

*Traitement quantique des noyaux*  
*Quantum treatment of the nuclei*

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# Classical Molecular Dynamics (“MD”)

Hamilton’s equations of motion for instance:

for atoms  $\alpha$ ,  $\alpha = 1, 2, \dots, N$

$$\begin{aligned}\dot{\mathbf{R}}_{\alpha} &\equiv \frac{d\mathbf{R}_{\alpha}}{dt} = \frac{\mathbf{P}_{\alpha}}{M_{\alpha}} \\ \dot{\mathbf{P}}_{\alpha} &\equiv \frac{d\mathbf{P}_{\alpha}}{dt} = -\nabla_{\mathbf{R}_{\alpha}} V(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{\alpha}, \dots, \mathbf{R}_N)\end{aligned}$$

solved by time-propagation, starting from the initial conditions

$$\begin{aligned}\mathbf{R}_{\alpha}(t = 0) &= \mathbf{R}_{\alpha}^{\circ} \\ \mathbf{P}_{\alpha}(t = 0) &= \mathbf{P}_{\alpha}^{\circ}\end{aligned}$$

State of the system at time  $t$ :  $\{\mathbf{R}_{\alpha}, \mathbf{P}_{\alpha}\} \rightarrow 6N$  variables:

- no real size problem: 150 000 atoms  $\longleftrightarrow$  8 MB
- constant  $T$ ,  $P$  simulations straightforward
- “on the fly” calculation of the potential

→ why not use ONLY classical mechanics?

# *Limitations of classical molecular dynamics*

Classical MD is based on two major assumptions:

- Born-Oppenheimer separation of nuclear and electronic motion
- classical description of nuclear motion

Hence it has some limitations:

- it cannot describe processes involving several coupled electronic states: electron transfer, non-radiative relaxation, photochemistry, collisional electronic relaxation, ...
- it cannot account for typical quantum effects (low T, H atoms): zero-point energy, zero-point delocalization, energy level quantification, tunneling

→ [Quantum molecular dynamics](#)

and methods combining the advantages of quantum and classical MD.

# *Syllabus*

Part I: Quantum Hamiltonian for the nuclei

Part II: Quantum dynamics with wave packets

Part II: Mixed quantum-classical dynamics

# *Part I*

## *Quantum Hamiltonian for the nuclei*

# Molecular Hamiltonian

Molecular system:  $N_n$  nuclei ( $Z_\alpha, M_\alpha, \mathbf{Q}_\alpha$ ),  $N_e$  electrons  $m_e, \mathbf{q}_j$

$$H = T_n + T_e + V$$

$$T_n = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N_n} \frac{1}{M_\alpha} \nabla_{\mathbf{Q}_\alpha}^2 \quad \text{nuclei kinetic energy}$$

$$T_e = -\frac{\hbar^2}{2m_e} \sum_{j=1}^{N_e} \nabla_{\mathbf{q}_j}^2 \quad \text{electron kinetic energy}$$

$$V = \sum_{\alpha=1}^{N_n} \sum_{\alpha' > \alpha}^{N_n} \frac{e^2 Z_\alpha Z_{\alpha'}}{|\mathbf{Q}_\alpha - \mathbf{Q}_{\alpha'}|} - \sum_{\alpha=1}^{N_n} \sum_{j=1}^{N_e} \frac{e^2 Z_\alpha}{|\mathbf{Q}_\alpha - \mathbf{q}_j|} + \sum_{j=1}^{N_e} \sum_{j' > j}^{N_e} \frac{e^2}{|\mathbf{q}_j - \mathbf{q}_{j'}|}$$

*electrostatic interaction*

$\{\mathbf{q}_j\}, \{\mathbf{Q}_\alpha\}$  Cartesian coordinates in space-fixed axes.

$$e^2 \equiv q_e^2 / 4\pi\epsilon_0$$

$H_{SO}$  can be added later

# Separation of the center of mass motion

Define the center of mass position  $\mathbf{R}_{\text{CM}} = \sum_{\alpha=1}^N \frac{M_{\alpha}}{M} \mathbf{Q}_{\alpha}$

and  $N_n + N_e - 1$  other **internal** coordinates, usually:

$$\mathbf{R}_{\beta} = \sum_{\alpha=1}^{N_n} a_{\beta\alpha} \mathbf{Q}_{\alpha}, \quad \beta = 1, \dots, N_n - 1$$

$$\mathbf{r}_j = \mathbf{q}_j + \sum_{\alpha=1}^{N_n} a_{j\alpha} \mathbf{Q}_{\alpha}, \quad j = 1, \dots, N_e$$

Total linear momentum  $\mathbf{P} = \frac{\hbar}{i} \sum_{\alpha=1}^N \nabla_{\mathbf{Q}_{\alpha}}$  with  $\nabla_{\mathbf{Q}_{\alpha}} = \frac{M_{\alpha}}{M} \nabla_{\mathbf{R}_{\text{CM}}} + \sum_{\beta=1}^{N-1} a_{\beta\alpha} \nabla_{\mathbf{R}_{\beta}}$

$$\mathbf{P} = \frac{\hbar}{i} \left[ \nabla_{\mathbf{R}_{\text{CM}}} + \sum_{\beta=1}^{N-1} \left( \sum_{\alpha=1}^N a_{\beta\alpha} \right) \nabla_{\mathbf{R}_{\beta}} \right]$$

**depends on the definition of the other coordinates!**  $\neq$  classical dynamics

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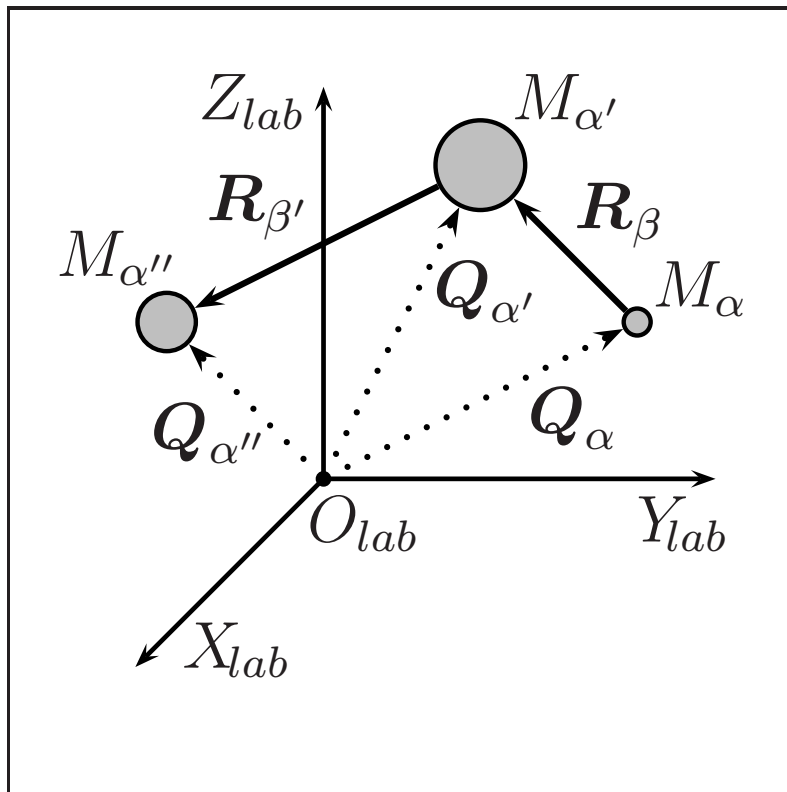
$$\mathbf{P} = \frac{\hbar}{i} \left[ \nabla_{\mathbf{R}_{\text{CM}}} + \sum_{\beta=1}^{N-1} \left( \sum_{\alpha=1}^N a_{\beta\alpha} \right) \nabla_{\mathbf{R}_{\beta}} \right]$$

**depends on the definition of the other coordinates!**  $\neq$  classical dynamics Unless...



# Internal coordinates

Unless  $\sum_{\alpha=1}^N a_{\beta\alpha} = 0 \quad \forall \beta = 1, \dots, N-1 \rightarrow \mathbf{R}_\beta$  internal coordinates



Laboratory frame and a possible choice of internal coordinates

Demonstration:

$$a_{\beta N} = - \sum_{\alpha=1}^{N-1} a_{\beta\alpha}$$

$$\begin{aligned} \mathbf{R}_\beta &= \sum_{\alpha=1}^N a_{\beta\alpha} \mathbf{Q}_\alpha = \sum_{\alpha=1}^{N-1} a_{\beta\alpha} \mathbf{Q}_\alpha + a_{\beta N} \mathbf{Q}_N \\ &= \sum_{\alpha=1}^{N-1} a_{\beta\alpha} \mathbf{Q}_\alpha - \sum_{\alpha=1}^{N-1} a_{\beta\alpha} \mathbf{Q}_N \\ &= \sum_{\alpha=1}^{N-1} a_{\beta\alpha} (\mathbf{Q}_\alpha - \mathbf{Q}_N) \end{aligned}$$

