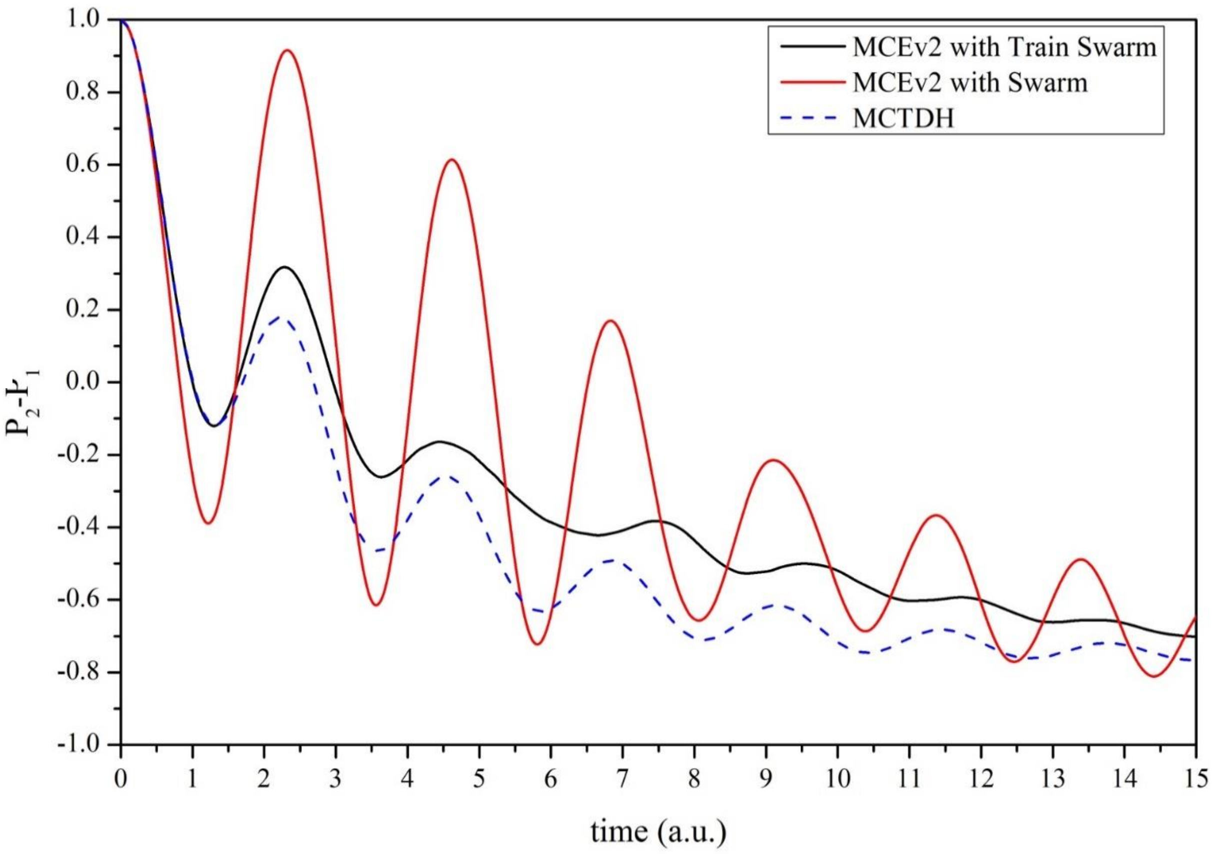


- MCE1 agrees very well with MCTDH
- MCE2 is way off !!!

Numerical test (Spin-Boson Model)

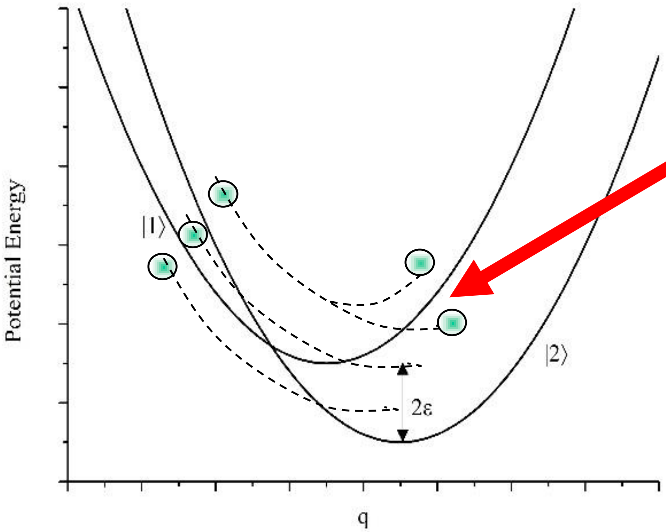


MCEv2 with swarm of trains

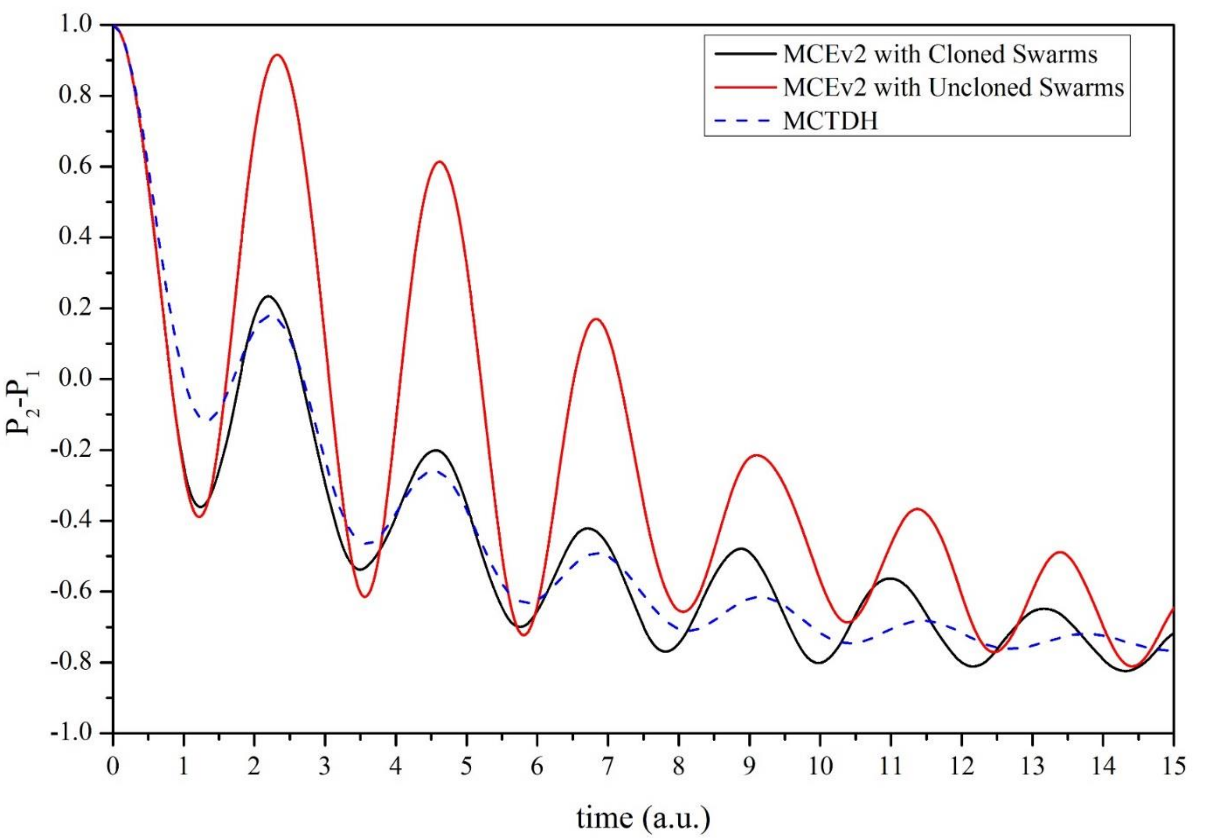


- MCEv2 with trains improves at initial time

Numerical test (Spin-Boson Model)



