

L9

Methods for dynamics simulations II: A hierarchy of methods

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Wavepacket propagation

$$\Phi(\mathbf{r}, \mathbf{R}) = \sum_{k=1}^{N_s} \chi_k(\mathbf{R}) \psi_k(\mathbf{r}; \mathbf{R})$$

$$\chi_k = \langle \psi_k | \Phi \rangle \text{ nuclear wave function}$$

$$\mathbf{H} = T_N + H_e$$

$$\left(i\hbar \frac{\partial}{\partial t} - \mathbf{H} \right) \Phi(\mathbf{r}, \mathbf{R}, t) = 0$$

Multiply by ψ_i at left and integrate in the electronic coordinates

$$\left[i\hbar \frac{\partial}{\partial t} - (T_N + E_i) \right] \chi_i + \sum_{k=1}^{N_s} \left(i\hbar \langle \psi_i | \frac{\partial}{\partial t} \psi_k \rangle - \langle \psi_i | T_N \psi_k \rangle \right) \chi_k = 0$$

Time dependent Schrödinger equation for the nuclei

Wave-packet propagation

Expand nuclear wave function in a basis of n_k functions ϕ_k for each coordinate R_k :

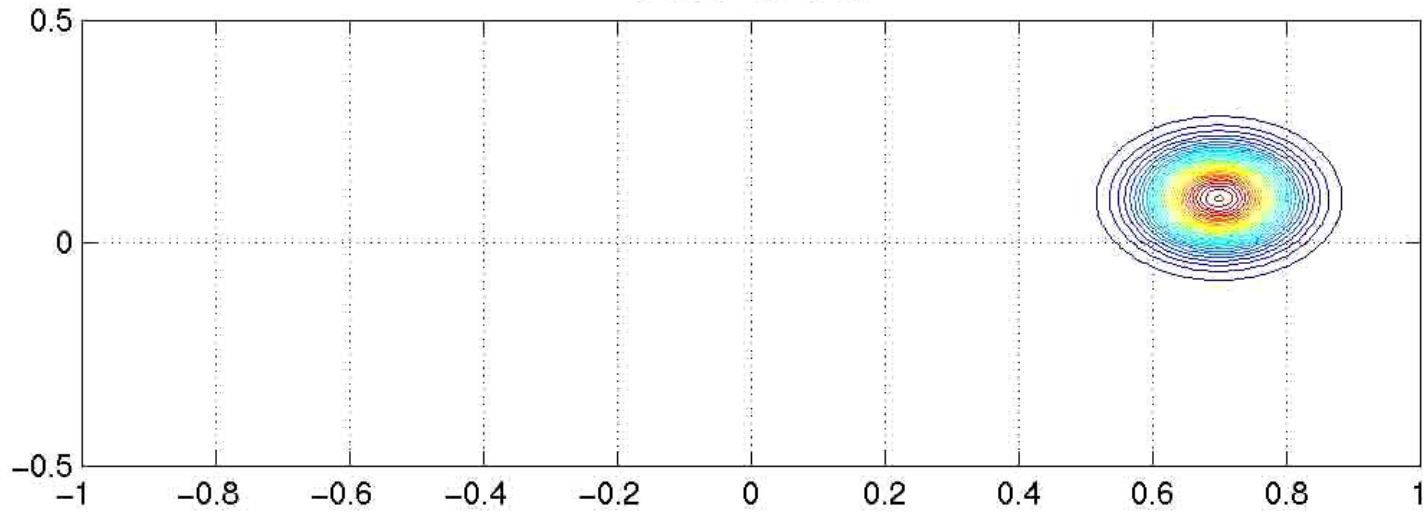
$$\chi_i(\mathbf{R}, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}^{(i)} \phi_{j_1}^{(1)}(R_1) \cdots \phi_{j_f}^{(f)}(R_f)$$

$$\left[i\hbar \frac{\partial}{\partial t} - (T_N + E_i) \right] \chi_i + \sum_{k=1}^{N_s} \left(i\hbar \left\langle \psi_i \left| \frac{\partial}{\partial t} \psi_k \right. \right\rangle - \langle \psi_i | T_N \psi_k \rangle \right) \chi_k = 0$$

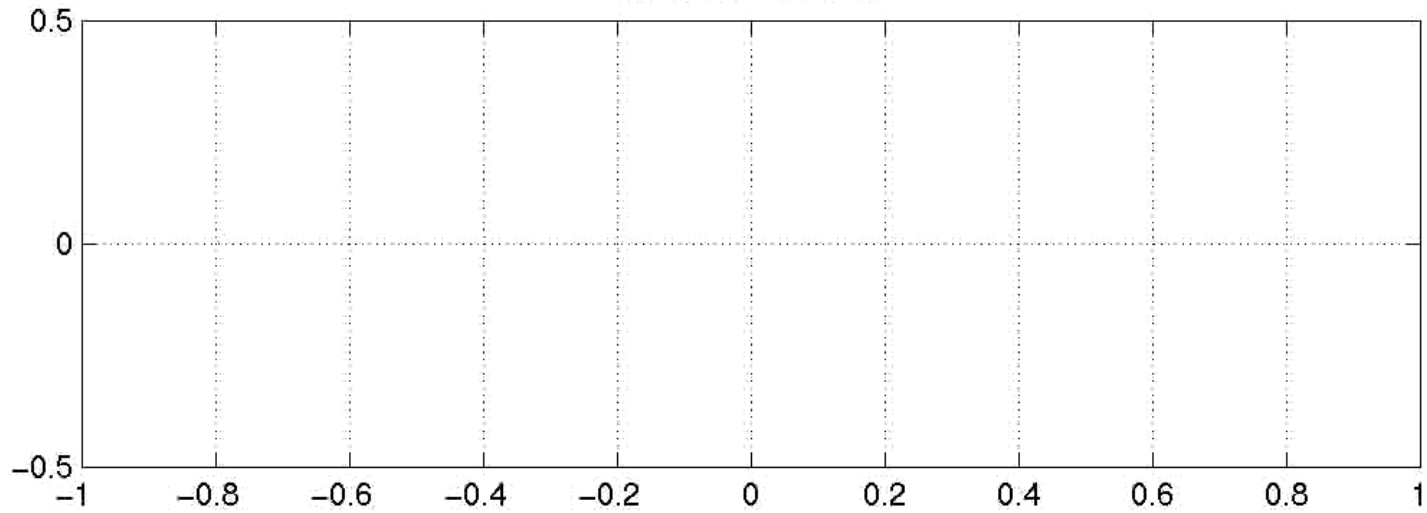
$$i\hbar \frac{\partial}{\partial t} \mathbf{A}^{(i)} = \sum_k \mathbf{H}^{ik} \mathbf{A}^{(k)}$$

