Introduction to Numerical Simulations and High Performance Computing: From Materials Science to Biochemistry

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Part 6:

Advanced Methods II

Path Integral and non-Adiabatic Methods

Beyond classical nuclei: Path Integral MD

Sometimes nuclei cannot be approximated as classical point-like particles. Textbook examples are:

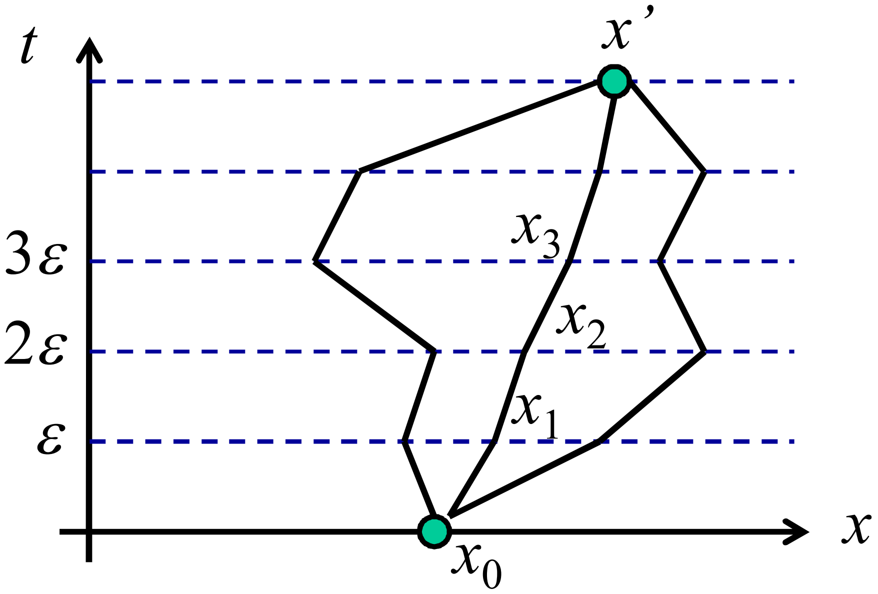
- Tunneling processes (mainly protons)
- Quantum broadening of nuclei comparable to (or larger than) thermal fluctuations

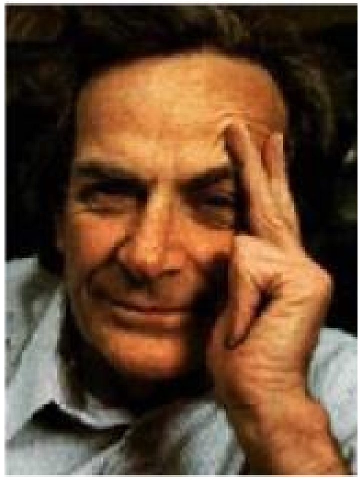
Proposed solution: Consider also (light) nuclei as quantum objects

First Principles Path Integral Molecular Dynamics (PIMD)

Path Integrals ?

A quantum particle travelling from an initial point x_0 at time t_0 can reach a point x' at time t' along any possible path joining the two points…





R.P. Feynman
1918 - 1988

…each weighted with its own probability exp (-iS), being S the action $S = \int dt\, L(x, \dot{x})$ of the system.

(R.P. Feynman, *Statistical Mechanics*, Addison Wesley, Massachusetts, 1972)

Well, yes… Path Integrals !

The probability amplitude of finding at (x', t') a particle started at (x_0, t_0) is then a sum of all possible weighted paths

$$\left\langle x,t\left|e^{-i(t-t')\hat{H}}\right|x',t'\right\rangle = \lim_{\substack{\varepsilon\to 0\\ n\to\infty}}\int dx_1dx_2...dx_{n-1}\, e^{-i\int_0^{\varepsilon}dt_1L}\, e^{-i\int_{\varepsilon}^{2\varepsilon}dt_2L}\cdot ...\cdot e^{-i\int_{(n-1)\varepsilon}^{n\varepsilon}dt_{n-1}L}$$

where $n\varepsilon = t'$, $x_0 = x(t_0)$ and $x' = x(t') = x(n\varepsilon)$. Formally we write

$$\mathcal{D}x(t) = \lim_{n\to\infty}\prod_{i=1}^{n-1}dx_i = \lim_{n\to\infty}dx_1dx_2...dx_{n-1}$$

$$\left\langle x,t\left|e^{-i(t-t')\hat{H}}\right|x',t'\right\rangle = \int_{x_0}^{x'}\mathcal{D}x(t)e^{-iS\left[x(t),\dot{x}(t)\right]}$$

Path Integral formulation of the partition function

The partition function $Z(\beta)$ of a system having a Hamiltonian $H = K + V$, i.e. a kinetic term $K = m\mathbf{v}^2/2$ (depending on the velocities) and a potential term V (depending on positions) at a temperature T ($\beta = 1/k_B T$) can be written as

$$Z(\beta) = \mathrm{Tr}\, e^{-\beta H} = \int dx_1 \langle x_1 | e^{-\beta(K+V)} | x_1 \rangle = \lim_{P\to\infty} \int dx_1 \langle x_1 | \Omega^P | x_1 \rangle$$

where we make use of the Trotter factorization

$$e^{-\beta(K+V)} = \lim_{P\to\infty} \left[e^{-\frac{\beta}{2P}V} e^{-\frac{\beta}{P}K} e^{-\frac{\beta}{2P}V} \right]^P = \lim_{P\to\infty} \Omega^P$$

Path Integral formulation of the partition function

Using the completeness relation $\mathbf{1} = \int dx \left| x \right\rangle \left\langle x \right|$ we get

$$Z(\beta) = \lim_{P\to\infty} \int dx_1 dx_2 \ldots dx_P \left\langle x_1 \left| \Omega \right| x_2 \right\rangle \left\langle x_2 \left| \Omega \right| x_3 \right\rangle \ldots \left\langle x_P \left| \Omega \right| x_1 \right\rangle$$

$$= \lim_{P\to\infty} \int \prod_{i=1}^{P} dx_i \left\langle x_i \left| \Omega \right| x_{i+1} \right\rangle_{P+1=1}$$

and each matrix element can be computed as

$$\left\langle x_i \left| \Omega \right| x_{i+1} \right\rangle = \left\langle x_i \left| e^{-\frac{\beta}{2P}V} e^{-\frac{\beta}{P}K} e^{-\frac{\beta}{2P}V} \right| x_{i+1} \right\rangle$$

$$= \left(\frac{mP}{2\pi\beta} \right) e^{-\left[\frac{mP}{2\beta}(x_{i+1}-x_i)^2 + \frac{\beta}{2P}\left(V(x_{i+1})+V(x_i)\right) \right]}$$