MCEv2 with swarm and cloning



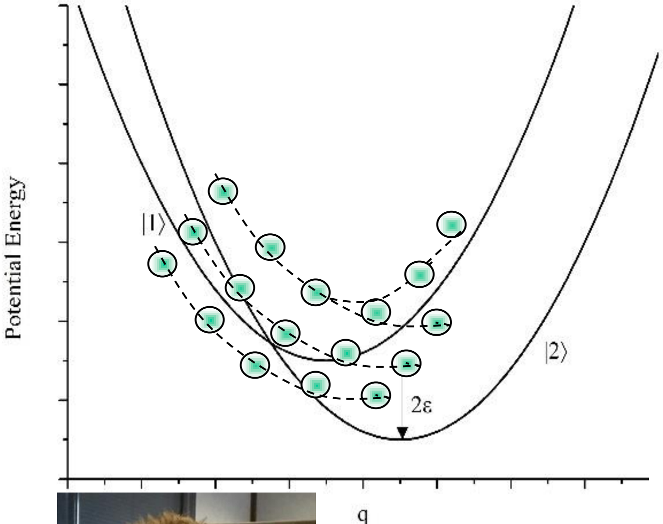
- MCEv2 with cloning improves at initial time

$$\left|\phi(t)\right\rangle = \left(a_1(t)\left|1\right\rangle + a_2(t)\left|2\right\rangle\right)\left|\mathbf{z}(t)\right\rangle$$

$$= \left(a_1(t)\left|1\right\rangle + 0\left|2\right\rangle\right)\left|\mathbf{z}(t)\right\rangle$$

$$+ \left(0\left|1\right\rangle + a_2(t)\left|2\right\rangle\right)\left|\mathbf{z}(t)\right\rangle$$

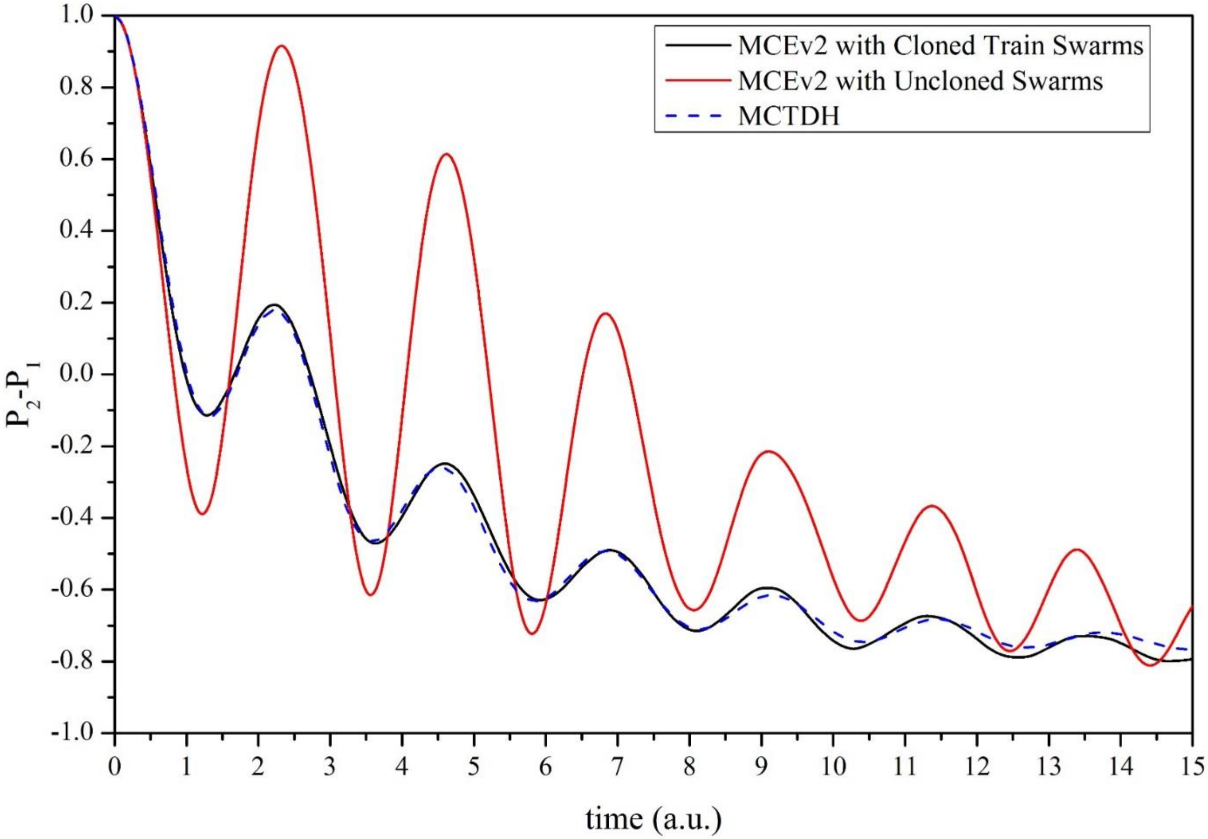
Numerical test (Spin-Boson Model)



Chris Symonds

- MCEv2 with all tricks applied agrees very well with MCTDH

MCEv2 with swarm of cloned trains



Numerical test (Spin-Boson Model)

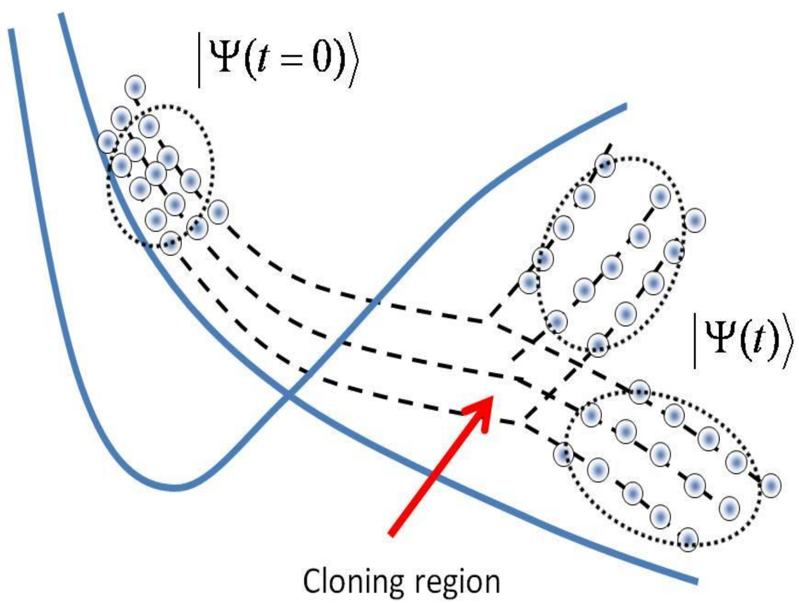
Comparison of MCEv1 and MCEv2

- MCEv1 converges very easily.
- MCEv2 is much harder to converge.
- But with all tricks and some efforts MCEv2 converges to the exact result.
- **Why bother ?**

Ab initio MCE is implemented in AIMS/MOLPRO (Stanford) and NEXMD (Los Alamos) codes

Dmitry Makhov, William Glover,
Sebastian Fernandez-Alberti

The MCE2 technique has been validated on model multidimensional systems and implemented as direct dynamics



1) **Trajectories with cloning are run “on the fly” one by one.**
2) **Trains allow to reuse electronic structure information**
3) **Coupling is done separately afterwards (post-processing)**