- Kosloff, J Phys Chem **92**, 2087 (1988)

Plus-level



Minus-level



$$\chi_i(\mathbf{R}, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}^{(i)}(t) \phi_{j_1}^{(1)}(R_1, t) \cdots \phi_{j_f}^{(f)}(R_f, t)$$

Variational method leads to equations of motion for A and ϕ .

Conventional: 1 – 4 degrees of freedom
MCTDH: 4 -12 degrees of freedom

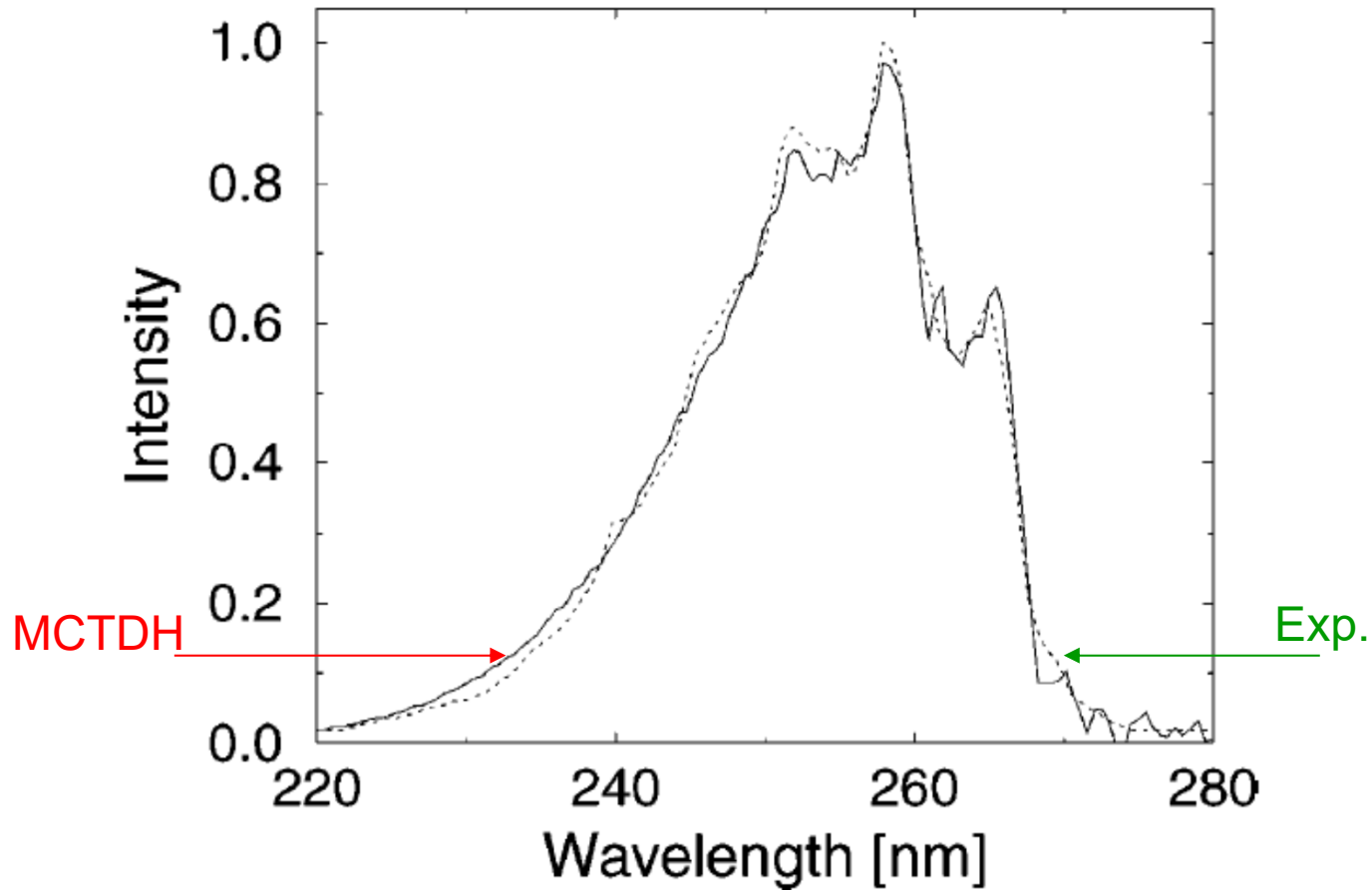
Heidelberg MCDTH program:

<http://www.pci.uni-heidelberg.de/tc/usr/mctdh/>

- Meyer and Worth, Theor Chem Acc **109**, 251 (2003)

UV absorption spectrum of pyrazine (24 degrees of freedom!)

$$I(\omega) = \omega \int_{-\infty}^{\infty} dt \langle \chi_1(0) | \chi_i(t) \rangle e^{i\omega t}$$



- Raab, et al. J. Chem. Phys. **110**, 936 (1999)