Path Integral formulation of the partition function

Hence, the partition function reads ($\omega_P^2 = P/\beta^2$)

$$Z(\beta) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta}\right)^{P/2}\int_{x_{P+1}=x_1} dx_1 \ldots dx_P\, e^{-\sum_{i=1}^{P}\left[\frac{mP}{2\beta}(x_{i+1}-x_i)^2+\frac{\beta}{P}V(x_i)\right]}$$

$$= \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta}\right)^{P/2}\int_{x_{P+1}=x_1}\prod_{i=1}^{P} dx_i\, e^{-\beta\sum_{i=1}^{P}\left[\frac{m}{2}\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}V(x_i)\right]}$$

$$= \int dx_1 \int_{x_1}^{x_1}\mathcal{D}x(\tau)\, e^{-S[x(\tau)]}$$

➡ map each QM particle onto an effective classical system of P beads coupled by a harmonic potential plus $V(x)$

Path Integral formulation in a Car-Parrinello Lagrangean scheme

$$\mathfrak{L} = \frac{1}{P}\sum_{\sigma=1}^{P}\left\{\sum_{i}\mu\left|\dot{\psi}_i^{\sigma}(\mathbf{x})\right|^2 - E^{DFT}\left[\psi_i^{\sigma},\mathbf{R}_I^{\sigma}\right] + \sum_{i,j}\left[\Lambda_{ij}\left(\left\langle\psi_i^{\sigma}\middle|\psi_j^{\sigma}\right\rangle - \delta_{ij}\right)\right]\right\}$$

$$+\sum_{\sigma=1}^{P}\left\{\sum_{I}\frac{M_I'^{\sigma}}{2}\left(\dot{\mathbf{R}}_I^{\sigma}\right)^2 - \sum_{I}\frac{M_I^{\sigma}}{2}\omega_P^2\left(\mathbf{R}_I^{\sigma}\right)^2\right\}$$

D. Marx and M. Parrinello,
Zeit. Phys. B **95**, 143 (1994)

- *M* and *M’* are different in order to keep on the same time scale all the modes involved in the QM treatment of the nuclei
- A Nosé-Hoover thermostat is added to ensure a canonical sampling and to control the adiabaticity

The Euler-Lagrange equations of motion:

$$\frac{1}{P}\mu\ddot{\psi}_i^\sigma(\mathbf{x}) = -\frac{1}{P}\frac{\delta E^{DFT}}{\delta\psi_i^{\sigma*}} + \frac{1}{P}\sum_j \Lambda_{ij}^\sigma \psi_j^\sigma(\mathbf{x}) - \frac{\mu}{P}\dot{\xi}_1^\sigma\dot{\psi}_i^\sigma(\mathbf{x})$$

$$Q_e^{(1)}\ddot{\xi}_1^\sigma = 2\left(\sum_i \mu\left|\dot{\psi}_i^\sigma(\mathbf{x})\right|^2 - E_e^{kin}\right) - Q_e^{(1)}\dot{\xi}_1^\sigma\dot{\xi}_2^\sigma$$

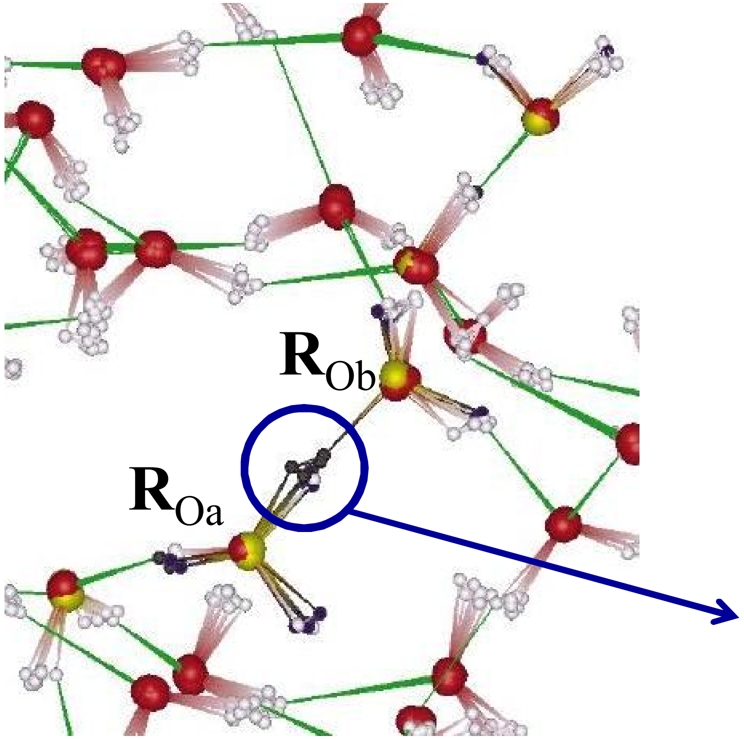
$$Q_e^{(\lambda)}\ddot{\xi}_\lambda^\sigma = [Q_e^{(\lambda-1)}\left(\dot{\xi}_{\lambda-1}^\sigma\right)^2 - \beta_e^{-1}] - Q_e^{(\lambda)}\dot{\xi}_\lambda^\sigma\dot{\xi}_{\lambda+1}^\sigma\left(1-\delta_{\lambda M}\right)$$

with $\lambda = 2,\ldots,M$ and for the QM nuclei we have

$$M_I'^\sigma\ddot{\mathbf{R}}_I^\sigma = -\frac{1}{P}\nabla_{\mathbf{R}_I^\sigma}E^{DFT} - \omega_P^2 M_I^\sigma\left(2\mathbf{R}_I^\sigma - \mathbf{R}_I^{\sigma+1} - \mathbf{R}_I^{\sigma+1}\right) - M_I'^\sigma\dot{s}_1^\sigma\dot{\mathbf{R}}_I^\sigma$$