Ab initio MCE is implemented in AIMS/MOLPRO (Stanford) and NEXMD (Los Alamos) codes

Dmitry Makhov and **Sebastian Fernandez-Alberti**

One more trick:

For postprocessing get nondiagonal elements of NACME and Potential Energy as average of the diagonal ones.

$$\langle \chi_m | V_I(\mathbf{R}) | \chi_n \rangle = \langle \chi_m | \chi_n \rangle \left(\frac{V_I(\overline{\mathbf{R}}_m) + V_I(\overline{\mathbf{R}}_n)}{2} \right) + \frac{\langle \chi_m | (\mathbf{R} - \overline{\mathbf{R}}_m) | \chi_n \rangle \nabla V_I(\overline{\mathbf{R}}_m) + \langle \chi_m | (\mathbf{R} - \overline{\mathbf{R}}_n) | \chi_n \rangle \nabla V_I(\overline{\mathbf{R}}_n)}{2}$$

$$\langle \chi_m | \mathbf{C}_{IJ}(\mathbf{R}) \mathbf{M}^{-1} \nabla | \chi_n \rangle = \frac{i}{2\hbar} \langle \chi_m | \chi_n \rangle \left(\overline{\mathbf{P}}_m \mathbf{M}^{-1} \mathbf{C}_{IJ}(\overline{\mathbf{R}}_m) + \overline{\mathbf{P}}_n \mathbf{M}^{-1} \mathbf{C}_{IJ}(\overline{\mathbf{R}}_n) \right)$$

Ab initio MCE is implemented in AIMS/MOLPRO (Stanford) and NEXMD (Los Alamos) codes

Nonadiabatic coupling derived from spatial dependence of electronic wave functions.

$$\left|j_I\right\rangle = \left|j_I(\mathbf{r};\mathbf{R})\right\rangle \Rightarrow \left\langle \varphi_I \middle| \nabla_R \middle| \varphi_J \right\rangle \quad \left\langle \varphi_I \middle| \nabla_R^2 \middle| \varphi_J \right\rangle$$

Nonadiabatic coupling derived from time dependence of electronic wave function attached to the nuclear wave packet.

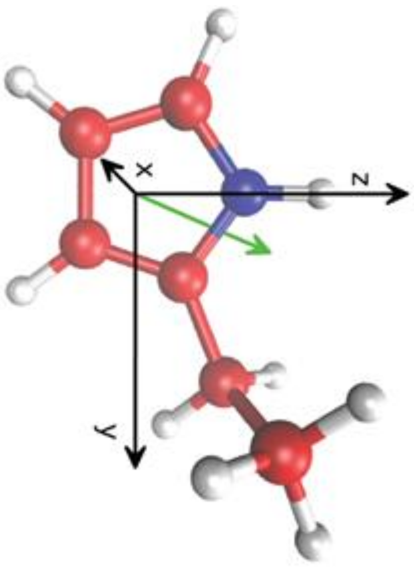
$$\left|\tilde{\varphi}_I^n\right\rangle = \left|\tilde{\varphi}_I^n\left(\mathbf{r};\overline{\mathbf{R}}_n(t)\right)\right\rangle \Rightarrow \left\langle \tilde{\varphi}_I^m \middle| \frac{\partial}{\partial t} \middle| \tilde{\varphi}_J^n \right\rangle$$

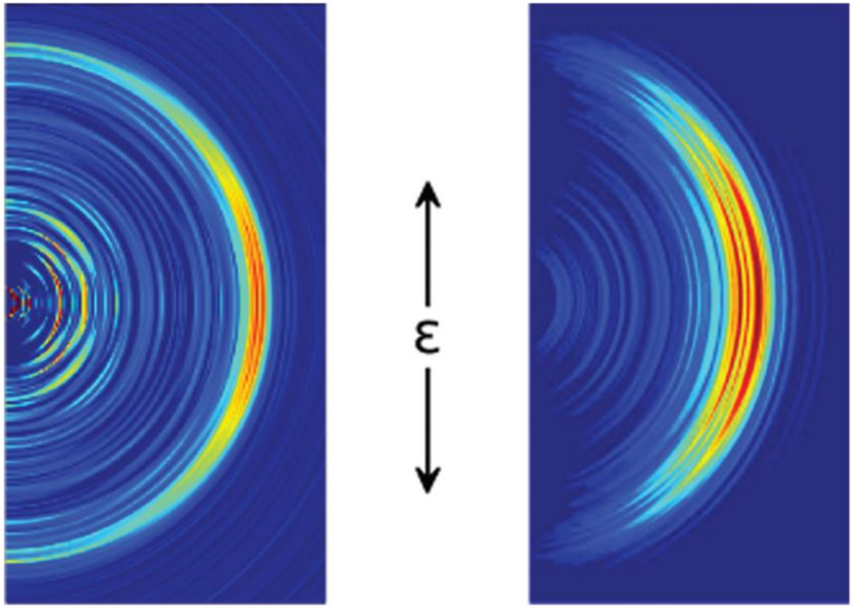
Benchmarking fully quantum MCE Theory Velocity Map Image

2-Ethylpyrrole

Experiment
Vas Stavros

Theory
Dmitry Makhov

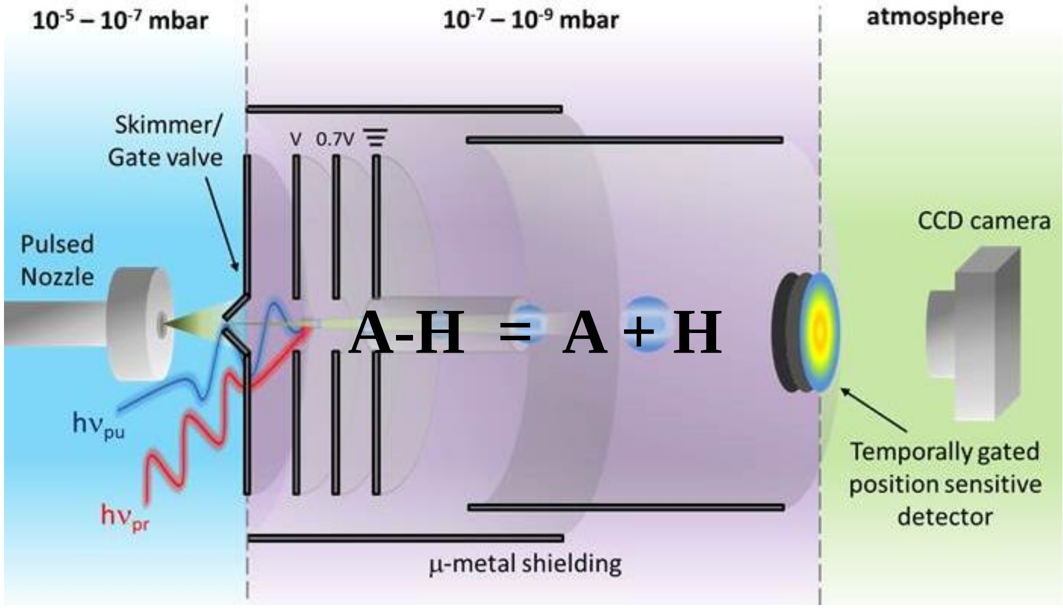


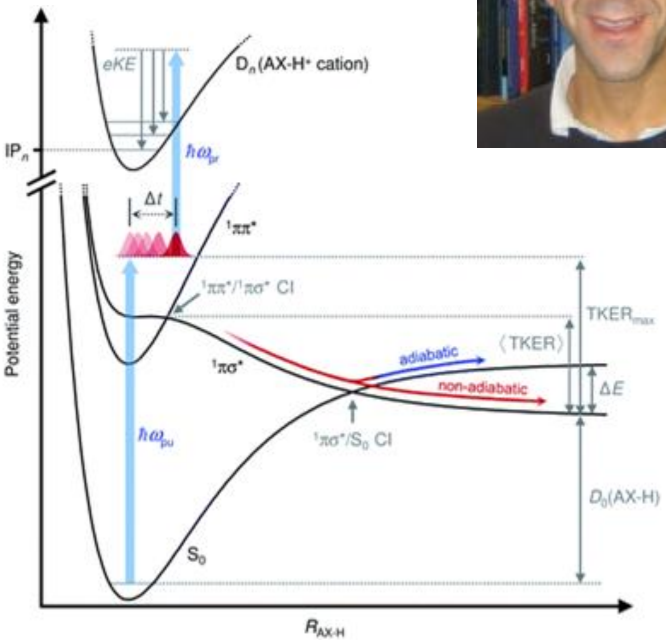


(a) (b)