Multiple spawning

Multiple spawning

Nuclear wavefunction is expanded in a Gaussian basis set centered at the classical trajectory $(\bar{\mathbf{R}}, \bar{\mathbf{P}})$

$$\chi_i(\mathbf{R}; t) = \sum_{m=1}^{N_i(t)} c_m^i(t) e^{i\gamma_m^i(t)} \prod_{\rho=1}^{3N_{at}} g_{m\rho}^i(R; \bar{R}_{m\rho}^i, \bar{P}_{m\rho}^i, \alpha_{m\rho}^i)$$

$$g_{m\rho}^i(R; \bar{R}_{m\rho}^i, \bar{P}_{m\rho}^i, \alpha_{m\rho}^i) = \left(\frac{2\alpha_{m\rho}^i}{\pi} \right)^{1/4} \exp\left(-\alpha_{m\rho}^i (R - \bar{R}_{m\rho}^i)^2 + i\bar{P}_{m\rho}^i (R - \bar{R}_{m\rho}^i) \right)$$

Notice that the number of Gaussian functions (N_i) depends on time.

- Ben-Nun, Quenneville, Martínez, J Phys Chem A **104**, 5161 (2000)

$$\chi_i(\mathbf{R}; t) = \sum_{m=1}^{N_i(t)} c_m^i(t) e^{i\gamma_m^i(t)} \prod_{\rho=1}^{3N_{at}} g_{m\rho}^i(R; \bar{R}_{m\rho}^i, \bar{P}_{m\rho}^i, \alpha_{m\rho}^i)$$



$$\left[i\hbar \frac{\partial}{\partial t} - T_N \right] \chi_i + \sum_{k=1}^{N_s} \left[-\chi_k \langle \psi_i | T_N \psi_k \rangle - \chi_k \langle \psi_i | H_e | \psi_k \rangle \right] = 0$$

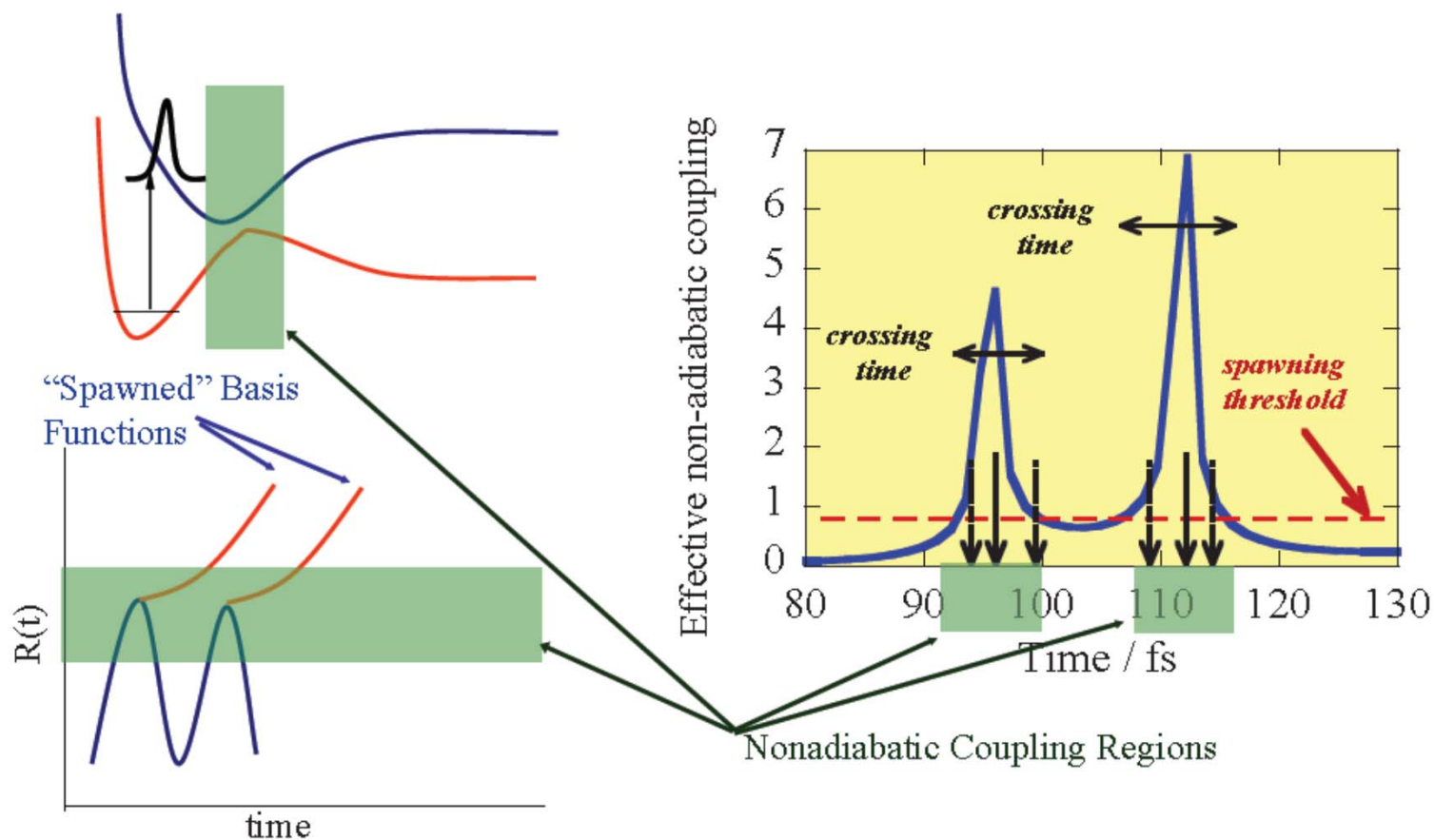
with $T_N \rightarrow 0$ and $\mathbf{S}_{mn}^{ij} = \langle \mathbf{g}_m^i | \mathbf{g}_n^j \rangle \delta_{ij}$

$$\frac{d\mathbf{C}^i}{dt} = -i(\mathbf{S}^{ii})^{-1} \left[(\mathbf{H}^{ii} - i\dot{\mathbf{S}}^{ii}) \mathbf{C}^i + \sum_{j \neq i} \mathbf{H}^{ij} \mathbf{C}^j \right]$$

Multiple spawning

The non-adiabatic coupling within \mathbf{H}^{ij} is computed and monitored along the trajectory.