and related thermostats

Example of application of PI-CPMD: proton propagation in water

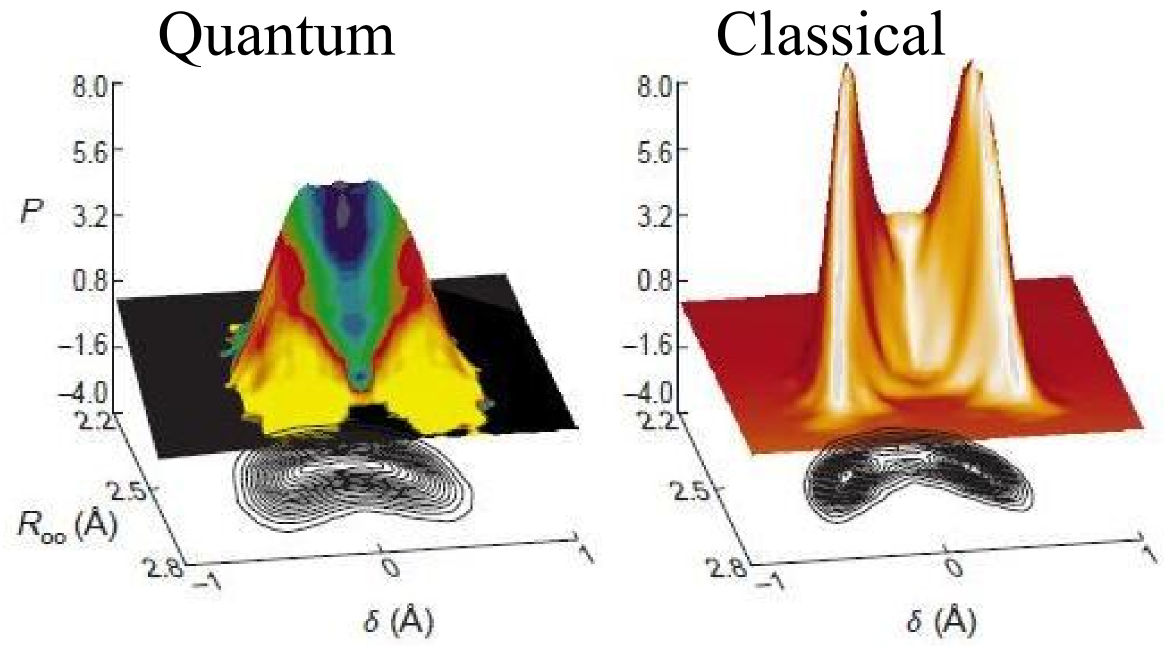


The proton is no longer a point-like object $\mathbf{R_H}(t)$ but a (quantum) probability distribution $\Phi(\mathbf{R_H})$.

Eigen/Zundel transition between oxygen Oa and Ob

M. Tuckerman et. al. *Science* **275,** 817 (1997)
D. Marx et al. *Nature* **397**, 601 (1999)

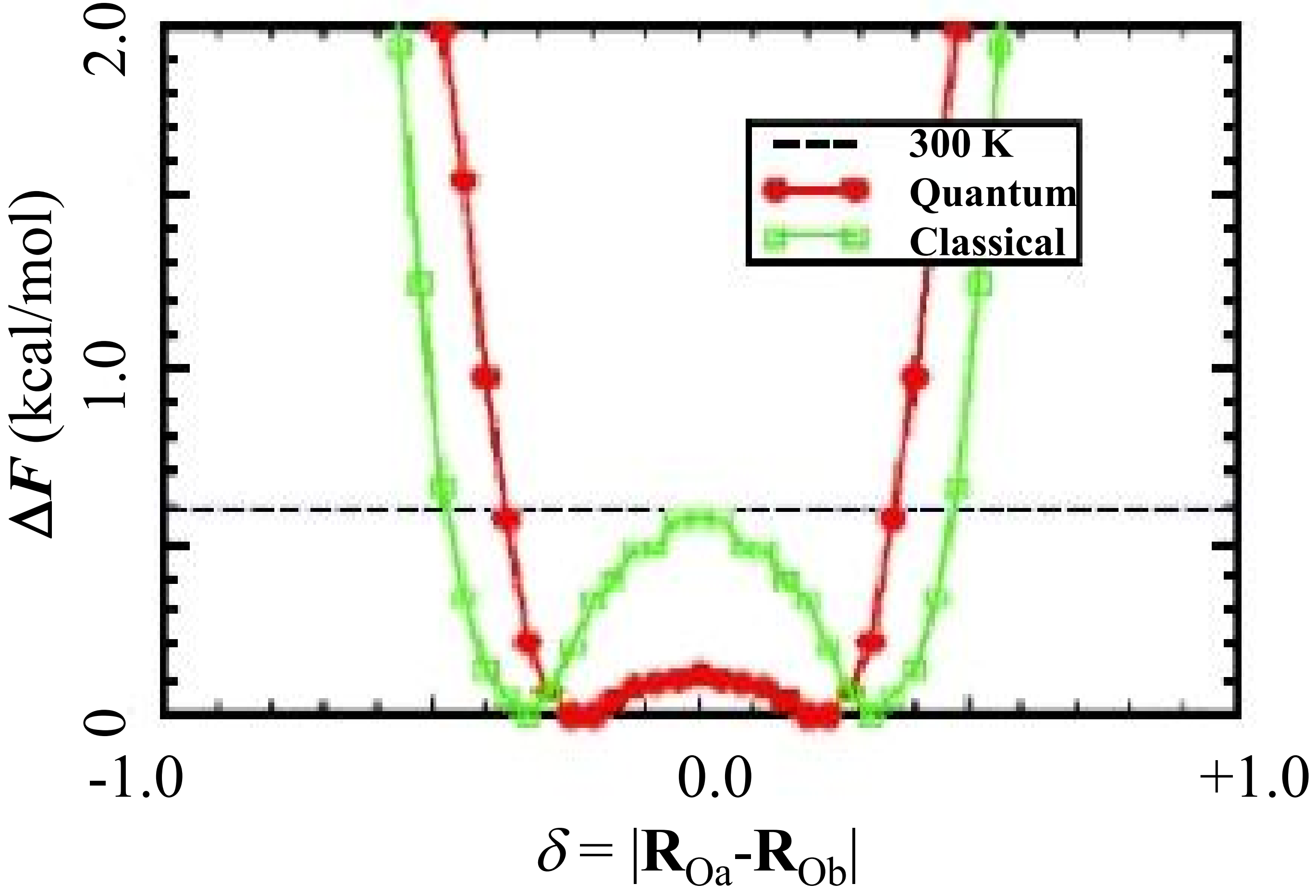
Example of application of PI-CPMD: Proton propagation in water


Quantum Classical

Probability distributions of proton position in terms of H^+ displacement $\delta = |\mathbf{R}_{Oa}-\mathbf{R}_{Ob}|$ relative to the Oa-H-Ob midpoint.