Time resolved Velocity Map Imaging

Vas Stavros (Warwick)



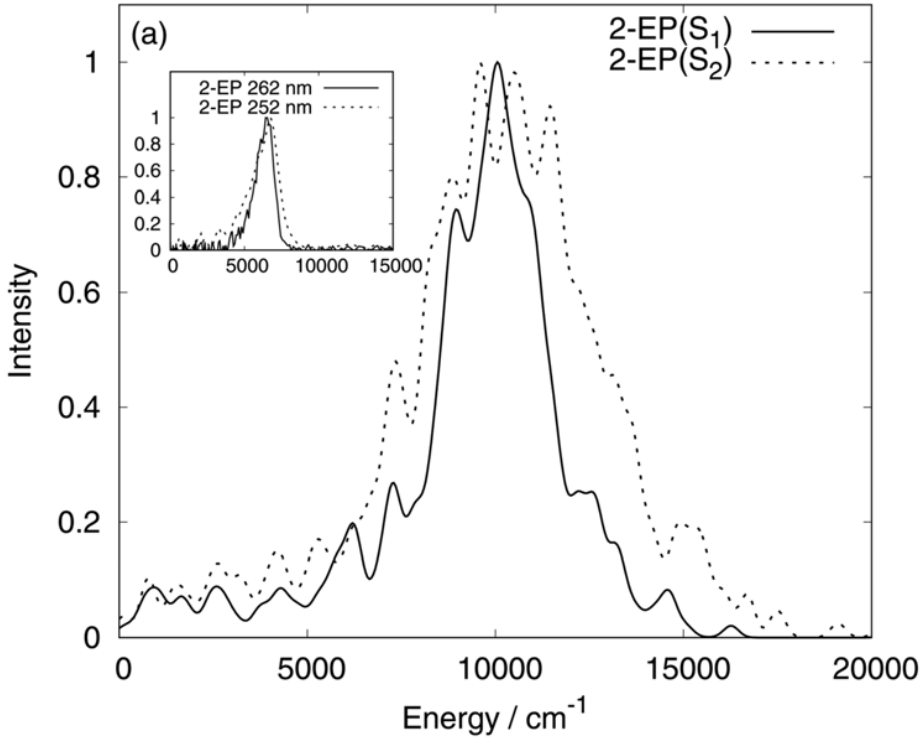


1) H and D dissociation kinetics (on the time scale of 10^2-10^3 fs with ~10 fs resolution), isotope effects.

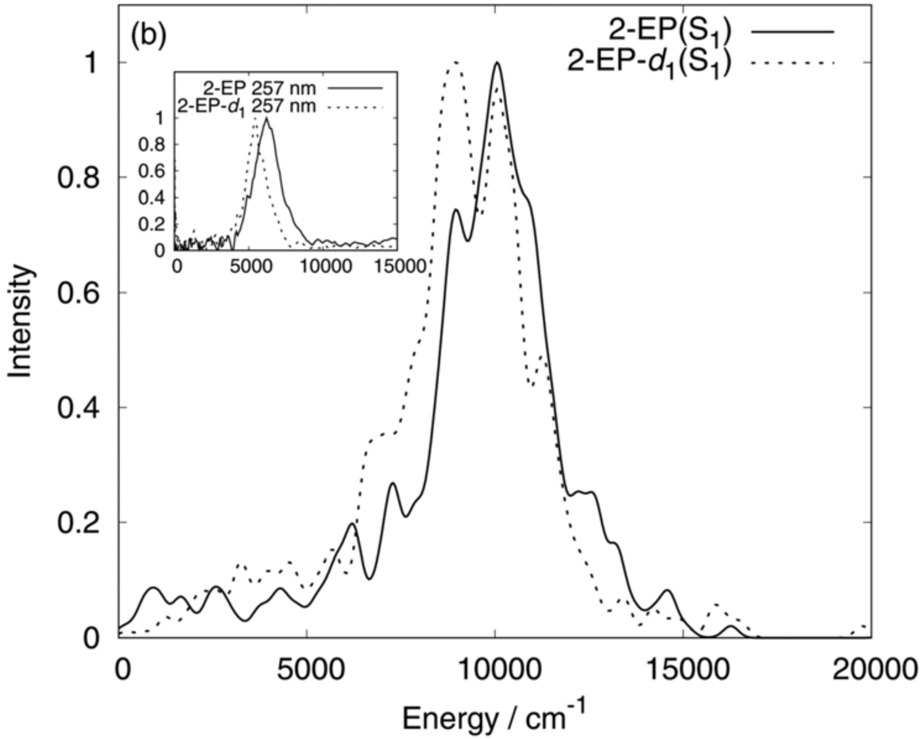
2) H and D product kinetic energy release distribution (TKER)

3) Spatial velocity distribution, Velocity Map Images (VMI)

Benchmarking fully quantum MCE Theory
2-EP TKER features

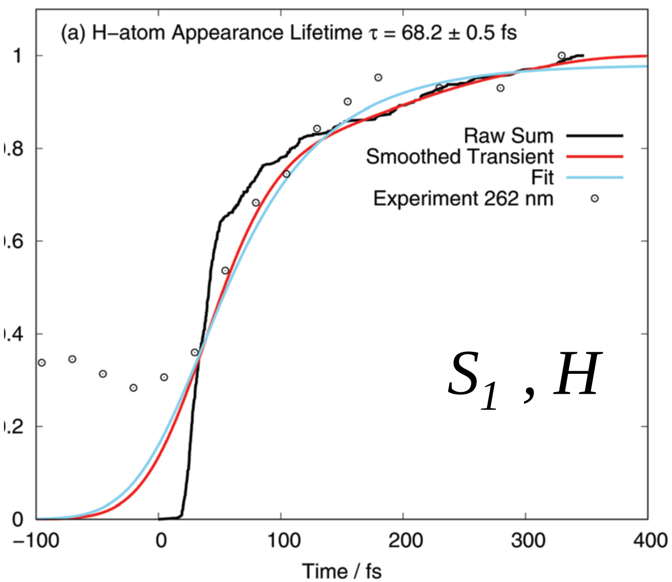


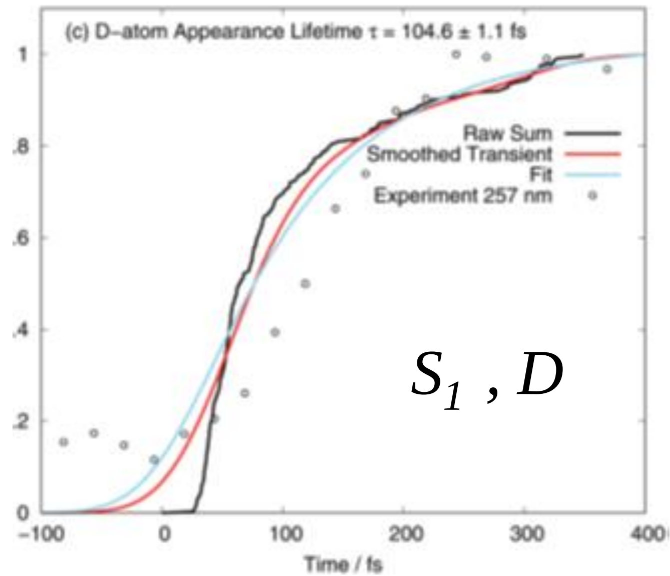
If excited to S2 state TKER spectrum gets broader.