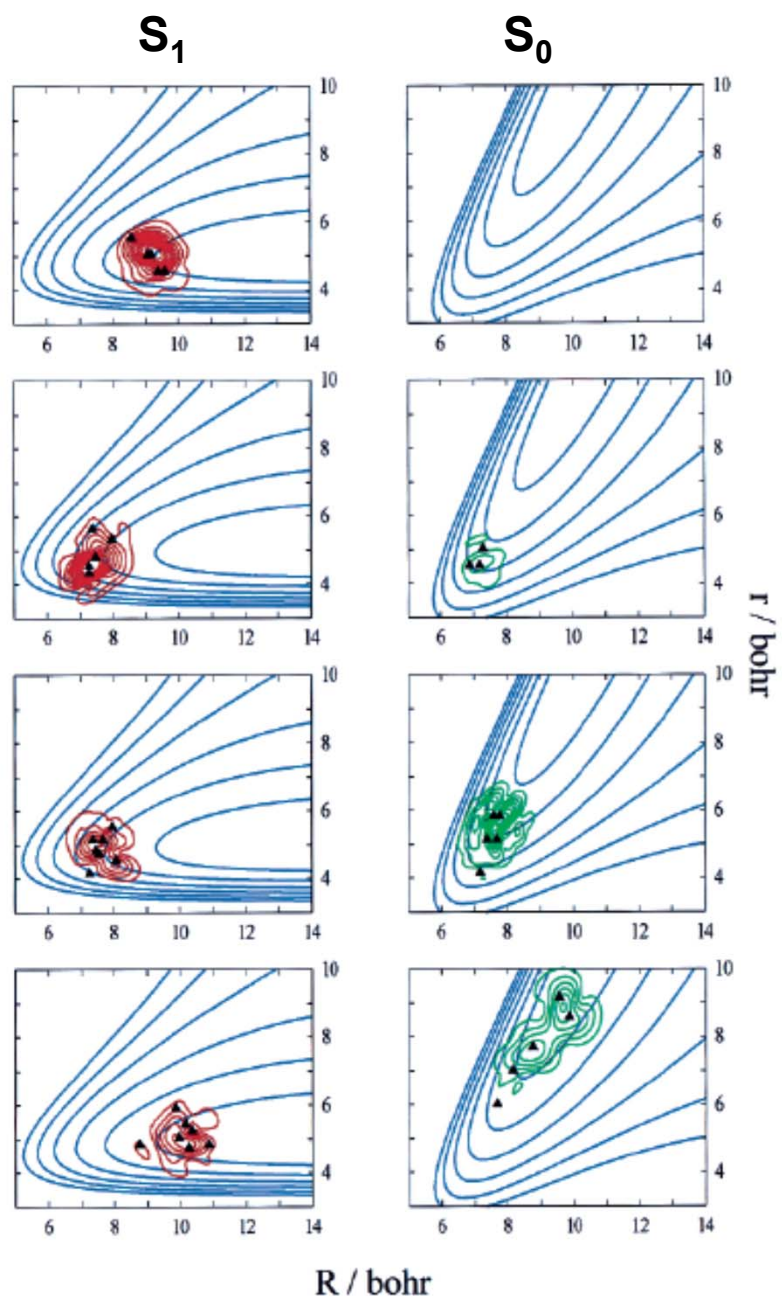
When it become larger than some pre-define threshold, new gaussian functions are created (spawned).