Proton propagation in water

Free energy profile as a function of δ: no single dominant structure



About Excited States

- Photoactive molecules are also the target of potential technological applications in molecular optoelectronics, photocatalysis and photo-biochemistry
- They involve electron excitations
- Time-dependent DFT (TDDFT) has been proposed as a way to include electron excitation (see M. E. Casida, *Recent Advances in Density Functional Methods*, Vol. 1, ed. by Chong, D.P., World Scientific, Singapore, 1995)
- Although TDDFT is computationally expensive…

About Excited States

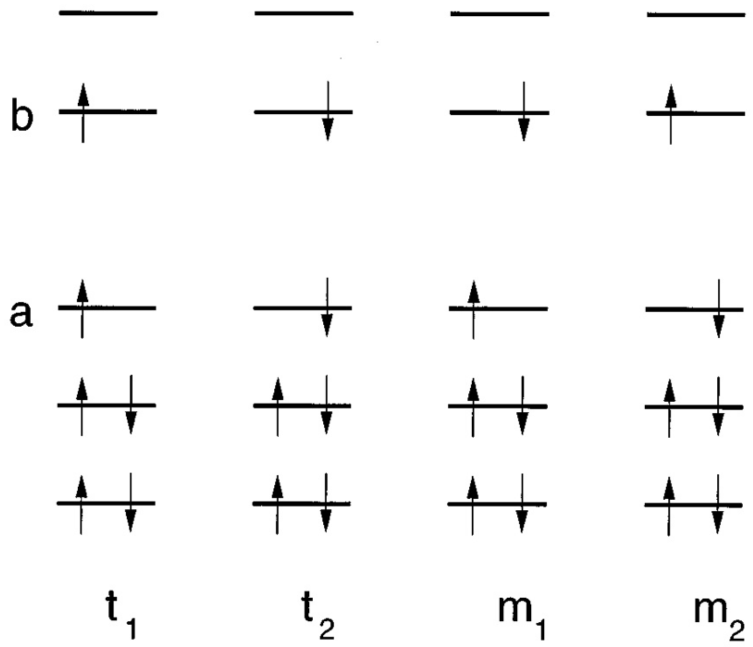
- Generally organic photoreactions involve mainly the first excited singlet state (S_1) and the lowest triplet state (T_1). Other excited states have a too short lifetime to be of real practical interest and can generally be neglected
- see N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Mill Valley1991

  A. Zewail* *Femtochemistry: Ultrafast Dynamics of the Chemical Bond*, World Scientific Series in 20th Century Chemistry, Vol. 3, World Scientific, Singapore 1994

* 1999 Chemistry Nobel Prize

The "minimal" excited states

- If a single valence electron is excited from the highest occupied (ground state) orbital **a** to the lowest unoccupied orbital **b**, four different determinants can be obtained according to the Pauli's principle



ROKS: Excited states@KS

- Instead of separate wavefunctions for the t and m states, it has been shown that it is possible to determine a single set of spin-restricted single-particle orbitals $\psi_i(\mathbf{x})$ for the states $i = 1,\ldots, N+1$ in such a way that

$$\rho(\mathbf{x}) = \rho_\alpha^m(\mathbf{x}) + \rho_\beta^m(\mathbf{x}) = \rho_\alpha^t(\mathbf{x}) + \rho_\beta^t(\mathbf{x})$$

- A new DFT functional, the restricted open shell Kohn-Sham (ROKS) functional, can be written as

$$H^{\mathrm{ROKS}}\left[\{\psi_i(\mathbf{x})\}\right] = 2E_m^{\mathrm{KS}}[\rho] - E_t^{\mathrm{KS}}[\rho] - \sum_{i,j=1}^{N+1} \varepsilon_{ij}\left(\int d^3x\,\psi_i^*(\mathbf{x})\psi_j(\mathbf{x}) - \delta_{ij}\right)$$

I. Frank, J. Hutter, D. Marx, M. Parrinello, *J. Chem. Phys*. **108**, 4060 (1998)

Total energy functionals for excited states

- The functionals with the superscript KS are Kohn-Sham total energy functionals with the difference reduced only to the exchange-correlation term

$$E_m^{\mathrm{KS}}\left[\{\psi_i\}\right] = E_k\left[\{\psi_i\}\right] + E_H\left[\rho\right] + E_{xc}[\rho_\alpha^m, \rho_\beta^m] + E_{eI}\left[\rho\right] + E_{II}$$

$$E_t^{\mathrm{KS}}\left[\{\psi_i\}\right] = E_k\left[\{\psi_i\}\right] + E_H\left[\rho\right] + E_{xc}[\rho_\alpha^t, \rho_\beta^t] + E_{eI}\left[\rho\right] + E_{II}$$

…and associated equations to solve (I)

- The minimization of the functional $H^{\mathrm{ROKS}}[\psi_i(\mathbf{x})]$ with respect to the orbitals leads to two sets of Schrödinger-like equations, one for the doubly occupied orbitals…

$$\left\{-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{y})}{|\mathbf{x}\text{ - }\mathbf{y}|} d^3y + V_{eI}(\mathbf{x}) + v_{xc}^{\alpha}\left[\rho_\alpha^m, \rho_\beta^m\right] + v_{xc}^{\beta}\left[\rho_\alpha^m, \rho_\beta^m\right]\right.$$

$$\left. -\frac{1}{2} v_{xc}^{\alpha}\left[\rho_\alpha^t, \rho_\beta^t\right] - \frac{1}{2} v_{xc}^{\beta}\left[\rho_\alpha^t, \rho_\beta^t\right]\right\}\psi_i(\mathbf{x}) = \sum_{j=1}^{N+1} \varepsilon_{ij}\psi_j(\mathbf{x})$$

$$v_{xc}^{\alpha} = \frac{\delta E_{xc}[\rho_\alpha^{m,t}, \rho_\beta^{m,t}]}{\delta \rho_\alpha^{m,t}} \quad , \quad v_{xc}^{\beta} = \frac{\delta E_{xc}[\rho_\alpha^{m,t}, \rho_\beta^{m,t}]}{\delta \rho_\beta^{m,t}}$$