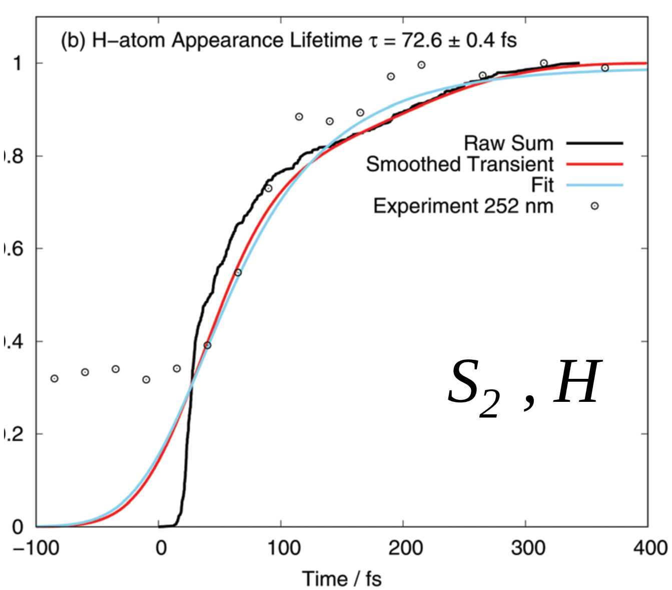


TKER spectrum of deuterated 2EP shifts to the left

Benchmarking fully quantum MCE Theory 2-EP kinetics







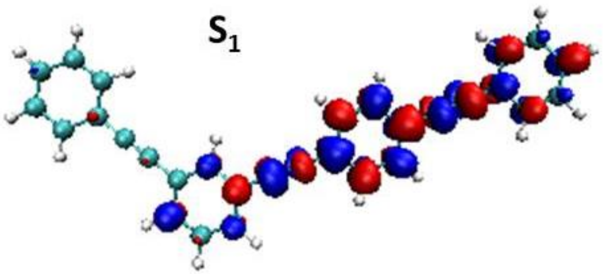
Quantitative agreement with experiment for appearance time when excited to S_1 and S_2 and for isotope effect.

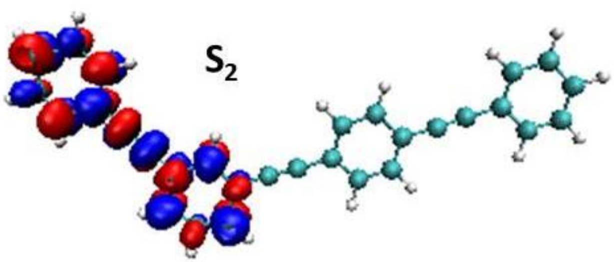
Ab initio Nonadiabatic dynamics of conjugated molecules (dendrimers)

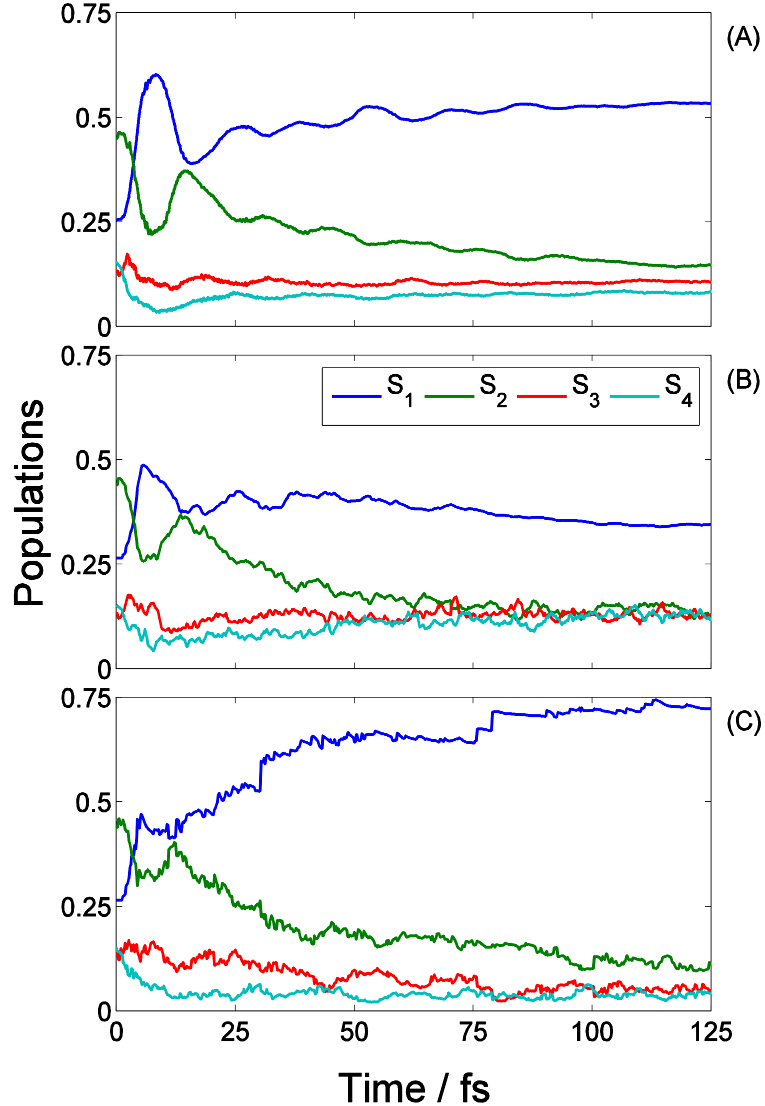
Sebastian Fernandez-Alberti (Argentina)

Sebastian Fernandez -Alberti

Sergei Tretiak







Quantum MCE

Ehrenfest

Surface hoping

More Applications of Coherent States

1) **Applying Gaussian CSs in a different context**

2) **Applying other types of CSs**

Bosonic systems are mapped to a set of coupled quantum oscillators. The Hamiltonian includes creation and annihilation operators. Use CSs !

Simulation of the Quantum Dynamics of Indistinguishable Bosons with the Coupled Coherent States Method

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(Dated: May 6, 2019)

$$\hat{H} = \hat{H}_{norm} = \sum_{m,n} h_{mn} \hat{a}_m^+ \hat{a}_n + \frac{1}{2} \sum_{klmn} \hat{a}_k^+ \hat{a}_l^+ W_{kl\,nm} \hat{a}_m \hat{a}_n$$