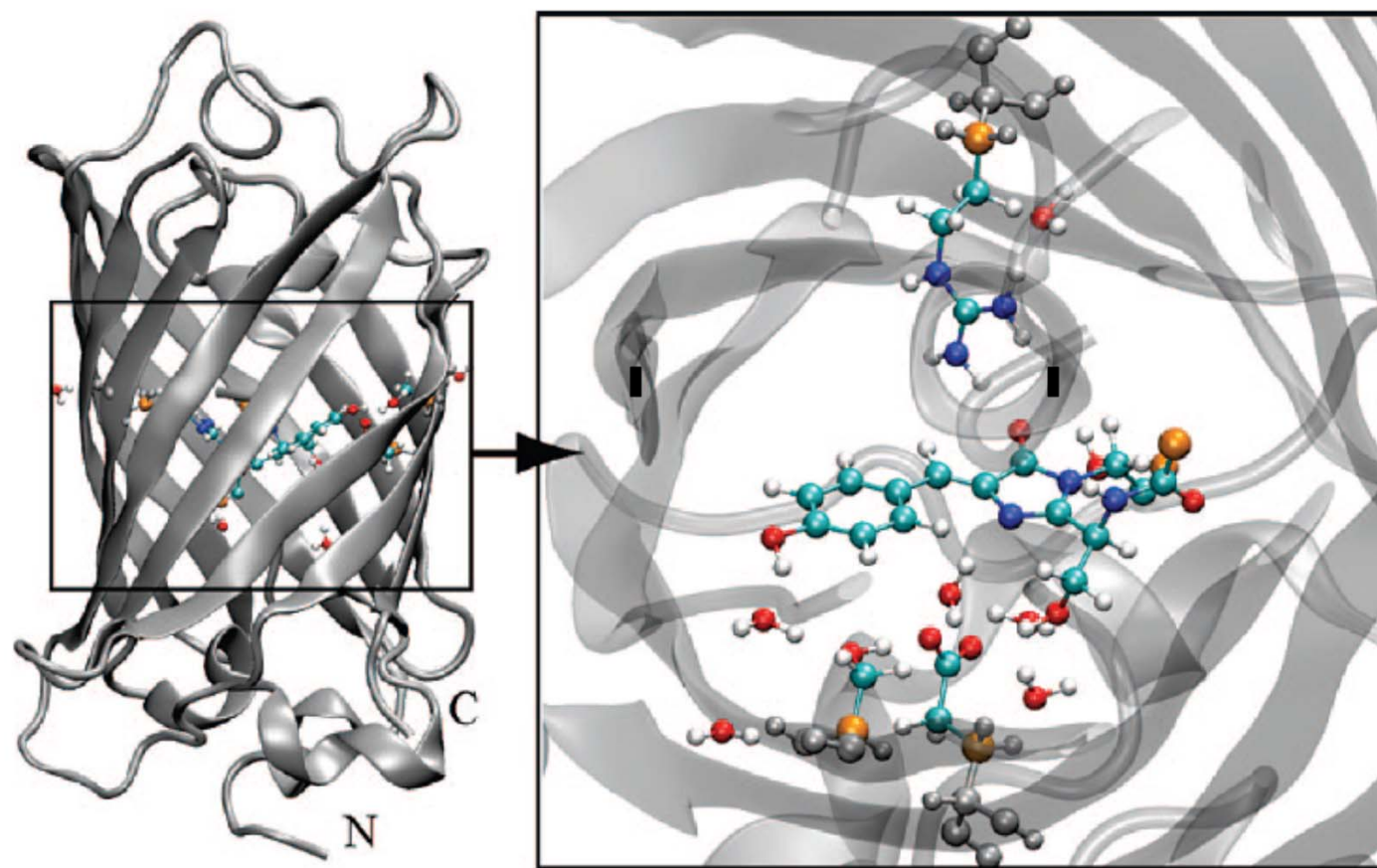
$$\mathbf{H}^{ij} = \langle \chi_i | H | \chi_j \rangle = \langle \chi_i | \left[T_N + E_i + \sum_k \hbar^2 \mathbf{h}_{ij} \cdot \nabla_M - \langle \psi_i | T_N \psi_J \rangle \right] | \chi_j \rangle$$

Saddle point approximation

$$\langle \chi_i | f | \chi_j \rangle \approx \langle \chi_i | \chi_j \rangle f(\bar{\mathbf{R}})$$



QM (FOMO-AM1)/MM

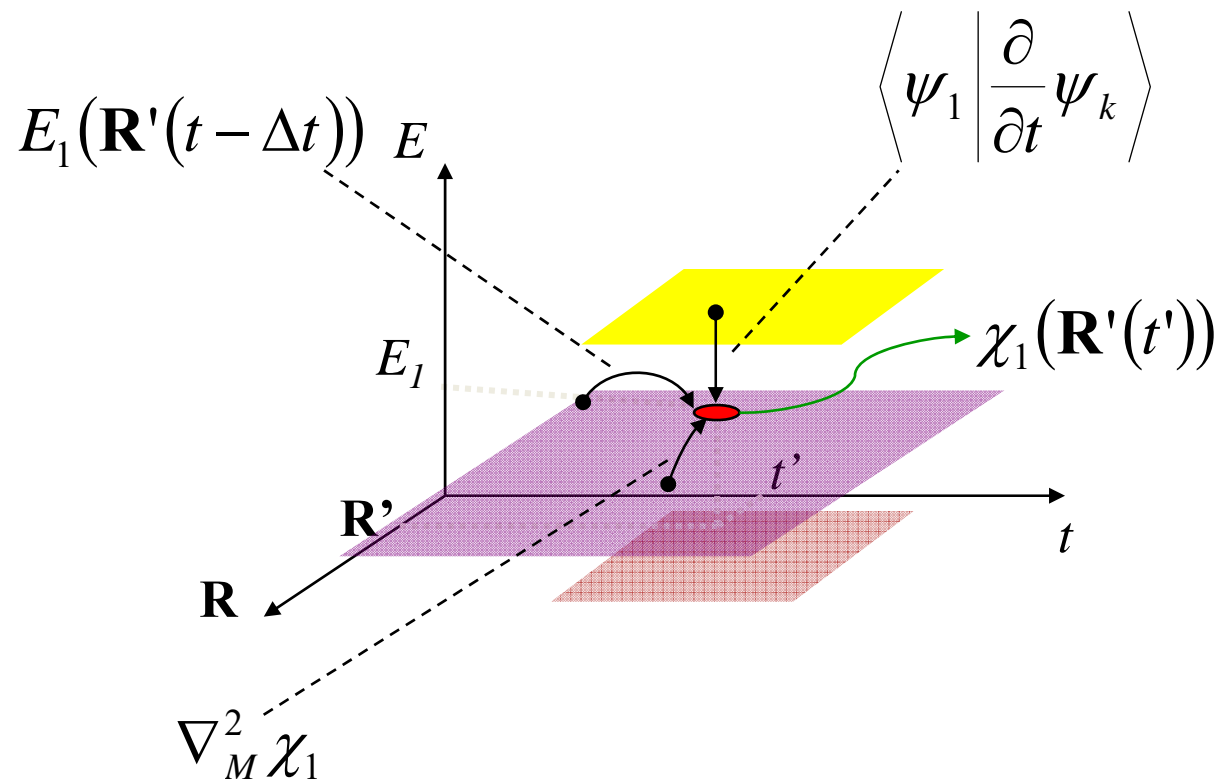


- Virshup et al. J. Phys. Chem. B **113**, 3280 (2009)