…and associated equations to solve (II)

- …and one for the singly occupied **a** and **b** states

$$\left\{\frac{1}{2}\left[-\frac{1}{2}\nabla^2+\int\frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d^3y+V_{eI}(\mathbf{x})\right]+v_{xc}^{\alpha}\left[\rho_{\alpha}^{m},\rho_{\beta}^{m}\right]-\frac{1}{2}v_{xc}^{\alpha}\left[\rho_{\alpha}^{t},\rho_{\beta}^{t}\right]\right\}\psi_a(\mathbf{x})$$

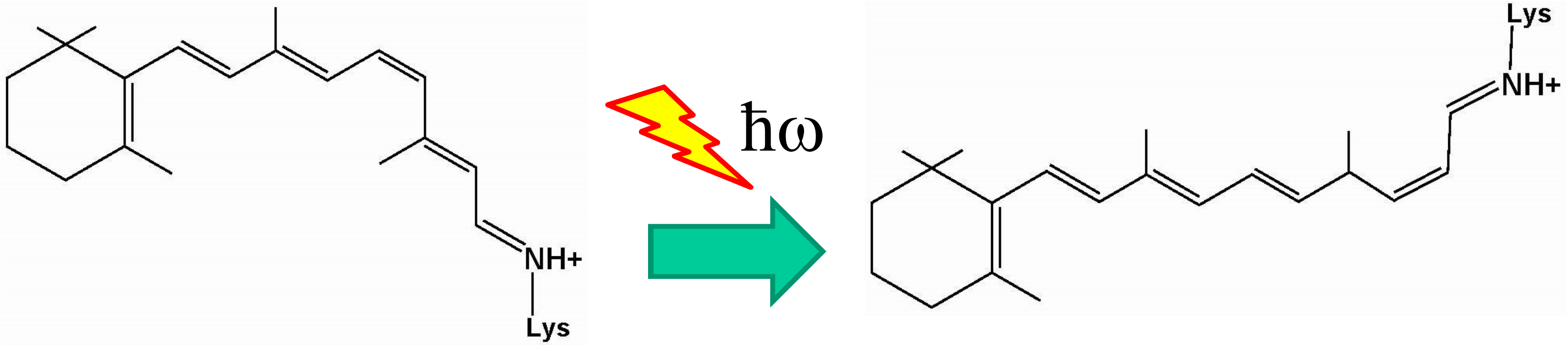
$$=\sum_{j=1}^{N+1}\varepsilon_{aj}\psi_j(\mathbf{x})$$

$$\left\{\frac{1}{2}\left[-\frac{1}{2}\nabla^2+\int\frac{\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d^3y+V_{eI}(\mathbf{x})\right]+v_{xc}^{\alpha}\left[\rho_{\alpha}^{m},\rho_{\beta}^{m}\right]-\frac{1}{2}v_{xc}^{\alpha}\left[\rho_{\alpha}^{t},\rho_{\beta}^{t}\right]\right\}\psi_a(\mathbf{x})$$

$$=\sum_{j=1}^{N+1}\varepsilon_{aj}\psi_j(\mathbf{x})$$

Where can it be used ?

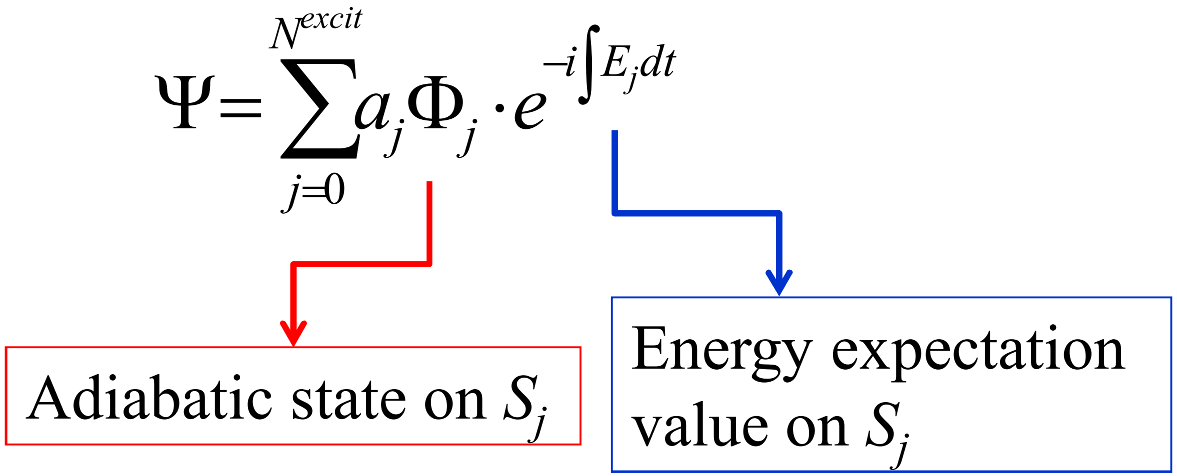
- This approach has been used to study the isomerization and energy changes of the rhodopsin chromophore.
- This is the photosensitive protein in the rod cells of the retina of vertebrates and the process of vision.
- It, involves the photoisomerization



as a response to the absorption of photons (in about 200 fs) and triggers a cascade of slower reactions that produce a specific biological signal (C. Molteni *et al*. JACS **121**, 12177 (1999)).