Phys. Rev. A **100**, 013607 2019

Bose condensate moving in a trap with CCSB

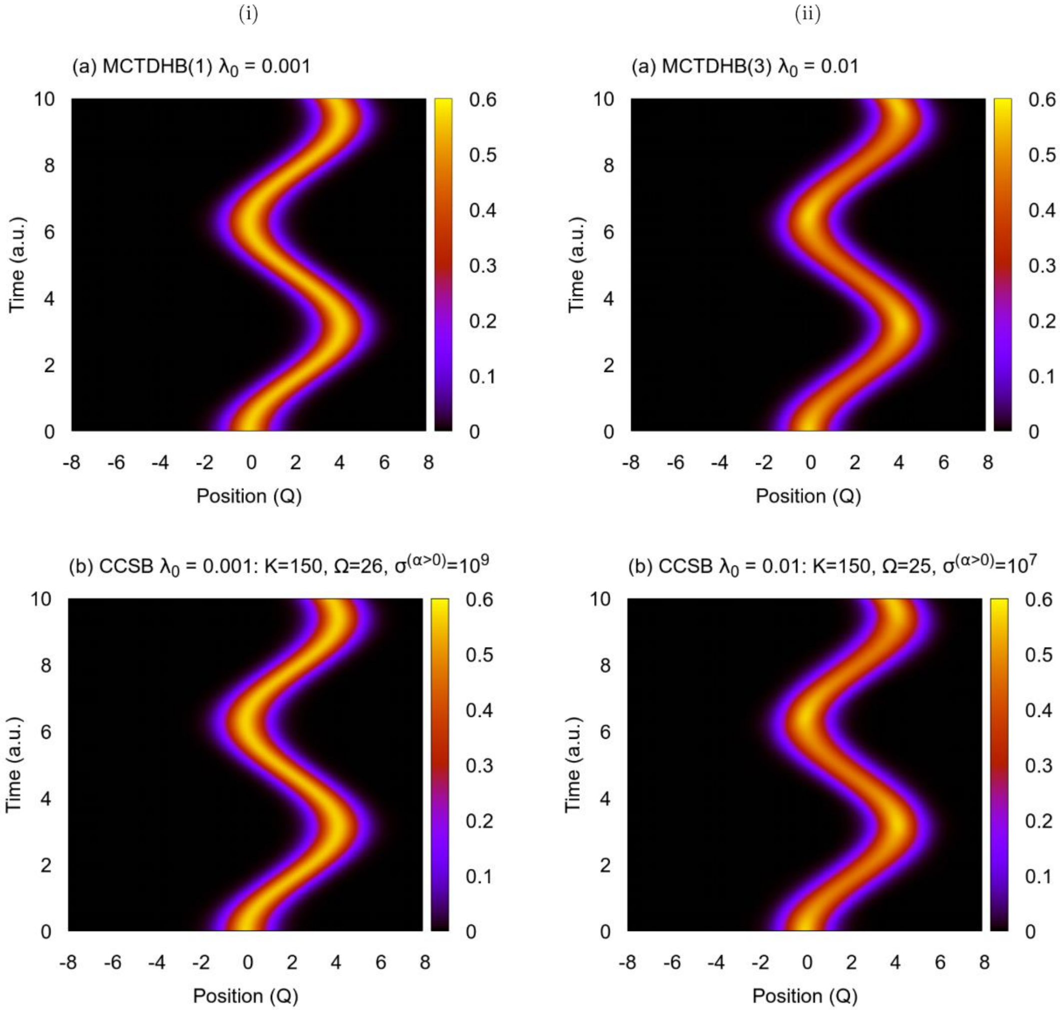


FIG. 3: Space-time representation of the evolution of the 1-body density for (a) MCTDHB and (b) CCSB calculations of Application 2 with interaction strengths (i) $\lambda_0 = 0.001$ and (ii) $\lambda_0 = 0.01$.

Creation and annihilation operators second quantization Hamiltonian, Fermions:

$$\hat{H} = \hat{H}_{norm} = \sum_{m,n} h_{mn} \hat{b}_m^+ \hat{b}_n + \frac{1}{2} \sum_{klmn} \hat{b}_k^+ \hat{b}_l^+ W_{kl\,nm} \hat{b}_m \hat{b}_n$$

$$\uparrow$$

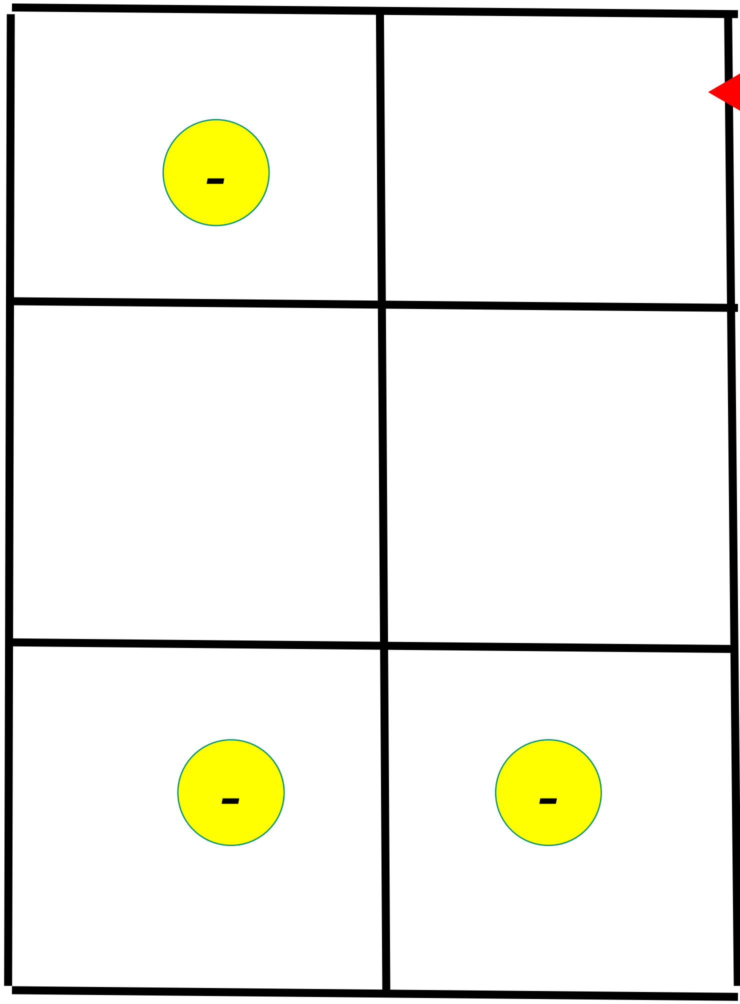
$$\frac{1}{r_{ee}}$$

USE SU-2 COHERENT STATE OF 2-LEVEL SYSTEM AND FRACTIONAL OCCUPATIONS OF ORBITALS

The Journal of Chemical Physics

1) 2018, **148,** 194109
2) In preparation

Electronic structure "on the fly" is expensive.



spin-orbital $\phi_i = \varphi_i \sigma_i$

Big problem: *There are many ways you can distribute the electrons via the boxes*

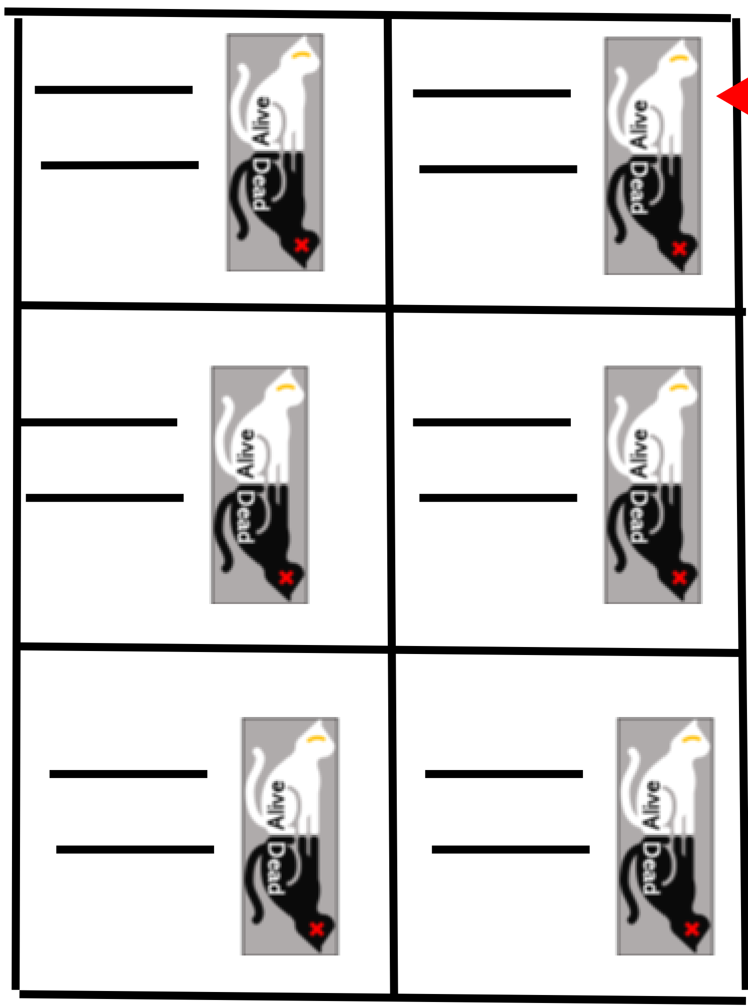
Number of configurations

Number of boxes

$$K = \frac{M_{spin-orb}!}{(M_{spin-orb} - N_e)!\, N_e!}$$

Number of electrons

An Alternative?