# Nuclei kinetic energy and the G matrix

Nuclei kinetic energy in the initial (cartesian) coordinates

$$T_n = -\frac{\hbar^2}{2} \sum_{\alpha=1}^N \frac{1}{M_\alpha} \nabla_{Q_\alpha}^2$$

Using  $\nabla_{Q_\alpha} = \frac{M_\alpha}{M} \nabla_{R_{CM}} + \sum_{\beta=1}^{N-1} a_{\beta\alpha} \nabla_{R_\beta}$

it can be written in the new coordinates  $\{\mathbf{R}_{CM}, \mathbf{R}_\beta, \beta = 1, N-1\}$

$$\begin{aligned} T_n &= -\frac{\hbar^2}{2M} \nabla_{R_{CM}}^2 - \frac{\hbar^2}{2} \sum_{\beta=1}^{N-1} \sum_{\beta'=1}^{N-1} g_{\beta,\beta'} \nabla_{R_\beta} \cdot \nabla_{R_{\beta'}} - \frac{\hbar^2}{2M} \sum_{\beta=1}^{N-1} \left( \sum_{\alpha=1}^N a_{\beta\alpha} \right) \nabla_{R_{CM}} \cdot \nabla_{R_\beta} \\ &= -\frac{\hbar^2}{2M} \nabla_{R_{CM}}^2 + T' \quad \text{with} \quad T'_n = -\frac{\hbar^2}{2} \sum_{\beta=1}^{N-1} \sum_{\beta'=1}^{N-1} g_{\beta,\beta'} \nabla_{R_\beta} \cdot \nabla_{R_{\beta'}} \end{aligned}$$

where  $T'_n$  only depends on  $\mathbf{R}_\beta$  and  $g_{\beta,\beta'} = \sum_{\alpha=1}^N \frac{a_{\beta\alpha} a_{\beta'\alpha}}{M_\alpha}$  define a symmetric matrix

## Example of the diatomic, triatomic molecule

Diatomic molecule:  $\mathbf{R} = \mathbf{R}_1 = \mathbf{Q}_2 - \mathbf{Q}_1$  i.e.  $a_{11} = -1$ ,  $a_{12} = 1$

This gives

$$g_{11} = \sum_{\alpha=1}^2 \frac{a_{1\alpha} a_{1\alpha}}{M_{\alpha}} = \frac{1}{M_1} + \frac{1}{M_2} = \frac{1}{\mu}$$

and the internal kinetic energy

$$T'_n = -\frac{\hbar^2}{2\mu} \nabla_R^2 \quad \text{with} \quad \mu = \frac{M_1 M_2}{M_1 + M_2} \quad \text{“reduced mass”}$$

Triatomic molecule in valence coordinates:  $\mathbf{R}_1 = \mathbf{Q}_2 - \mathbf{Q}_1$ ,  $\mathbf{R}_2 = \mathbf{Q}_2 - \mathbf{Q}_3$

$$T'_n = -\frac{\hbar^2}{2\mu_1} \nabla_{R_1}^2 - \frac{\hbar^2}{2\mu_2} \nabla_{R_2}^2 + \frac{\hbar^2}{M_2} \nabla_{R_1} \cdot \nabla_{R_2} \quad \text{with} \quad \mu_1 = \frac{M_1 M_2}{M_1 + M_2} \quad \text{and} \quad \mu_2 = \frac{M_3 M_2}{M_3 + M_2}$$

## Center of mass frame

Choosing the center of mass of the nuclei as origin for the electrons gives

$$T' = -\frac{\hbar^2}{2} \left[ \sum_{\beta=1}^{N_n-1} \sum_{\beta'=1}^{N_n-1} g_{\beta\beta'} \nabla_{R_\beta} \cdot \nabla_{R_{\beta'}} + \left( \frac{1}{m_e} + \frac{1}{M_n} \right) \sum_{j=1}^{N_e} \nabla_{r_j}^2 + \frac{1}{M_n} \sum_{j=1}^{N_e} \sum_{j' \neq j}^{N_e} \nabla_{r_j} \cdot \nabla_{r_{j'}} \right]$$

Neglecting the terms in  $1/M_n$  gives

$$T' = -\frac{\hbar^2}{2} \left[ \sum_{\beta=1}^{N_n-1} \sum_{\beta'=1}^{N_n-1} g_{\beta\beta'} \nabla_{R_\beta} \cdot \nabla_{R_{\beta'}} + \frac{1}{m_e} \sum_{j=1}^{N_e} \nabla_{r_j}^2 \right]$$

# Diatomic molecule Hamiltonian (SF axes)

$$H = -\frac{\hbar^2}{2\mu} \nabla_R^2 - \frac{\hbar^2}{2m_e} \sum_{j=1}^{N_e} \nabla_{r_j}^2 + \frac{e^2 Z_1 Z_2}{R} - \sum_{\alpha=1}^2 \sum_{j=1}^{N_e} \frac{e^2 Z_\alpha}{|\mathbf{r}_j - \gamma_\alpha \mathbf{R}|} + \sum_{j' > j} \frac{e^2}{|\mathbf{r}_{j'} - \mathbf{r}_j|}$$

with  $\mu = M_1 M_2 / (M_1 + M_2)$ ,  $\gamma_1 = -M_2 / (M_1 + M_2)$  and  $\gamma_2 = M_1 / (M_1 + M_2)$

Introducing the kinetic angular momentum of the nuclei

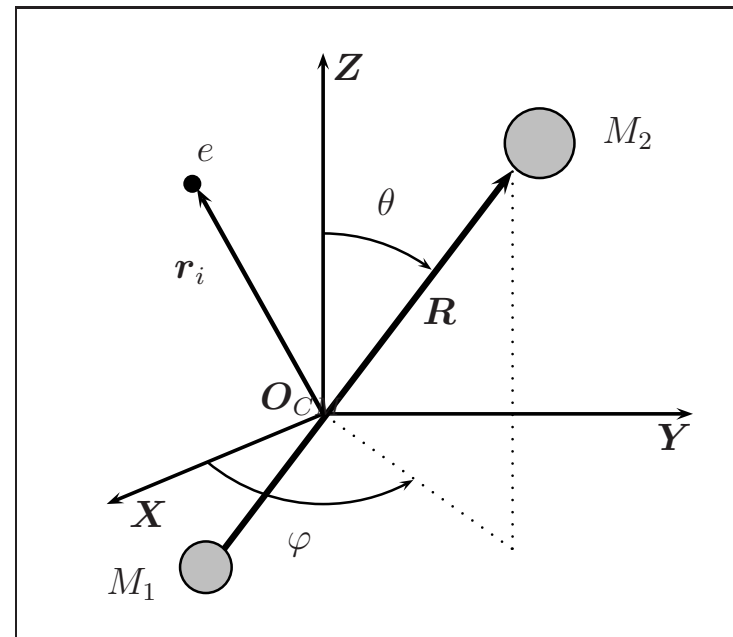
$$\mathbf{O} = \mathbf{R} \times \frac{\hbar}{i} \nabla_R$$

the kinetic energy of the nuclei is

$$T_n = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\mathbf{O}^2}{2\mu R^2}$$

with

$$\mathbf{O}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right)$$

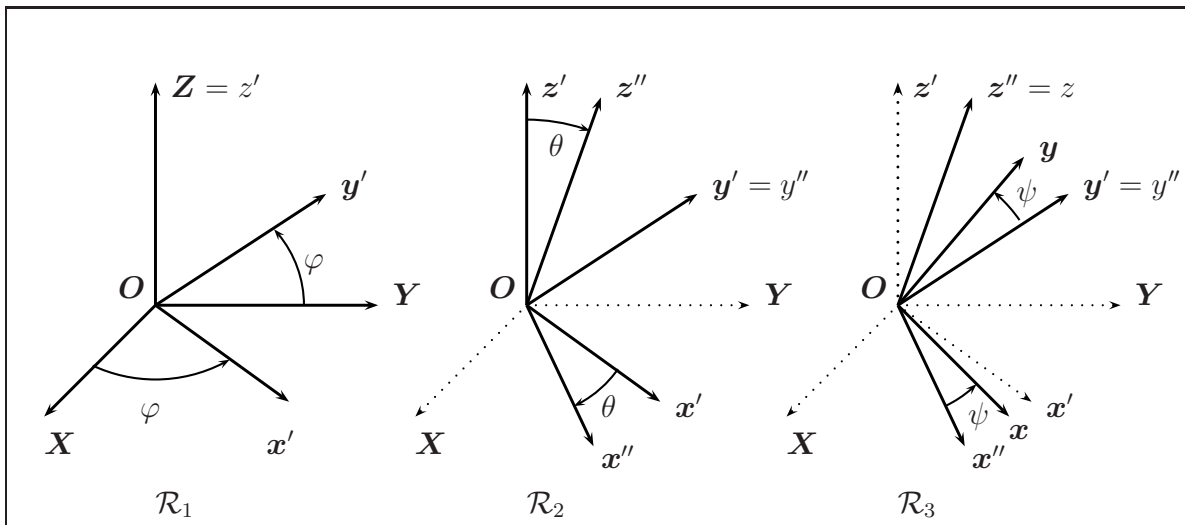


# Molecular (rotating) frame (BF axes)

$R$  plays a special role  $\rightarrow$  attach new axes to  $R$ , such that  $z // R$