Semi-classical propagation

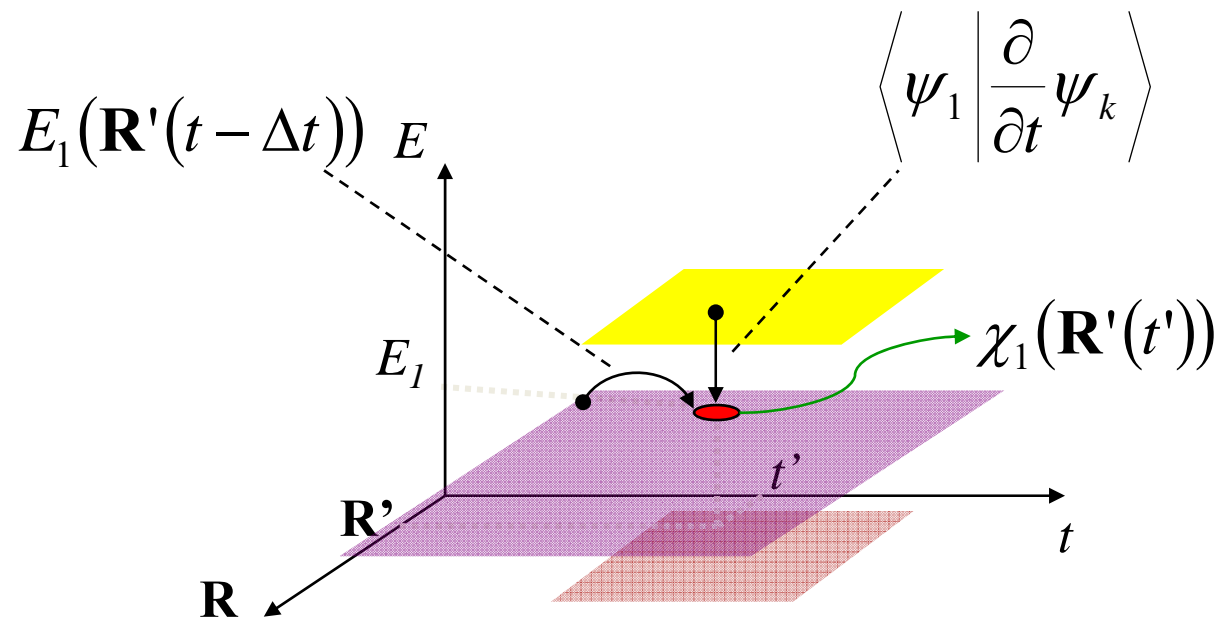
$$\left[i\hbar \frac{\partial}{\partial t} - (T_N + E_i) \right] \chi_i + \sum_{k=1}^{N_s} \left(i\hbar \left\langle \psi_i \left| \frac{\partial}{\partial t} \psi_k \right. \right\rangle - \langle \psi_i | T_N \psi_k \rangle \right) \chi_k = 0$$



Global nature of the nuclear wavefunction

LIGHT AND
MOLECULES

$$T_N \chi_i = \frac{\hbar}{2M} \nabla_M^2 \chi_i \rightarrow 0 \quad \left[i\hbar \frac{\partial}{\partial t} - (E_i) \right] \chi_i + \sum_{k=1}^{N_s} \left(i\hbar \left\langle \psi_i \left| \frac{\partial}{\partial t} \psi_k \right. \right\rangle \right) \chi_k = 0$$



Within this approximation, the nuclear wavefunction is local: it does not depend on the wavefunction values at other positions of the space

This opens two possibilities:

- 1) On-the-fly approaches (global PESs are no more needed)**
- 2) Classical independent trajectories approximations**

However, because of the non-adiabatic coupling between different electronic states, the problem cannot be reduced to the Newton's equations

We use, therefore, Mixed Quantum-Classical Dynamics approaches (MQCD)

$$\mathbf{F}(\mathbf{R}^c) = -\nabla_N \langle \Phi(t) | H_e | \Phi(t) \rangle$$

With $\Phi(t) = \sum_{k=1}^{N_s} \chi_k(t) \psi_k(\mathbf{r}; \mathbf{R}^c(t))$

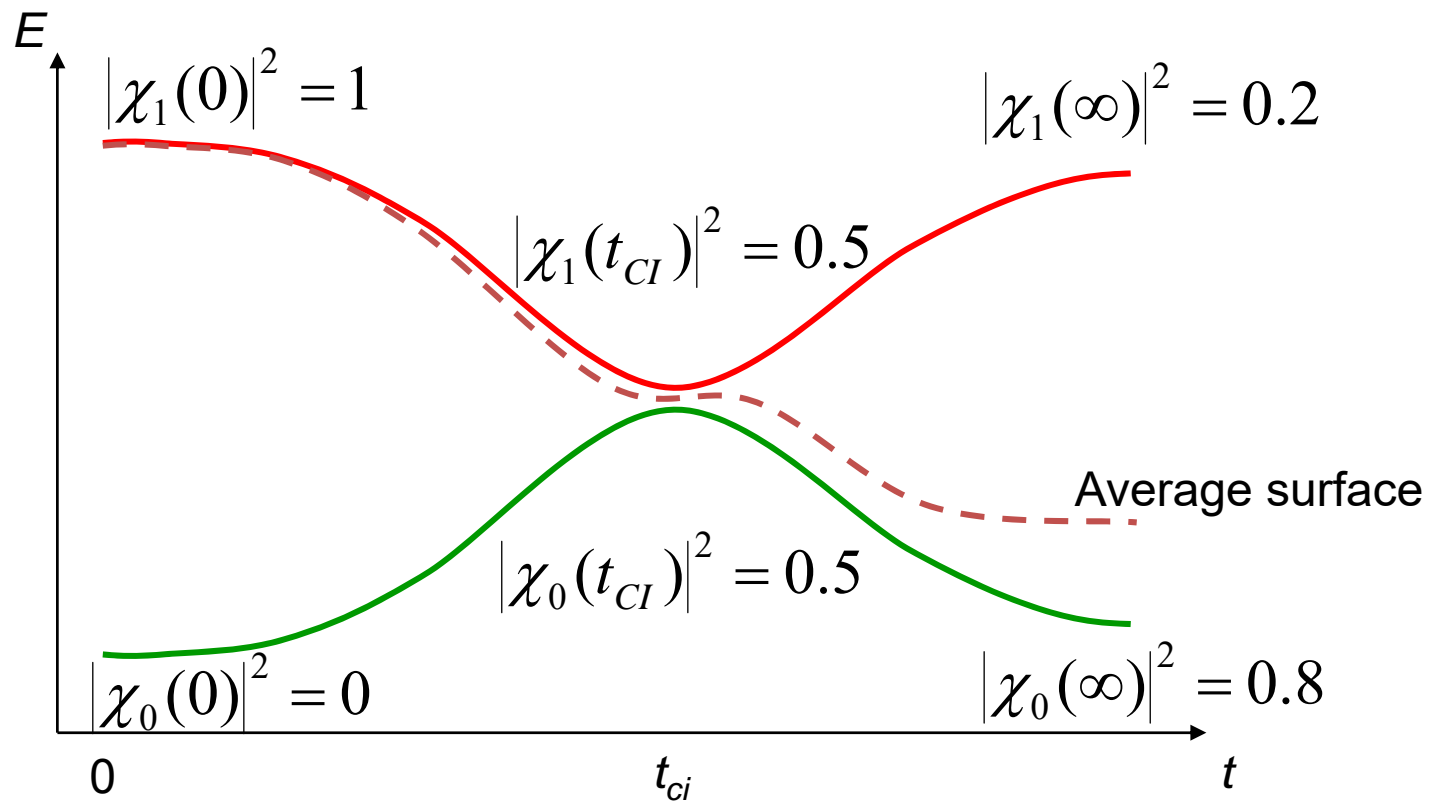
$\{\psi_i\}$ which solves: $(H_e - E)\psi_i = 0$ (adiabatic basis)