spin-orbital

Zombie electron at every orbital
SU(2) Coherent State

$$\left|\zeta_m\left(a_{1m}, a_{2m}\right)\right\rangle = a_{1m}\left|1_m\right\rangle + a_{0m}\left|0_m\right\rangle$$

alive *dead*

The Journal of Chemical Physics
1) 2018, **148,** 194109
2) In preparation (almost ready)

Generalised SU2 Coherent State, Zomie State

$$\left|\Psi(t)\right\rangle = \sum_n A^{(n)}(t)\left|\overline{\zeta}^{(n)}(t)\right\rangle$$

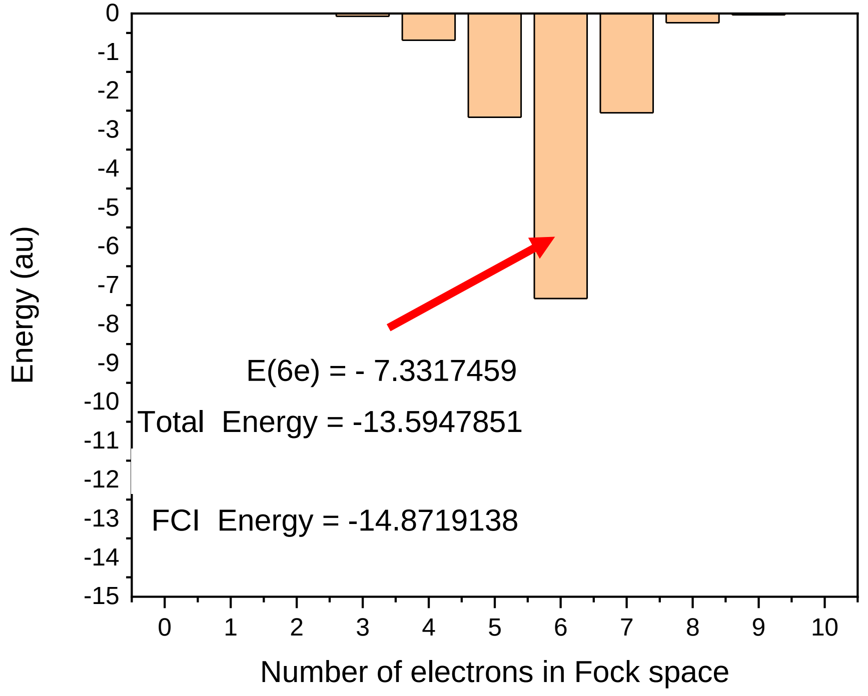
$$\left|\overline{\zeta}(t)\right\rangle = \prod_m \left(a_{0m}(t)\left|0_m\right\rangle + a_{1m}(t)\left|1_m\right\rangle\right)$$

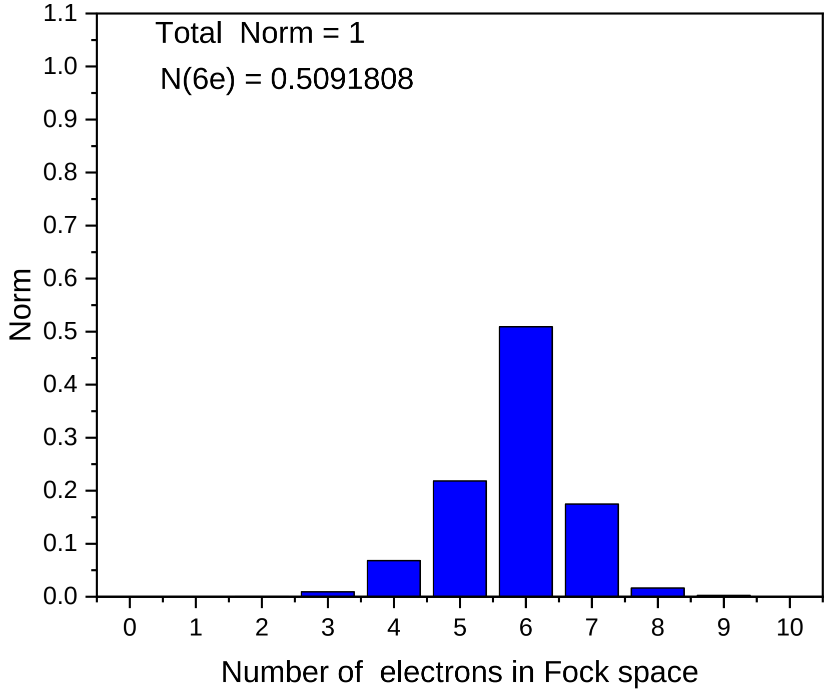
$$e^{-\beta\hat{H}}\left|\Psi(t)\right\rangle = \left|Ground\ State\right\rangle$$

Oliver Bramley

Tim Hele

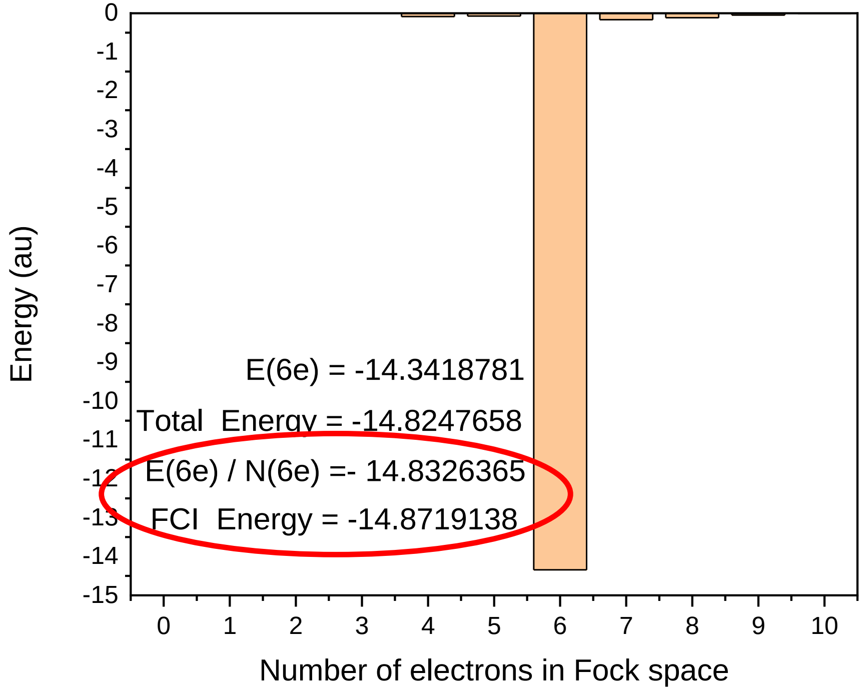
Energy and norm distribution in Fock Space
(Li_2 , 6e, 10 Spin-Orbitals. Random basis of 20 ZSs,)