Space-fixed (SF) axes  $(O, X, Y, Z)$  to body-fixed (BF) axes  $(O, x, y, z) : \mathcal{R}(\varphi, \theta, \psi)$

$$\mathcal{R} = \begin{pmatrix} \cos \theta \cos \varphi \cos \psi - \sin \varphi \sin \psi & -\cos \theta \cos \varphi \sin \psi - \sin \varphi \cos \psi & \sin \theta \cos \varphi \\ \cos \theta \sin \varphi \cos \psi + \cos \varphi \sin \psi & -\cos \theta \sin \varphi \sin \psi + \cos \varphi \cos \psi & \sin \theta \sin \varphi \\ -\sin \theta \cos \psi & \sin \theta \sin \psi & \cos \theta \end{pmatrix}$$



$$\begin{pmatrix} A_X \\ A_Y \\ A_Z \end{pmatrix} = \mathcal{R} \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix}$$

$$\begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \mathcal{R}^T \begin{pmatrix} A_X \\ A_Y \\ A_Z \end{pmatrix}$$

# Kinetic energy in the molecular frame

By applying the chain rule for derivation, it is obtained

$$\begin{aligned}\frac{\partial}{\partial \theta} &\rightarrow \frac{\partial}{\partial \theta} - \frac{i}{\hbar} (\cos \psi L_y + \sin \psi L_x) \\ \frac{\partial}{\partial \varphi} &\rightarrow \frac{\partial}{\partial \varphi} - \frac{i}{\hbar} (\cos \theta L_z - \sin \theta (\cos \psi L_x - \sin \psi L_y))\end{aligned}$$

hence the expression for  $O^2$  is very cumbersome.

Remarkably, the expression for the electronic orbital angular momentum is simple

$$\mathbf{L} = \frac{\hbar}{i} \sum_{j=1}^{N_e} \mathbf{r}_j \times \nabla_{r_j} \quad \left\{ \begin{array}{l} L_x = \frac{\hbar}{i} \sum_j \left( \frac{\partial}{\partial z_j} y_j - \frac{\partial}{\partial y_j} z_j \right) \\ L_y = \frac{\hbar}{i} \sum_j \left( \frac{\partial}{\partial x_j} z_j - \frac{\partial}{\partial z_j} x_j \right) \\ L_z = \frac{\hbar}{i} \sum_j \left( \frac{\partial}{\partial y_j} x_j - \frac{\partial}{\partial x_j} y_j \right) \end{array} \right.$$

# Total angular momentum and centrifugal energy

Introduce  $\mathbf{N} = \mathbf{O} + \mathbf{L}$  total angular momentum without spin: commutes with  $H$   
→ it is possible to find eigenfunctions of  $H$ ,  $\mathbf{N}^2$ , and  $N_Z$

Then  $\mathbf{O}^2 = \mathbf{N}^2 + \mathbf{L}^2 - 2\mathbf{L} \cdot \mathbf{N}$  and

$$H = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\mathbf{N}^2}{2\mu R^2} - \frac{\hbar^2}{2m_e} \sum_{j=1}^{N_e} \nabla_{r_j}^2 + V(\{\mathbf{r}_k\}; R) + H_c$$

where  $H_c$  is the Coriolis coupling:

$$H_c = \frac{\mathbf{L}^2 - 2\mathbf{L} \cdot \mathbf{N}}{\mu R^2}$$

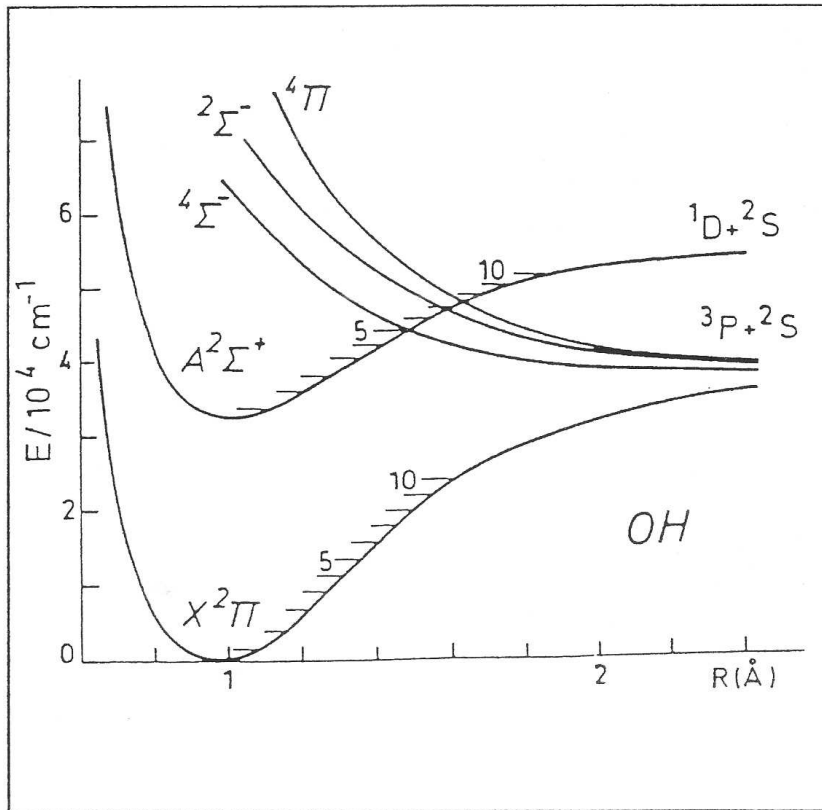
which couples  $\mathbf{L}$  with nuclear motion (rotation and vibration).



## *The diatomic problem*

$$H = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\mathbf{J}^2}{2\mu R^2} + H_c + H_e$$

# Electronic wave function for diatomics



$L_z$  commutes with  $H_e$   
 (cylindrical symmetry about  $\mathbf{R}$ )  
 Hence electronic wave functions can  
 be chosen as eigenfunctions of  $L_z$

$$H_e \phi_{\Lambda\alpha}(\{\mathbf{r}_k\}; R) = U_\alpha(R) \phi_{\Lambda\alpha}(\{\mathbf{r}_k\}; R)$$

$$L_z \phi_{\Lambda\alpha}(\{\mathbf{r}_k\}; R) = \hbar \Lambda \phi_{\Lambda\alpha}$$

Potential energy curves  $U_\alpha(R)$  for OH. (from H. Lefebvre-Brion and R.W. Field, "The spectra and dynamics of diatomic molecules", Academic Press, 2004)

# Born-Oppenheimer approximation for diatomics

$$\Psi_{\Lambda}(\mathbf{R}, \{\mathbf{r}_k\}) = F_{\Lambda}(R, \theta, \varphi) \phi_{\Lambda}(\{\mathbf{r}_k\}; R)$$

We suppose that  $\phi_{\Lambda}(\{\mathbf{r}_k\}; R)$  is known,  
we look for  $F_{\Lambda}(R, \theta, \varphi)$

It is a solution of the Schrödinger equation for vibration and rotation:

$$\left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\mathbf{N}_{\Lambda}^2}{2\mu R^2} + U_{\Lambda}(R) \right] F_{\Lambda}(\mathbf{R}) = E F_{\Lambda}(\mathbf{R})$$

with

$$\mathbf{N}_{\Lambda}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} - 2i \frac{\cot \theta}{\sin \theta} \Lambda \frac{\partial}{\partial \varphi} - \frac{1}{\sin^2 \theta} \Lambda^2 \right)$$

# Rotational wave functions for diatomics

$N^2$  and  $N_Z$ , but also  $N_z$ , commute with  $H$

This is because  $N_z = L_z$  since  $O_z = 0$

( $O = R \times P_R$  is necessarily perpendicular to  $R$ )

Hence we can find eigenfunctions of  $H$ ,  $N^2$ ,  $N_Z$  and  $N_z$  simultaneously.