Doing CPMD-like dynamics with more than one PES

- If the ground state $\boldsymbol{S_0}$ and the ROKS excited $\boldsymbol{S_1}$ surface are two accessible states (e.g. photochemistry) it is possible to adopt a Tully scheme (J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990); *ibid.* **55**, 562 (1971))
- The electronic wavefunction for the whole system reads

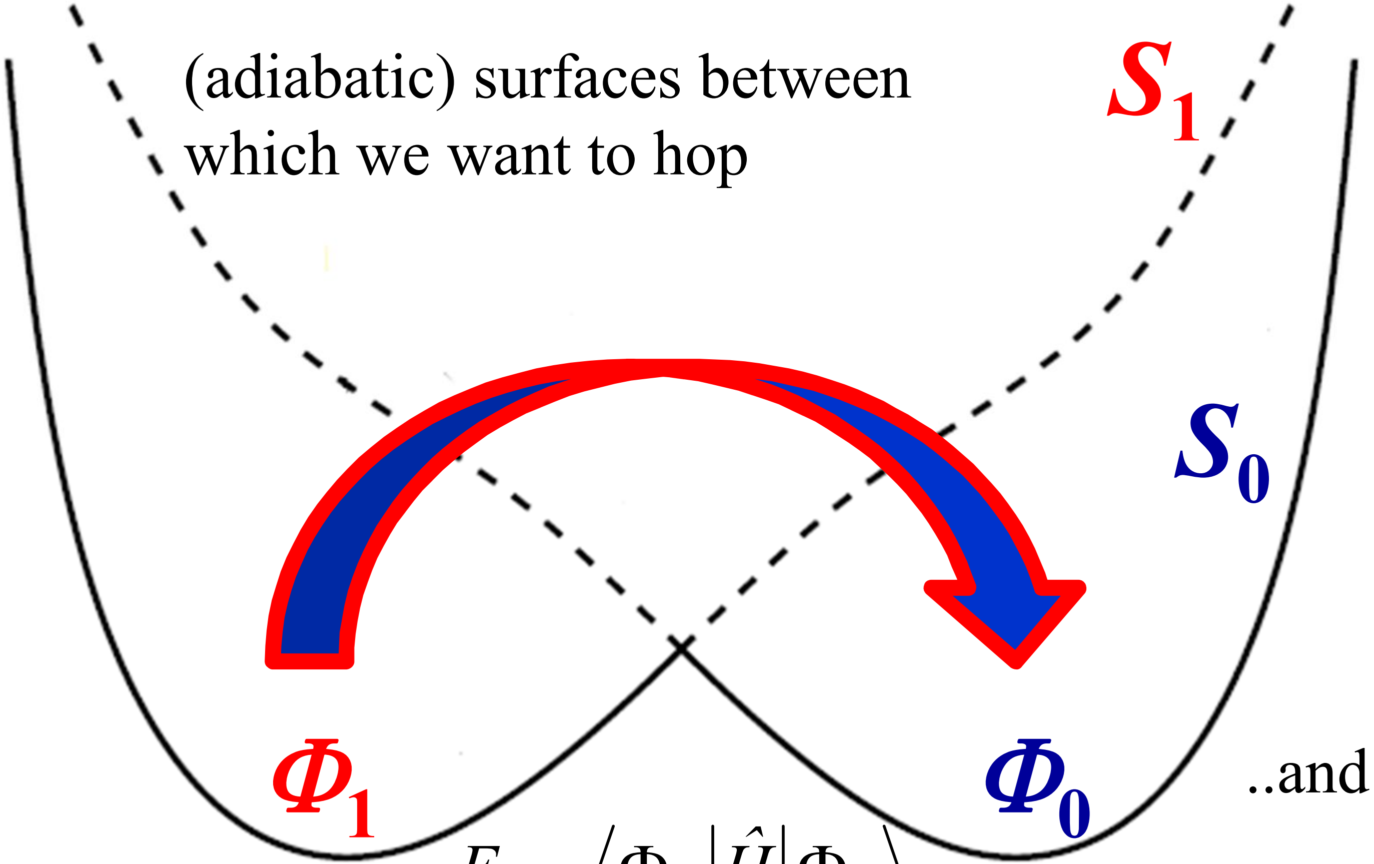


$$\Psi=\sum_{j=0}^{N^{excit}} a_j\Phi_j\cdot e^{-i\int E_j dt}$$

Adiabatic state on S_j

Energy expectation value on S_j

Doing CPMD-like dynamics with more than one PES



(adiabatic) surfaces between
which we want to hop

..and a_j?

$$E_j = \langle \Phi_j | \hat{H} | \Phi_j \rangle$$

Doing CPMD-like dynamics with more than one PES

- a_j are determined by the solution of the time-dependent Schrödinger equation

$$\hat{H}\Psi = i\frac{\partial}{\partial t}\Psi$$

- For the closed shell KS ground state $\boldsymbol{S_0}$

$$\Phi_0 = \left|\varphi_1^0 \varphi_1^{*0} \ldots \varphi_n^0 \varphi_n^{*0}\right\rangle$$

- And for the excited ROKS $\boldsymbol{S_1}$

$$\Phi_1 = \frac{1}{\sqrt{2}}\left[\left|\varphi_1^1 \varphi_1^{*1} \ldots \varphi_n^1 \varphi_{n+1}^{*1}\right\rangle + \left|\varphi_1^1 \varphi_1^{*1} \ldots \varphi_n^{*1} \varphi_{n+1}^1\right\rangle\right]$$

- n = half the (even) number of electrons

Doing CPMD-like dynamics with more than one PES

- These Φ_0 and Φ_1 are normalized on **S_0** and **S_1**, respectively but they are not orthogonal to each other
- It is possible to define the quantities

$$S_{ij} = \left\langle \Phi_i \middle| \Phi_j \right\rangle \neq \delta_{ij} \qquad S_{01} = S_{10} = S \qquad S_{ii} = 1$$

$$D_{ij} = \left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \Phi_j \right\rangle = \left\langle \Phi_i \middle| \dot{\Phi}_j \right\rangle \quad D_{ij} = -D_{ji} \qquad D_{ii} = 0$$

Non-adiabatic coupling matrix → easy to do: wfs velocities are directly available in CPMD

Doing CPMD-like dynamics with more than one PES

- Solving $\Psi^* \hat{H} \Psi = i \Psi^* \frac{\partial}{\partial t} \Psi$ for $\Psi = \sum_{j=0}^{1} a_j \Phi_j \exp\left(-i \int E_j dt\right)$ gives

$$\left\{ \begin{aligned} \dot{a}_0 &= \frac{1}{S^2 - 1}\left[i a_1 \frac{p_1}{p_0} S\left(E_0 - E_1\right) + a_1 D_{01} \frac{p_1}{p_0} - a_0 D_{10} S \right] \\ \dot{a}_1 &= \frac{1}{S^2 - 1}\left[a_0 D_{10} \frac{p_0}{p_1} - a_1 D_{01} S - i a_1 S^2 \left(E_0 - E_1\right) \right] \end{aligned} \right.$$

Doltsinis & Marx, *Phys. Rev. Lett.* **88**, 166402 (2002)

Doing CPMD-like dynamics with more than one PES

- Note that $p_j = e^{-i\int E_j dt}$

$$E_j = \langle \Phi_j | \hat{H} | \Phi_j \rangle = H_{jj} \qquad H_{01} = H_{10} = E_0 S$$

- If the wavefunctions were eigenfunctions of the KS Hamiltonian, then $|a_0|^2$ and $|a_1|^2$ would be occupation numbers
- …but they are not. So what ?