$$\mathbf{F}(\mathbf{R}^c) = -\sum_{k=1}^{N_s} \underbrace{|\chi_k(t)|^2}_{\text{Weighted average over all gradients}} \nabla E_k^c - \sum_{kj} \chi_j \chi_k^* (E_j^c - E_k^c) \langle \psi_k | \nabla \psi_j \rangle$$

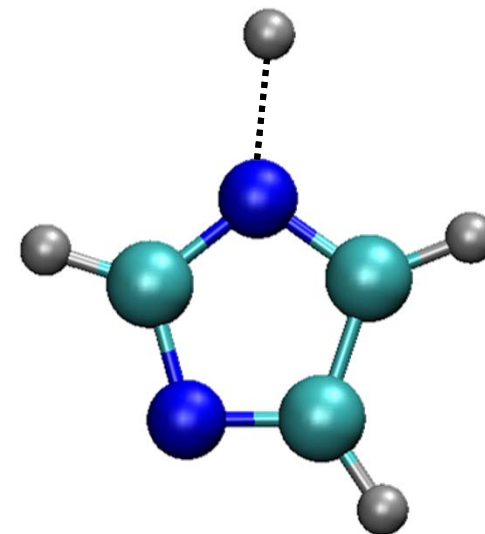
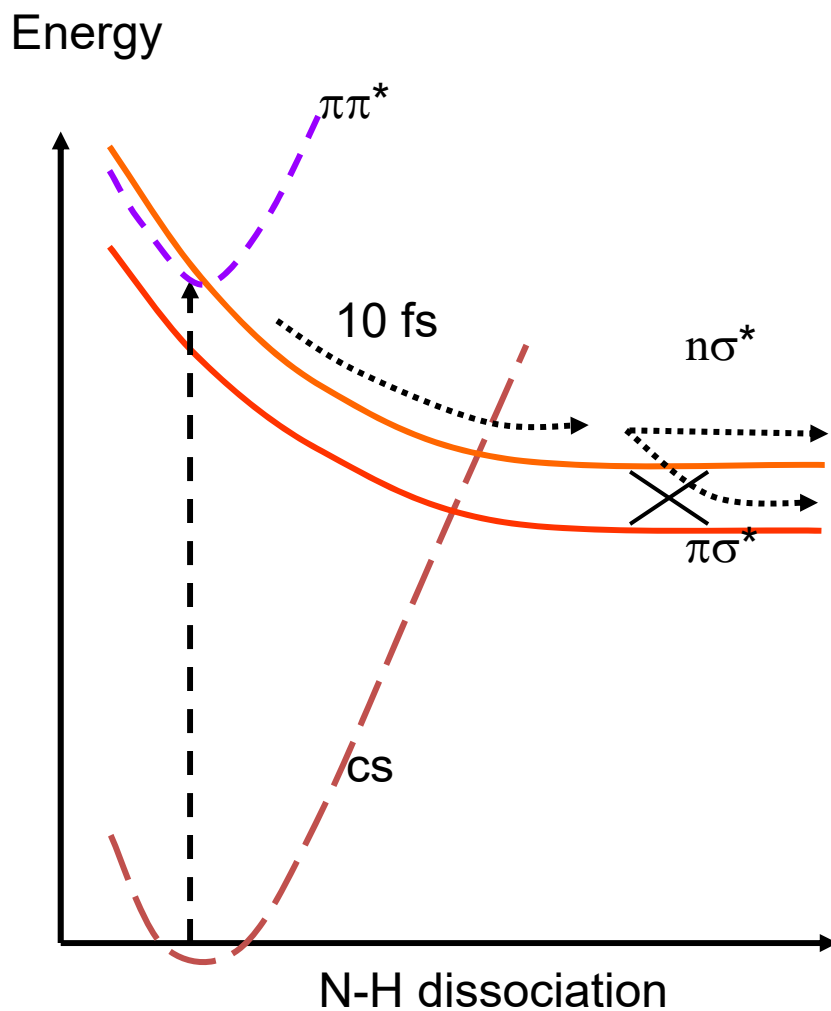
Weighted average over all gradients

- Meyer and Miller, J. Chem. Phys. **70**, 3214 (1979)

Ehrenfest (Mean Field) Dynamics



Ehrenfest dynamics fails for dissociation



The problem with the Ehrenfest dynamics is the lack of decoherence.

$$\rho = \begin{bmatrix} |\chi_0|^2 & \chi_0^* \chi_1 \\ \chi_1^* \chi_0 & |\chi_1|^2 \end{bmatrix}$$

The non-diagonal terms should quickly go to zero because of the coupling among the several degrees of freedom.