We write  $F_\Lambda(R, \theta, \varphi) = G(R) \mathcal{R}_{M\Lambda}^N(\varphi, \theta)$  where  $\mathcal{R}_{M\Lambda}^N = \frac{e^{iM\varphi}}{\sqrt{2\pi}} \Theta_{M\Lambda}^N(\theta)$ ,

$\Theta_{M\Lambda}^N(\theta)$  being a solution of

$$\left[ -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{M^2 - 2\Lambda M \cos \theta + \Lambda^2}{\sin^2 \theta} \right] \Theta_{M\Lambda}^N(\theta) = N(N+1) \Theta_{M\Lambda}^N(\theta)$$

**Properties:**

$$\int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \mathcal{R}_{M'\Lambda}^{N'*} \mathcal{R}_{M\Lambda}^N = \delta_{N'N} \delta_{M'M}$$

$$N^2 \mathcal{R}_{M\Lambda}^N = \hbar^2 N(N+1) \mathcal{R}_{M\Lambda}^N; \quad N_Z \mathcal{R}_{M\Lambda}^N = \hbar M \mathcal{R}_{M\Lambda}^N; \quad N_z \mathcal{R}_{M\Lambda}^N = \hbar \Lambda \mathcal{R}_{M\Lambda}^N$$

$$\mathcal{R}_{M\Lambda}^N(\varphi, \theta) = \sqrt{\frac{2N+1}{4\pi}} D_{M\Lambda}^{N*}(\varphi, \theta, 0); \quad \mathcal{R}_{M\Lambda=0}^N = Y_{NM}(\theta, \varphi)$$

# Vibrational wave functions for diatomics

We are now left with

$$\left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\hbar^2}{2\mu R^2} N(N+1) + U(R) \right] G(R) = E G(R)$$

It is more convenient to work with

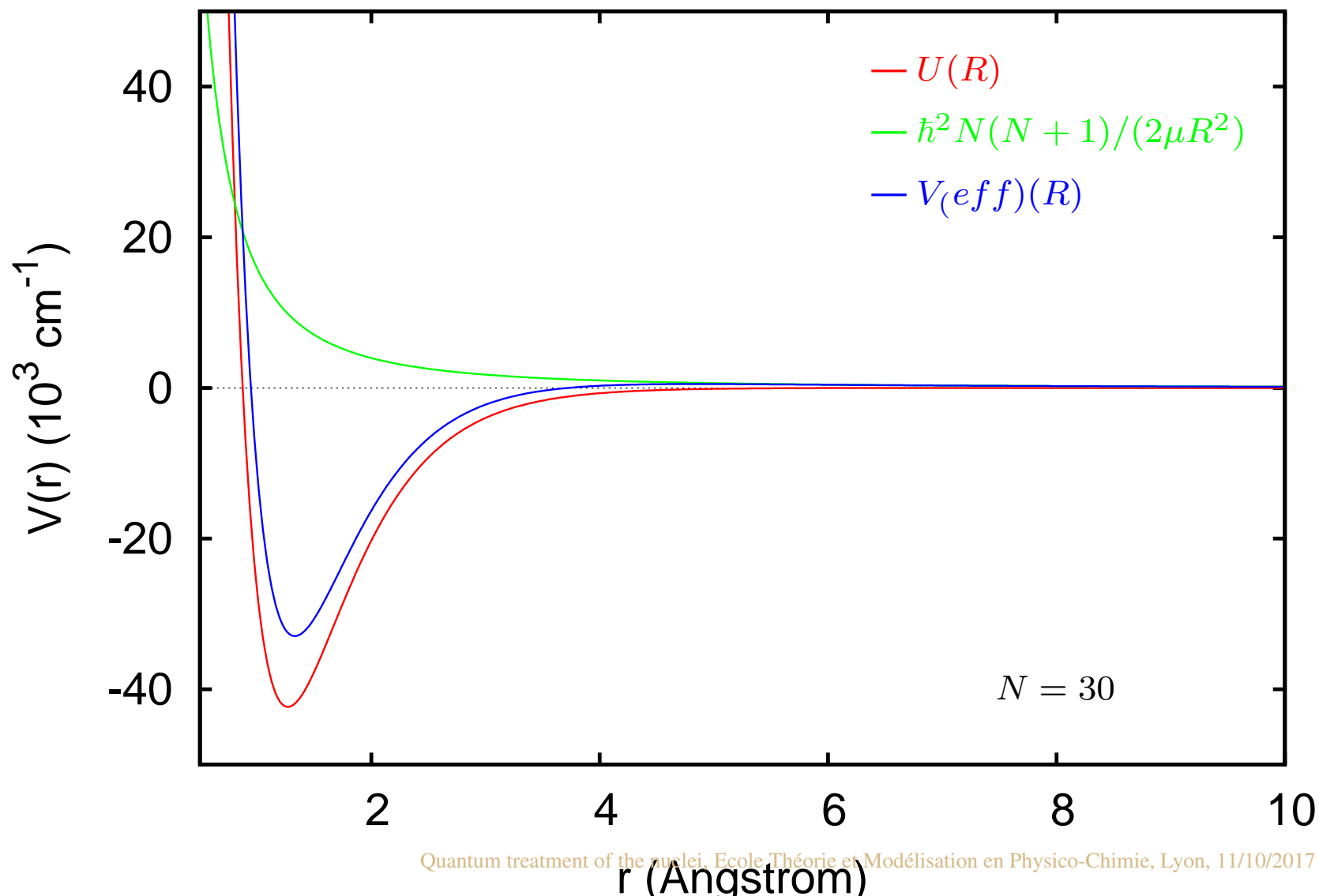
$$G(R) = \frac{\chi(R)}{R} \quad \text{hence} \quad \int_0^\infty G'^*(R) G(R) R^2 dR = \int_0^\infty \chi'^*(R) \chi(R) dR$$

and  $\chi(R)$  is a solution of

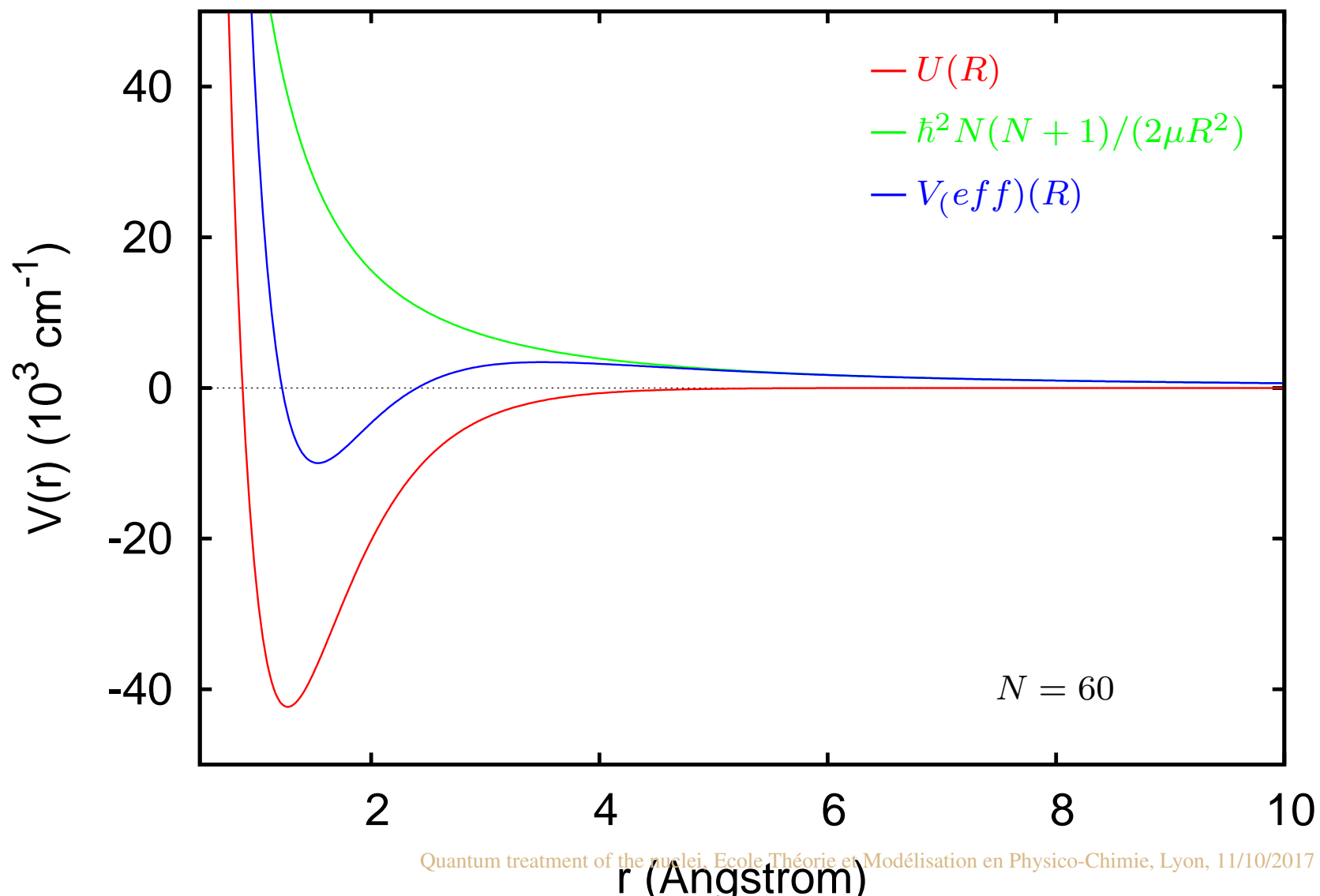
$$\left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu R^2} N(N+1) + U(R) \right] \chi(R) = E \chi(R)$$