Doltsinis & Marx, *Phys. Rev. Lett*. **88**, 166402 (2002)

Doing CPMD-like dynamics with more than one PES

- Expand on an orthonormal auxiliary set of wfs Φ'_j

$$\Psi = d_0 \Phi'_0 + d_1 \Phi'_1 \equiv b_0 \Phi_0 + b_1 \Phi_1 \qquad b_j = a_j p_j$$

⇓

$$d_0^2 + d_1^2 = 1$$

true state population

$$\Phi'_j = c_{0j} \Phi_0 + c_{1j} \Phi_1$$

$$\mathbf{c}_0 = \begin{pmatrix} c_{00} \\ c_{10} \end{pmatrix} \quad \mathbf{c}_1 = \begin{pmatrix} c_{01} \\ c_{11} \end{pmatrix}$$

Eigenvectors of
$H\,\mathbf{c}_i = E_i\,\mathbf{S}\,\mathbf{c}_i$

Doing CPMD-like dynamics with more than one PES

- Hence, we get

$$E_0' = E_0 \qquad E_1' = \frac{E_1 - S^2 E_0}{1 - S^2} \quad \boxed{> E_1 \ \text{if} \ E_0 < E_1}$$

$$\mathbf{c}_0 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \mathbf{c}_1 = \begin{pmatrix} -S \\ 1 \end{pmatrix}$$

- and the orthonormal auxiliary wavefunctions and occupations

$$\Phi_0' = \Phi_0 \qquad \Phi_1' = \frac{-S\,\Phi_0 + \Phi_1}{\sqrt{1 - S^2}}$$

$$|d_0|^2 = |b_0|^2 + S^2 |b_1|^2 + 2S\,Re\left(b_0^* b_1\right) \qquad |d_1|^2 = \left(1 - S^2\right)|b_1|^2$$

Doing CPMD-like dynamics with more than one PES

- Transitions from one surface to the other is done according to the fewest switches criterion of Tully:

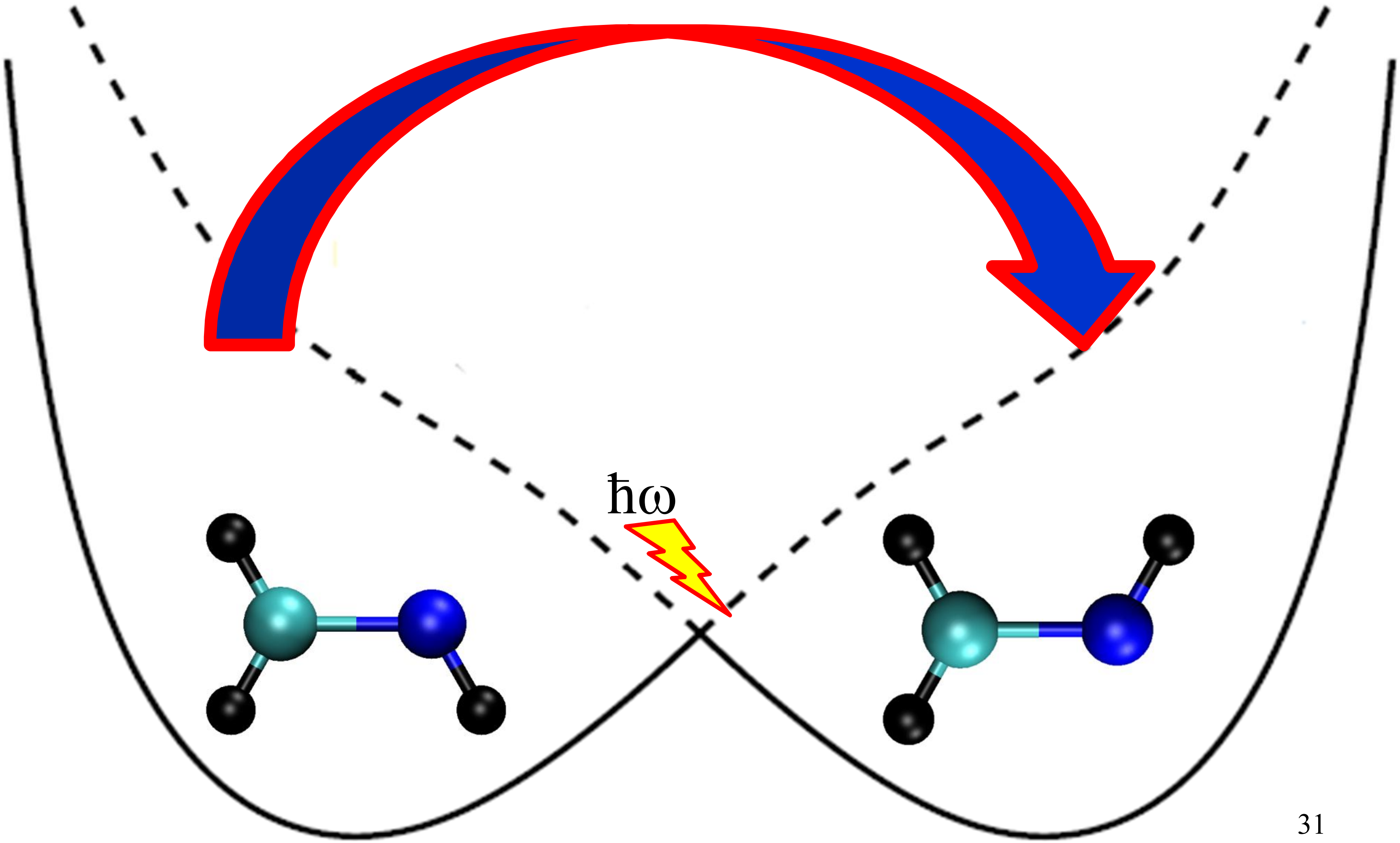
$$p_i = -\Delta t \frac{d|d_i|^2 / dt}{|d_i|^2}$$