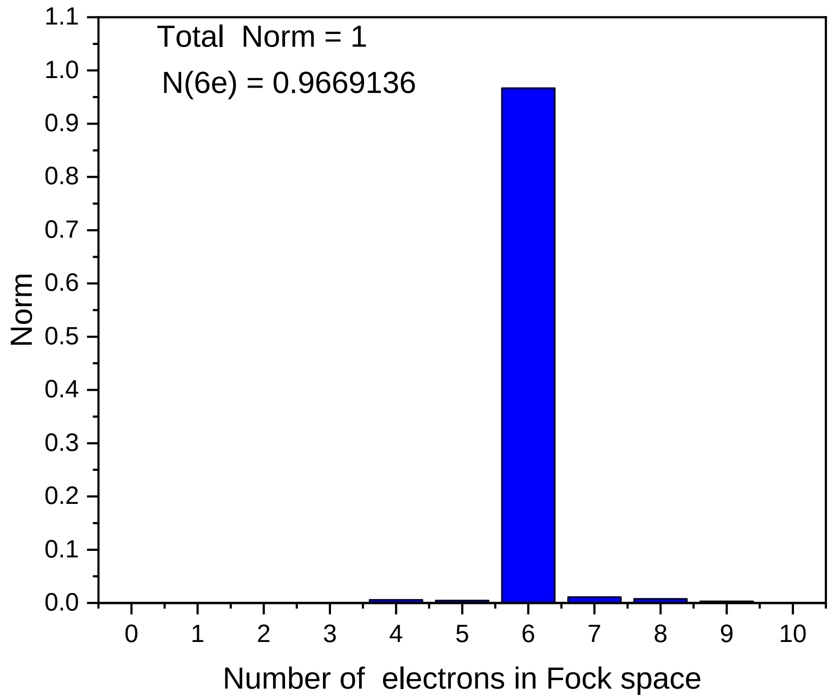




Zombie states wave function $\left|\Psi(t)\right\rangle = \sum A^{(n)}(t)\left|\bar{\zeta}^{(n)}(t)\right\rangle$ contains contribution from all possible numbers of electrons from 0 to 10

Energy and norm distribution in Fock Space
(Li$_2$, 6e, 10 Spin-Orbitals. Random **biased** basis of 20 ZSs)



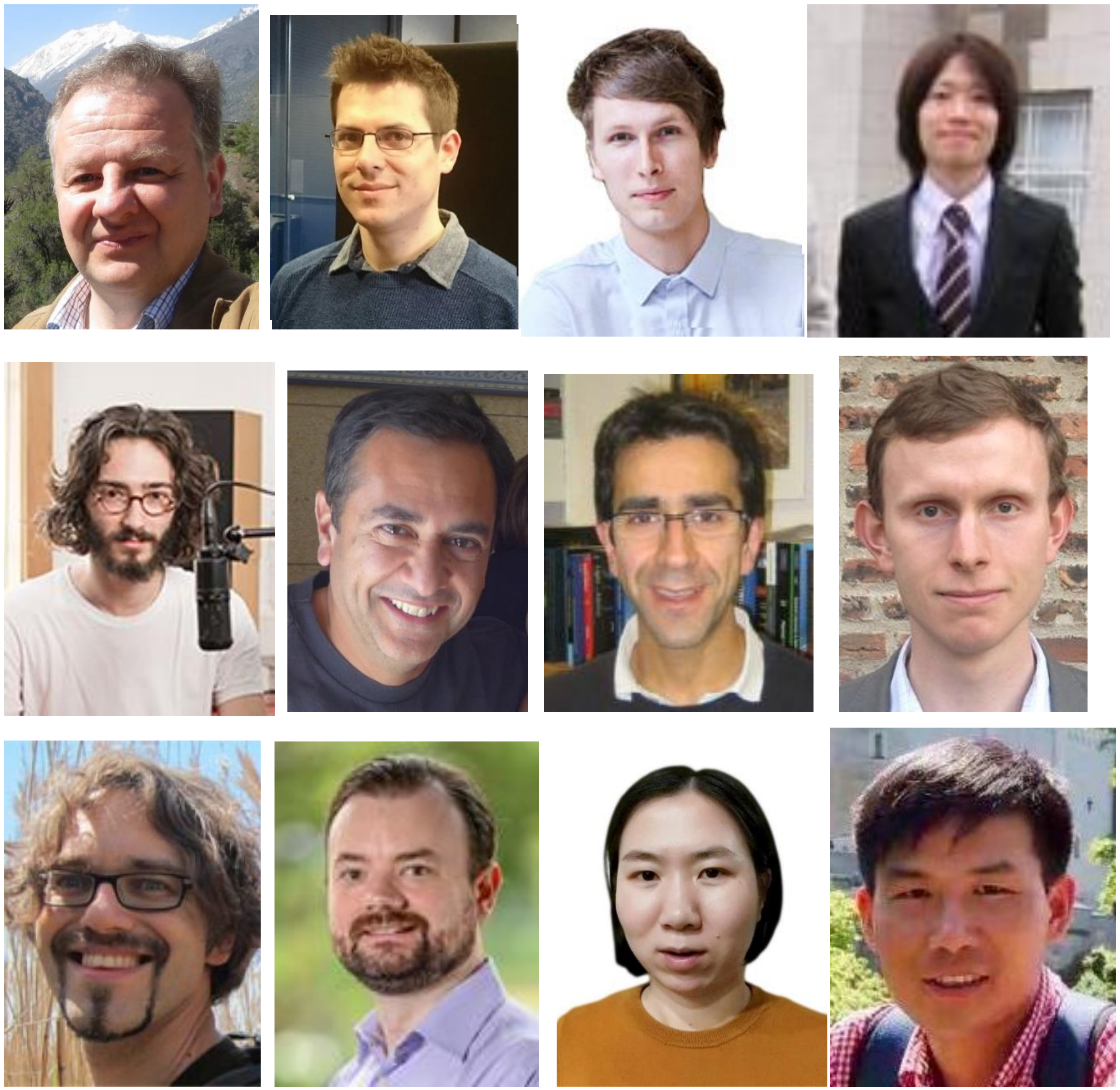


Lower orbitals are almost alive and higher orbitals are almost dead

Very short conclusion:

Coherent States basis can be very useful for multidimensional Quantum Mechanics

Group members and collaborators



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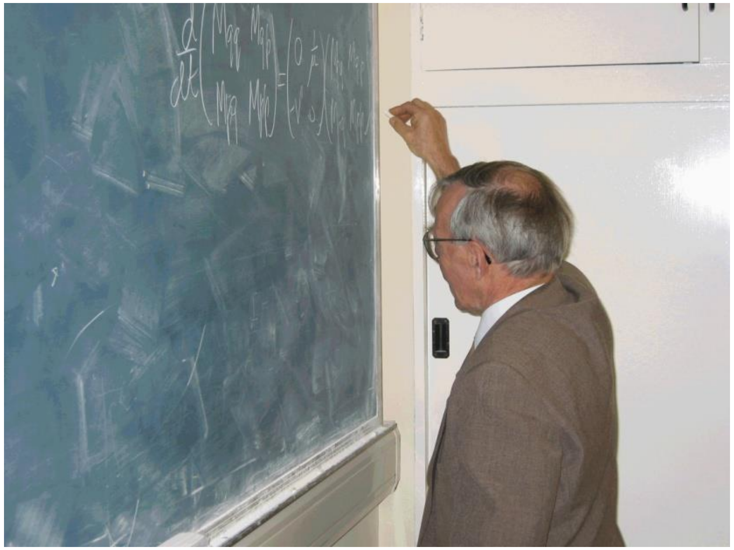
Thank you:



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