$\hbar^2 N(N+1)/(2\mu R^2)$  is called the *centrifugal potential*

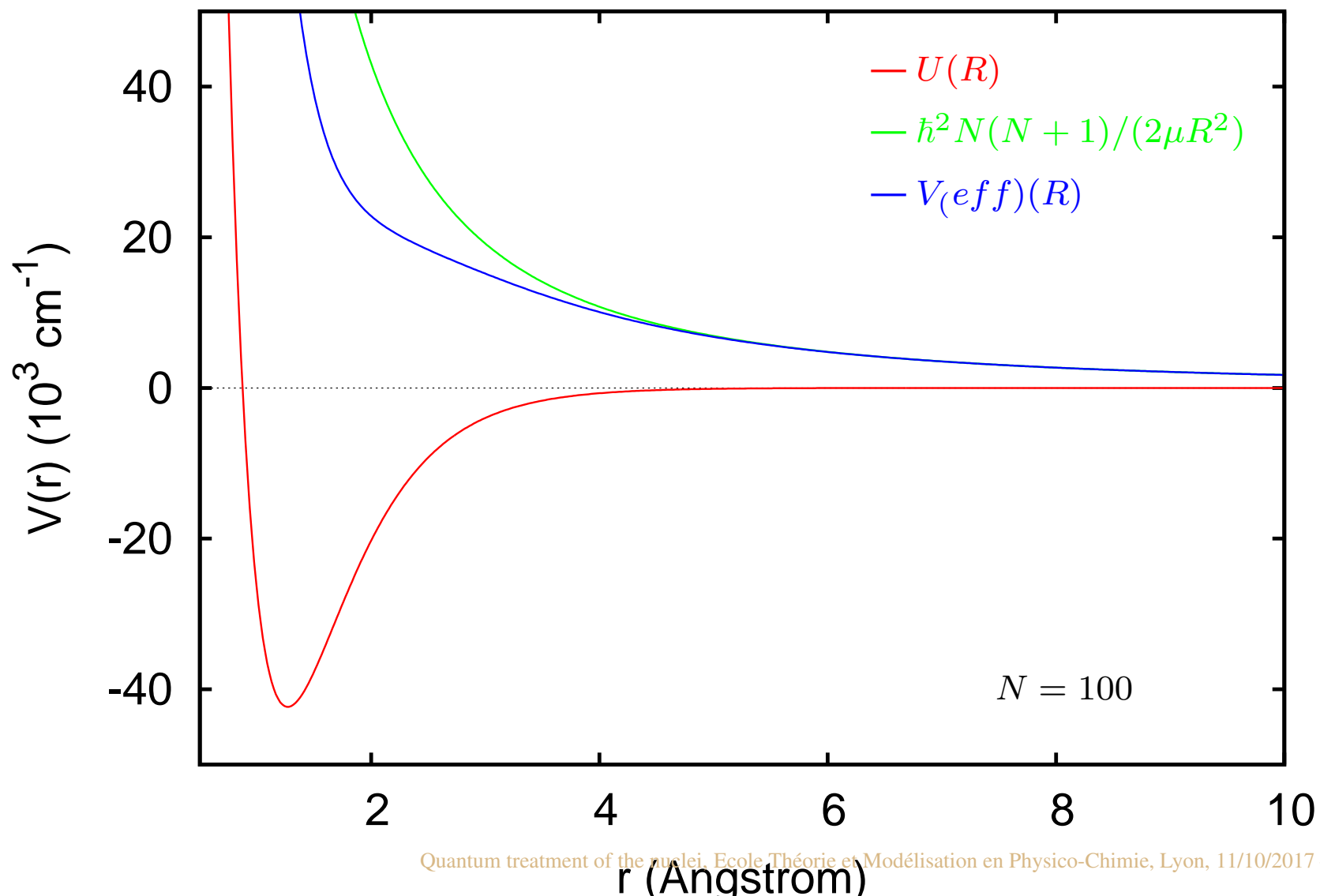
# HCl Centrifugal potential



# HCl Centrifugal potential



# HCl Centrifugal potential





# Harmonic and rigid rotor approximations

**First approximation:** Expand  $U(R)$  around its minimum:

$$U(R) = -\mathcal{D}_e + \frac{1}{2}k_e(R - R_e)^2 \quad \text{where} \quad k_e = \left( \frac{\partial^2 U}{\partial R^2} \right)_{R_e}$$

$R_e$  equilibrium position ( $(\partial U / \partial R)_{R_e} = 0$ ),

$\mathcal{D}_e$  dissociation energy of the molecule

$k_e$  force constant.

**Second approximation:** replace centrifugal potential by its value at  $R_e$

$$\left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{2}k_e(R - R_e)^2 \right] \chi(R) = \left[ E + \mathcal{D}_e - \frac{\hbar^2 N(N+1)}{2\mu R_e^2} \right] \chi(R)$$

It is a harmonic oscillator equation for  $\chi(R)$  with eigenvalues  $\hbar\omega_e(v + 1/2)$

$$E_{vN} = -\mathcal{D}_e + B_e N(N+1) + \hbar\omega_e\left(v + \frac{1}{2}\right); \quad v = 0, 1, 2, \dots$$

$$B_e = \frac{\hbar^2}{2\mu R_e^2} \quad \text{rotational constant} \quad \text{and} \quad \omega_e = \sqrt{\frac{k_e}{\mu}} \quad \text{vibrational frequency}$$

$$\Psi_{\alpha\Lambda_\alpha vNM}(\mathbf{R}, \{\mathbf{r}_j\}) = \frac{1}{R} \chi_v^\alpha(R) \mathcal{R}_{M\Lambda}^N(\varphi, \theta) \phi_{\alpha\Lambda_\alpha}(\{\mathbf{r}_j\}; R)$$

## *Part II*

# *Quantum dynamics with wave packets*

# Time-dependent Schrödinger equation

$$H\Psi(R, t) = i\hbar \frac{d\Psi(R, t)}{dt}$$

Example: expand  $\Psi(R, t)$  in eigenfunctions  $\phi_n$  of  $H$ :

$$\Psi(R, t) = \sum_n c_n(t) \phi_n(R) \quad \text{with} \quad H\phi_n(R) = E_n \phi_n(R)$$

$$H\Psi(R, t) = \sum_n c_n(t) E_n \phi_n(R) = i\hbar \sum_n \frac{dc_n}{dt} \phi_n(R)$$

$$\dot{c}_n(t) \equiv \frac{dc_n}{dt} = -\frac{i}{\hbar} E_n c_n t \quad \rightarrow \quad c_n(t) = e^{-iE_n t/\hbar}$$

Formally, the time-dependent Schrödinger equation can be solved as

$$\frac{d\Psi}{\Psi} = -\frac{i}{\hbar} H dt \quad \rightarrow \quad \Psi(R, t) = e^{-\frac{i}{\hbar} H t} \Psi(R, 0)$$

Example: if  $\Psi(R, t = 0) = \phi_n(R)$ , then  $\Psi(R, t) = e^{-iE_n t/\hbar} \phi_n(R)$

# How to propagate wave packets?

position eigenstates

momentum eigenstates

$$\hat{x}|x\rangle = x|x\rangle \quad \langle x|x'\rangle = \delta(x - x') \quad \hat{p}|p\rangle = p|p\rangle \quad \langle p|p'\rangle = \delta(p - p')$$

$$\hat{V}(x)|x\rangle = V(x)|x\rangle \quad T \equiv \frac{\hat{p}^2}{2m}|p\rangle = \frac{p^2}{2m}|p\rangle$$

They form complete (continuous) basis sets:  $\hat{1} = \int dx|x\rangle\langle x| = \int dp|p\rangle\langle p|$

Expand any state vector as

$$f = \int dx|x\rangle\langle x|f\rangle = \int dx|x\rangle f(x) \quad f = \int dp|p\rangle\langle p|f\rangle = \int dp|p\rangle f(p)$$

in coordinate space

in momentum space

They are related by Fourier transforms:

$$\frac{\hbar}{i} \frac{d\langle x|p\rangle}{dx} = p\langle x|p\rangle \rightarrow \langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

$$\langle p|f\rangle = \langle p| \left( \int dx|x\rangle\langle x| \right) |f\rangle = \int dx \langle p|x\rangle \langle x|f\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dx e^{ipx/\hbar} f(x)$$

## How to propagate wave packets? (II)

$$\Psi(R, t) = e^{-\frac{i}{\hbar} H t} \Psi(R, 0) \quad e^{-\frac{i}{\hbar} H t} = 1 + \left(-i \frac{t}{\hbar}\right) H + \frac{1}{2!} \left(-i \frac{t}{\hbar}\right)^2 H^2 + \dots$$

$\Psi(R, t)$  expressed on a grid in  $R$ :  $\Psi(R_k, t)$

$H = T + V$  but  $T$  and  $V$  do not commute

Hence divide  $t$  in small intervals  $\Delta t$  :