Δt = CPMD time step

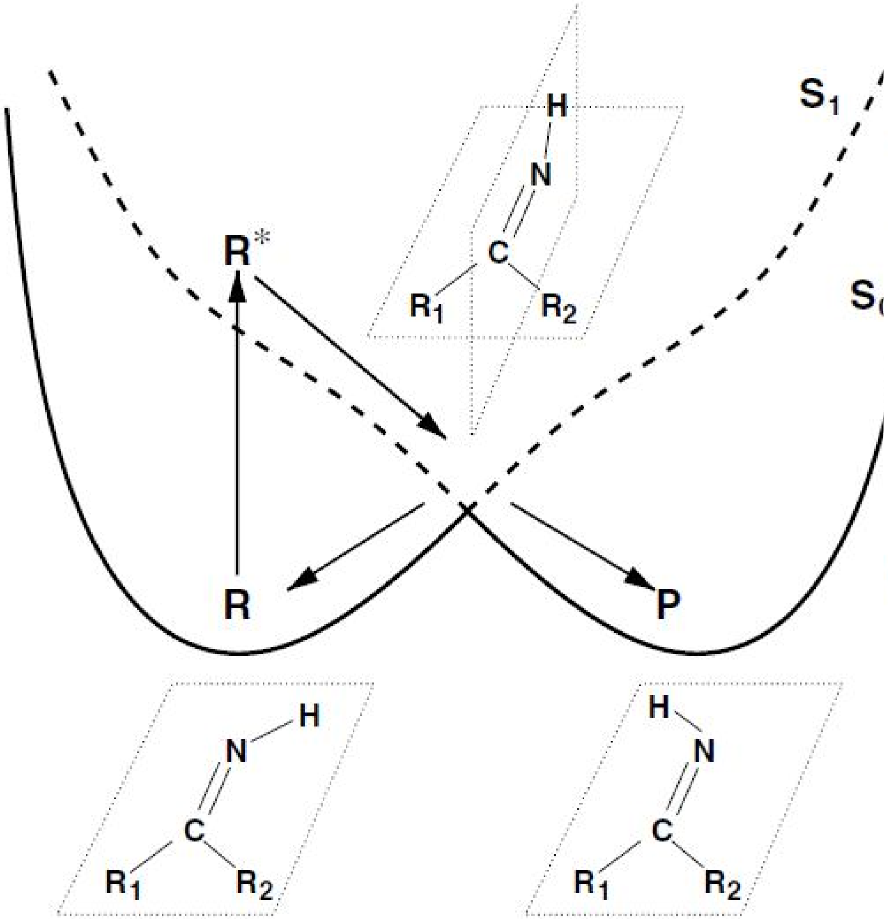
select a random number *rnd*[]=ζ. If $\zeta > p_i$ then

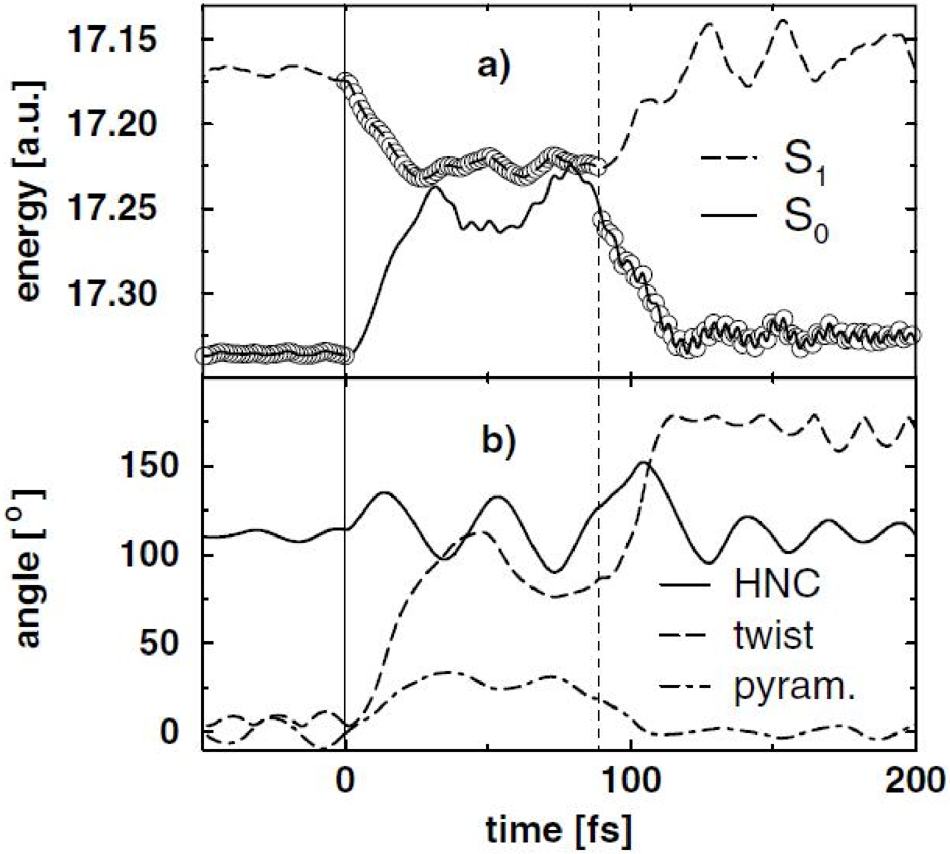
- jump from ***i*** to ***j*** if E_j-E_i < T_i = kinetic energy in the ***i*** state
- and do not hop if T_i is insufficient to compensate for the jump $E_j - E_i$ → ***Tully's forbidden transitions***
- Warning: The accessible time scale is of the order of fs (as in TD-DFT, Ehrenfest MD, etc.)

Example of application: Photo-isomerization of formaldimine



Example of application: Photo-isomerization of formaldimine





Doltsinis & Marx, *Phys. Rev. Lett*. **88**, 166402 (2002)

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