The approximation $\chi_i(\mathbf{R}(t)) \sim \chi_i(t)$ does not describe this behavior adequately.

Ad hoc corrections may be imposed.

- Zhu, Jasper and Truhlar, J Chem Phys **120**, 5543 (2004)

$$\mathbf{F}(\mathbf{R}^c) = -\nabla_N E_i$$

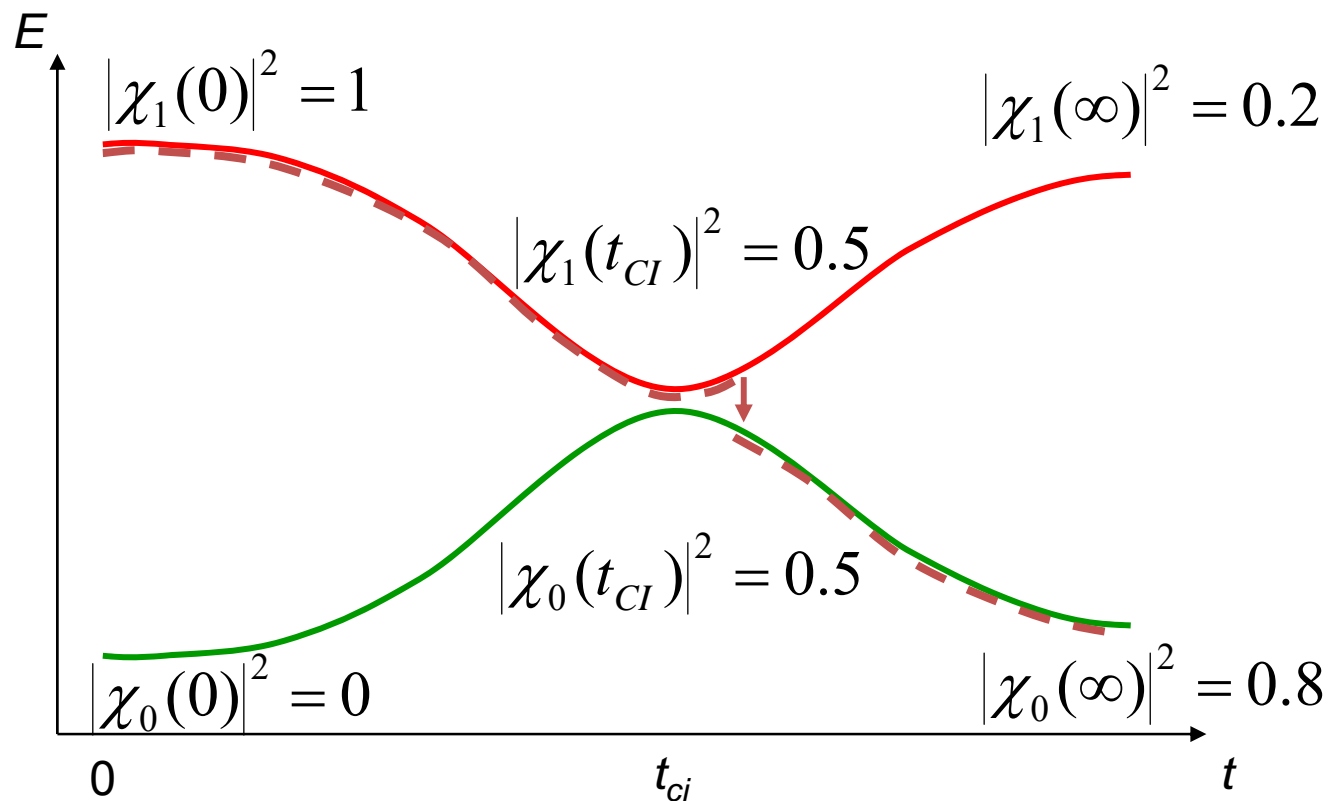
Dynamics runs always on a single surface (diabatic or adiabatic).

Every time step a stochastic algorithm decides based on the non-adiabatic transition probabilities on which surface the molecule will stay.

The wavepacket information is recovered repeating the procedure for a large number of independent trajectories.

Because the dynamics runs on a single surface, the decoherence problem is largely reduced (but not eliminated).

- Tully, J. Chem. Phys. **93**, 1061 (1990)



Quantum

Wave packet (MCTDH)

$$\chi_i(\mathbf{R}, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}^{(i)}(t) \phi_{j_1}^{(1)}(R_1, t) \cdots \phi_{j_f}^{(f)}(R_f, t)$$

Multiple spawning

$$\chi_i(\mathbf{R}; t) = \sum_{m=1}^{N_i(t)} c_m^I(t) e^{i\gamma_m^i(t)} \prod_{\rho=1}^{3N_{at}} g_{m\rho}^i(R; \bar{R}_{m\rho}^i, \bar{P}_{m\rho}^i, \alpha_{m\rho}^i)$$

Mean field; Surface hopping

$$|\chi_i(\mathbf{R}; t)|^2 = \rho_i(\mathbf{R}(t))$$

Classical

- There are many methods available for nonadiabatic dynamics simulations.
- They have different range of applications.
- They span a spectrum from pure quantum mechanical to semi-classical approaches.