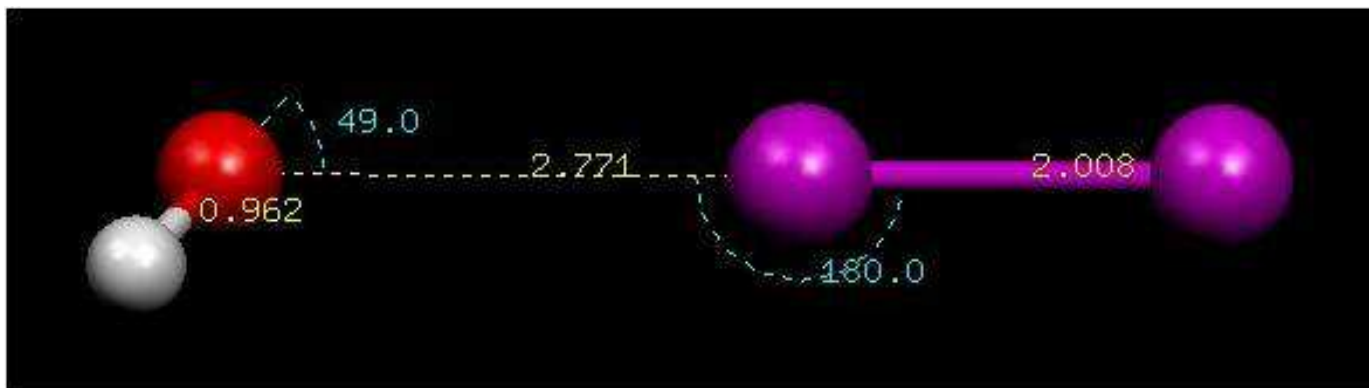
$$e^{-\frac{i}{\hbar} H t} = e^{-\frac{i}{\hbar} H \Delta t} e^{-\frac{i}{\hbar} H \Delta t} e^{-\frac{i}{\hbar} H \Delta t} \dots$$

and use “split operator” method

$$e^{-\frac{i}{\hbar} H \Delta t} = e^{-\frac{i}{\hbar} V \Delta t / 2} e^{-\frac{i}{\hbar} T \Delta t} e^{-\frac{i}{\hbar} V \Delta t / 2}$$

for each time step, with  $V$  evaluated in position space and  $T$  in momentum space  $\rightarrow$  FFT

## Example: $H_2O \cdots Cl_2$ photodissociation

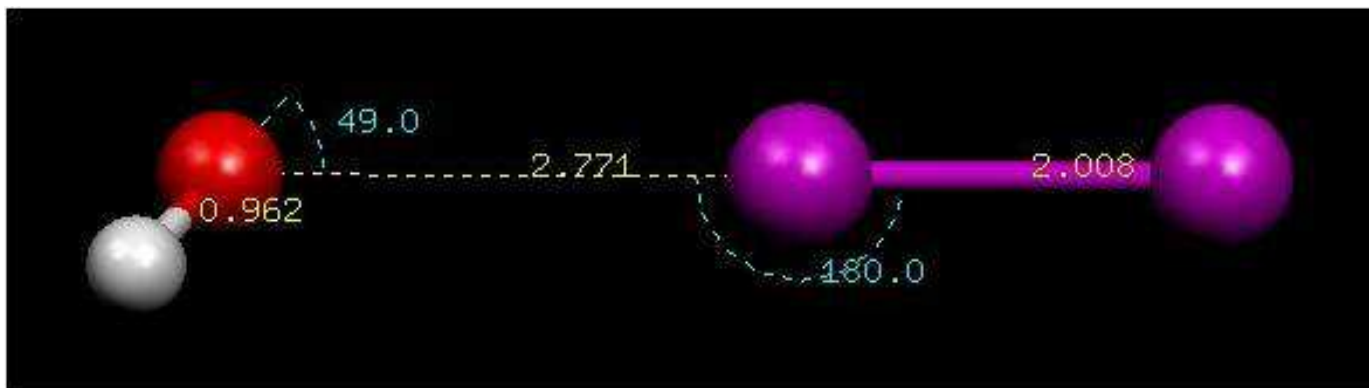


*Ab initio* optimization of the structure [MP2/AVTZ et CCSD(T)]

→ “halogen bond”:  $D_e = 917 \text{ cm}^{-1}$

$R(O-Cl) = 2.771 \text{ \AA}$  instead of  $R(Cl) + R(O) = 1.52 + 1.75 = 3.27 \text{ \AA}$ .

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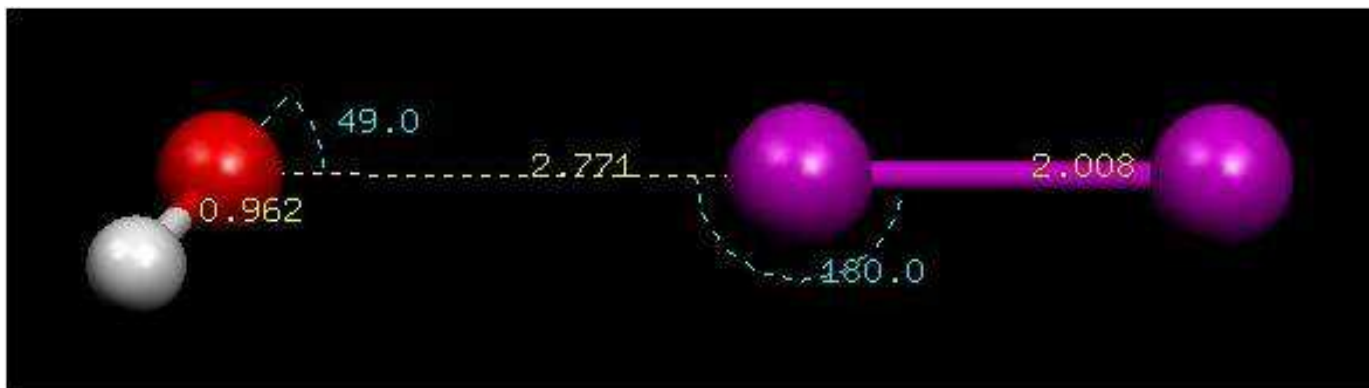
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interaction of one O lone pair with the empty  $\sigma^*$  orbital of  $X_2$



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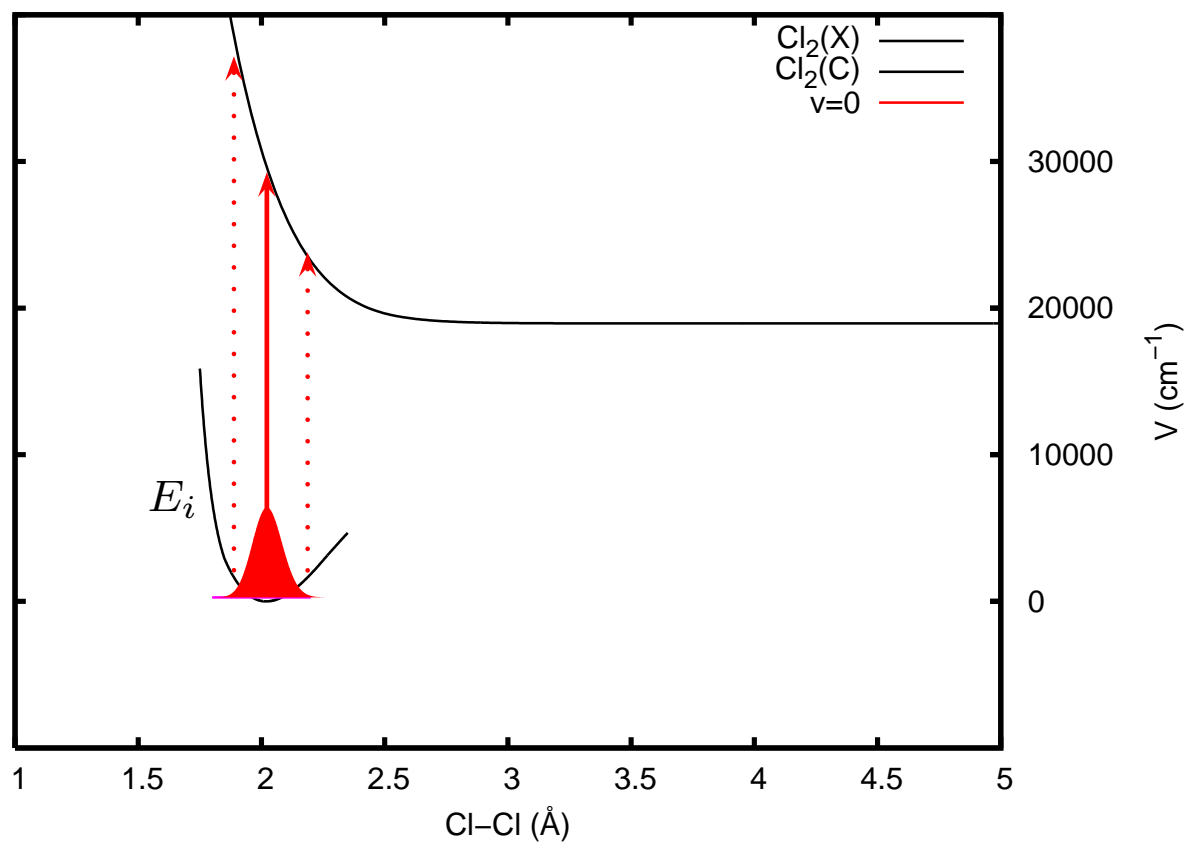
2D model :

- $r$  is the halogen intramolecular coordinate
- $R$  is the water- $X_2$  (COM) intermolecular distance

Hernández-Lamonedá et al., *J. Phys. Chem.* **112**, 89 (2008)

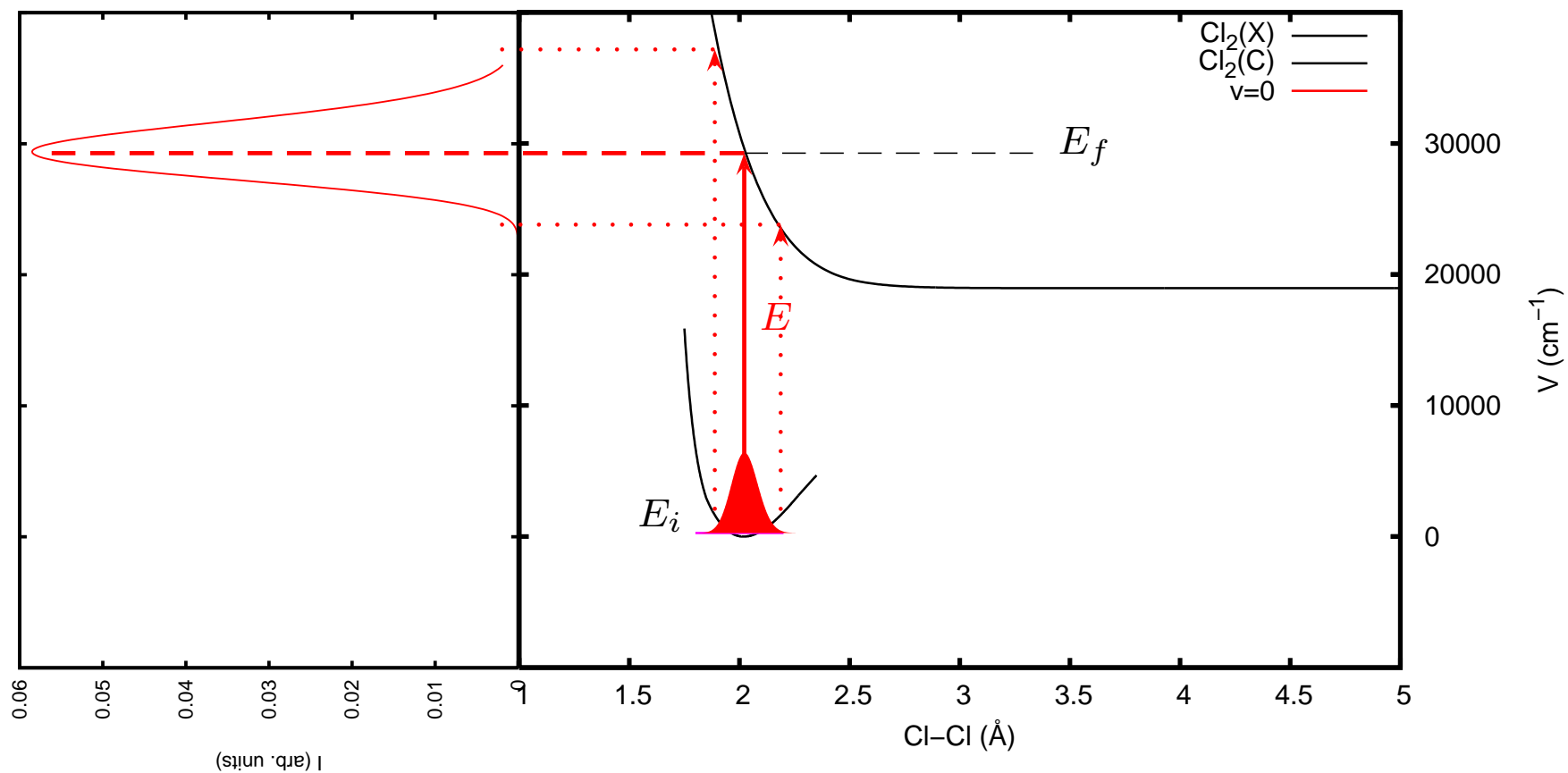


# $Cl_2$ Absorption spectrum: Bound to continuum

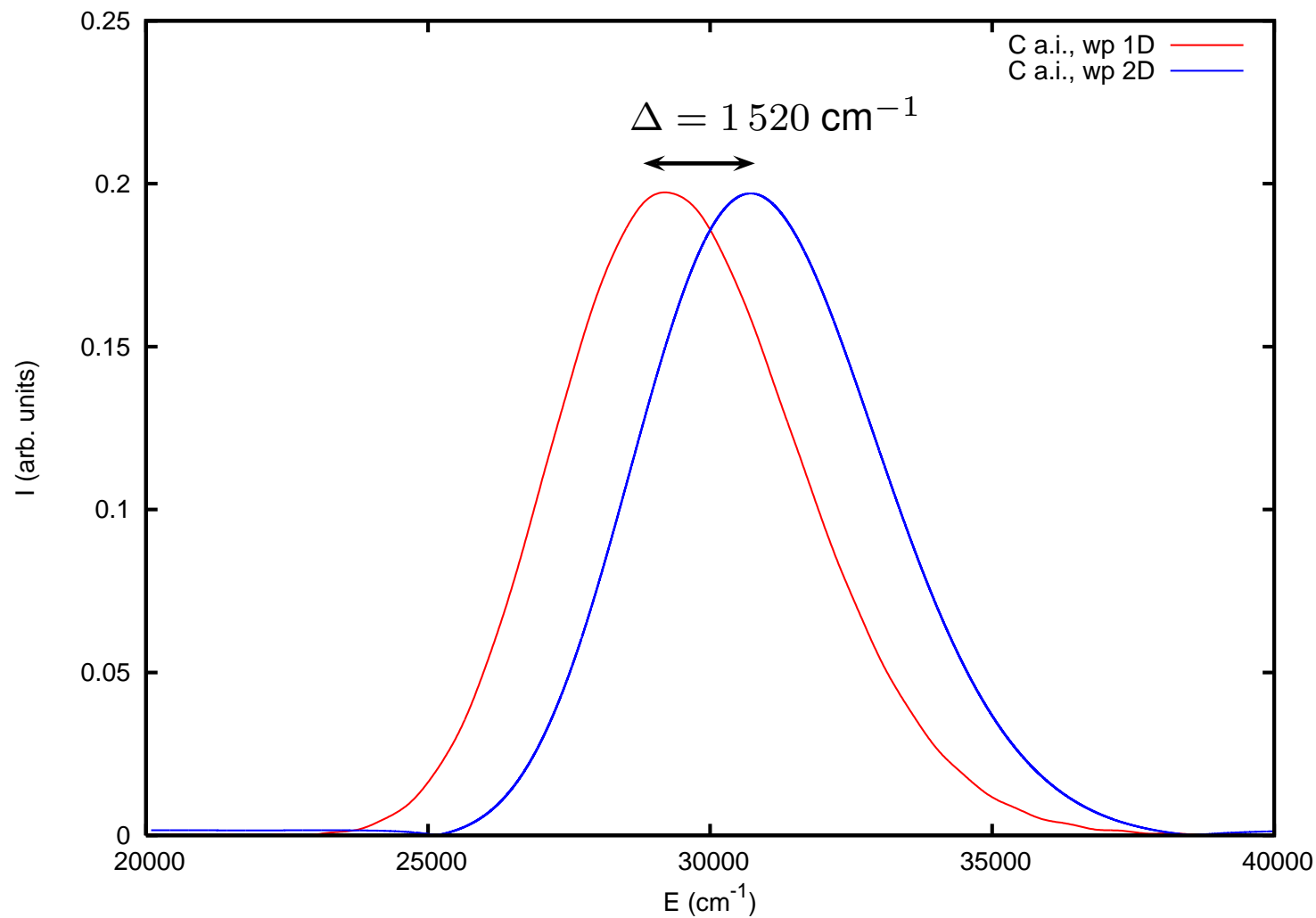


# Reflection principle

$$I(\mathbf{E}) \propto |\langle \Psi_f | \mu | \Psi_i \rangle|^2 \delta(E - (E_f - E_i)) \simeq |\mu \Psi_i(R_{c.t.p.}[E_f])|^2 \delta(E - (E_f - E_i))$$



# $H_2O \cdots Cl_2$ absorption spectrum



**NO** broadening!

# Photodissociation with wave packets

Photodissociation cross section:

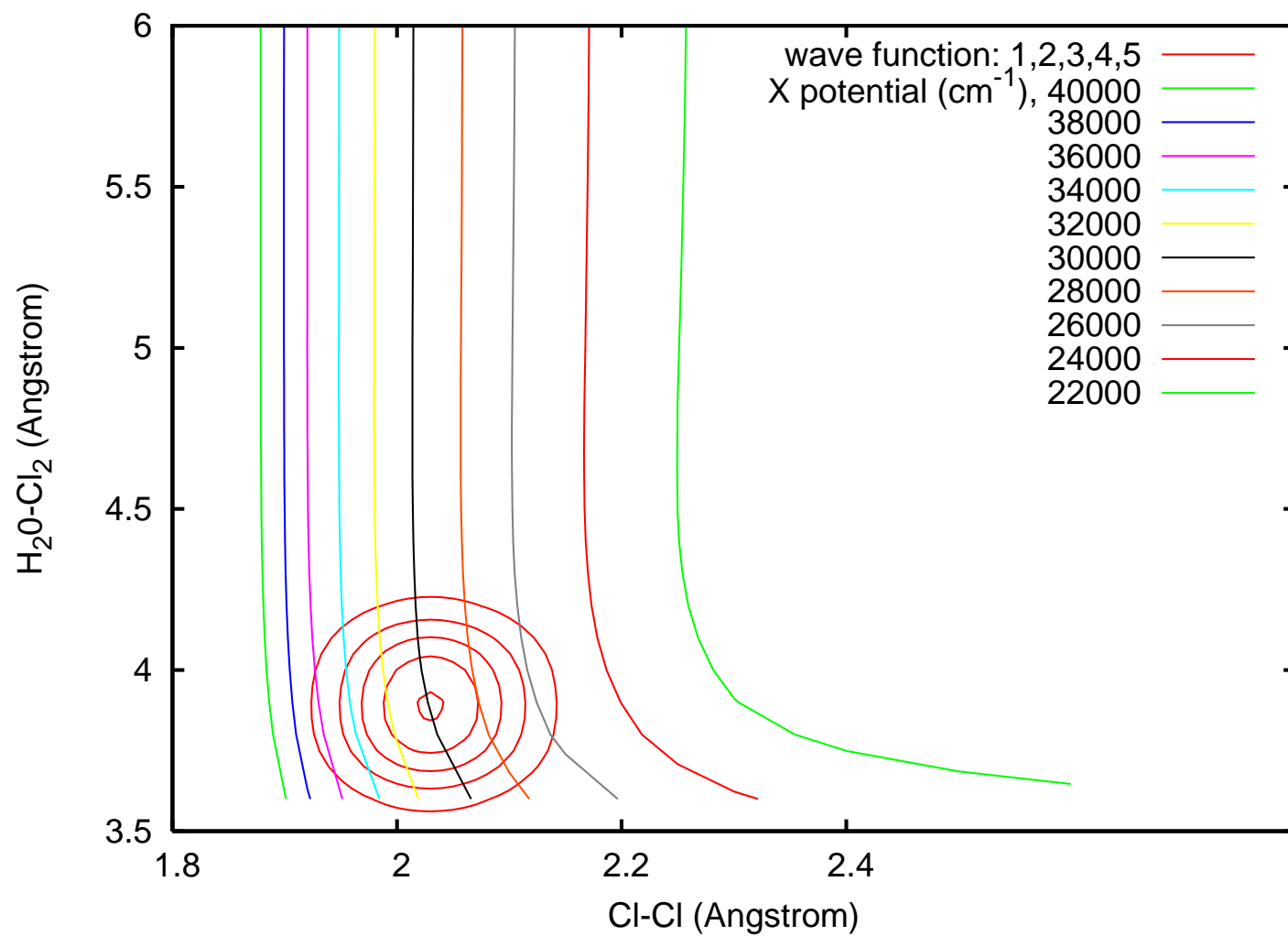
$$\begin{aligned}\sigma(\hbar\omega_{ph}) &\propto |\langle \Psi_i | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} | \Psi_{f, \frac{E}{\hbar} = \omega_{ph}} \rangle|^2 = \int dE |\langle \Psi_i | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} | \Psi_{f, E} \rangle|^2 \delta\left(\frac{E}{\hbar} - \omega_{ph}\right) \\ &= \int dE \langle \Psi_i | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} | \Psi_{f, E} \rangle \langle \Psi_{f, E} | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} | \Psi_i \rangle \frac{1}{2\pi} \int dt e^{-i\left(\frac{E}{\hbar} - \omega_{ph}\right)t} \\ &= \frac{1}{2\pi} \int dt e^{i\omega_{ph}t} \int dE \langle \Psi_i | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} | e^{-iH_f t/\hbar} \Psi_{f, E} \rangle \langle \Psi_{f, E} | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} | \Psi_i \rangle \\ &= \frac{1}{2\pi} \int dt e^{i\omega_{ph}t} \langle \Psi_i | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} e^{-iH_f t/\hbar} | \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} \Psi_i \rangle\end{aligned}$$

Can be calculated as the Fourier transform of the autocorrelation function of  $\boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} \Psi_i$ :

$$\begin{aligned}\tilde{\Psi}_f(t=0) &= \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} \Psi_i \\ \tilde{\Psi}_f(t) &= e^{-iH_f t/\hbar} \tilde{\Psi}_f(t=0) = e^{-iH_f t/\hbar} \boldsymbol{\mu} \cdot \boldsymbol{\varepsilon} \Psi_i \\ \sigma(\hbar\omega_{ph}) &= \frac{1}{2\pi} \int dt e^{i\omega_{ph}t} \langle \tilde{\Psi}_f(t=0) | \tilde{\Psi}_f(t) \rangle\end{aligned}$$

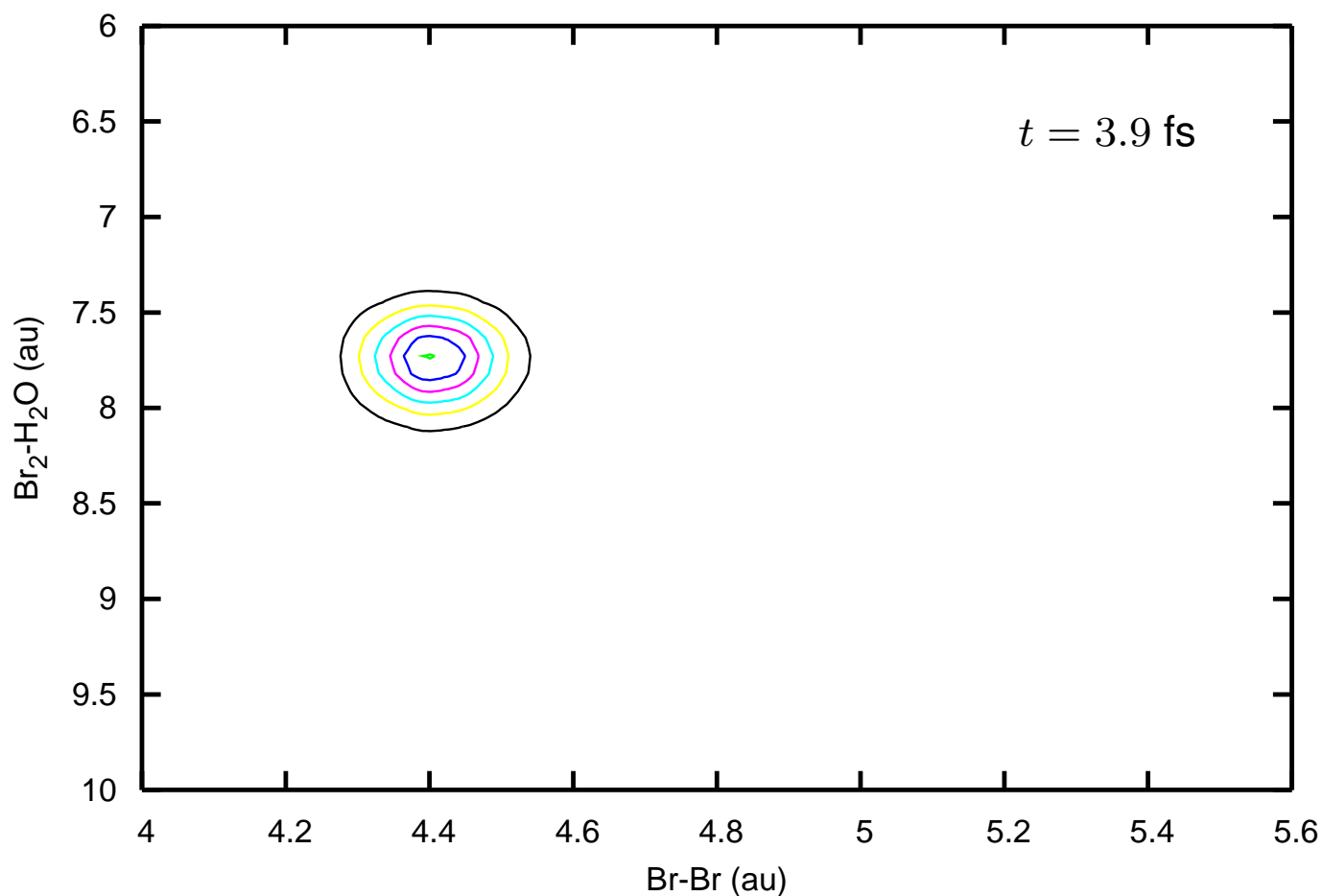
# Why no broadening?

Example of  $H_2O \cdots Cl_2$



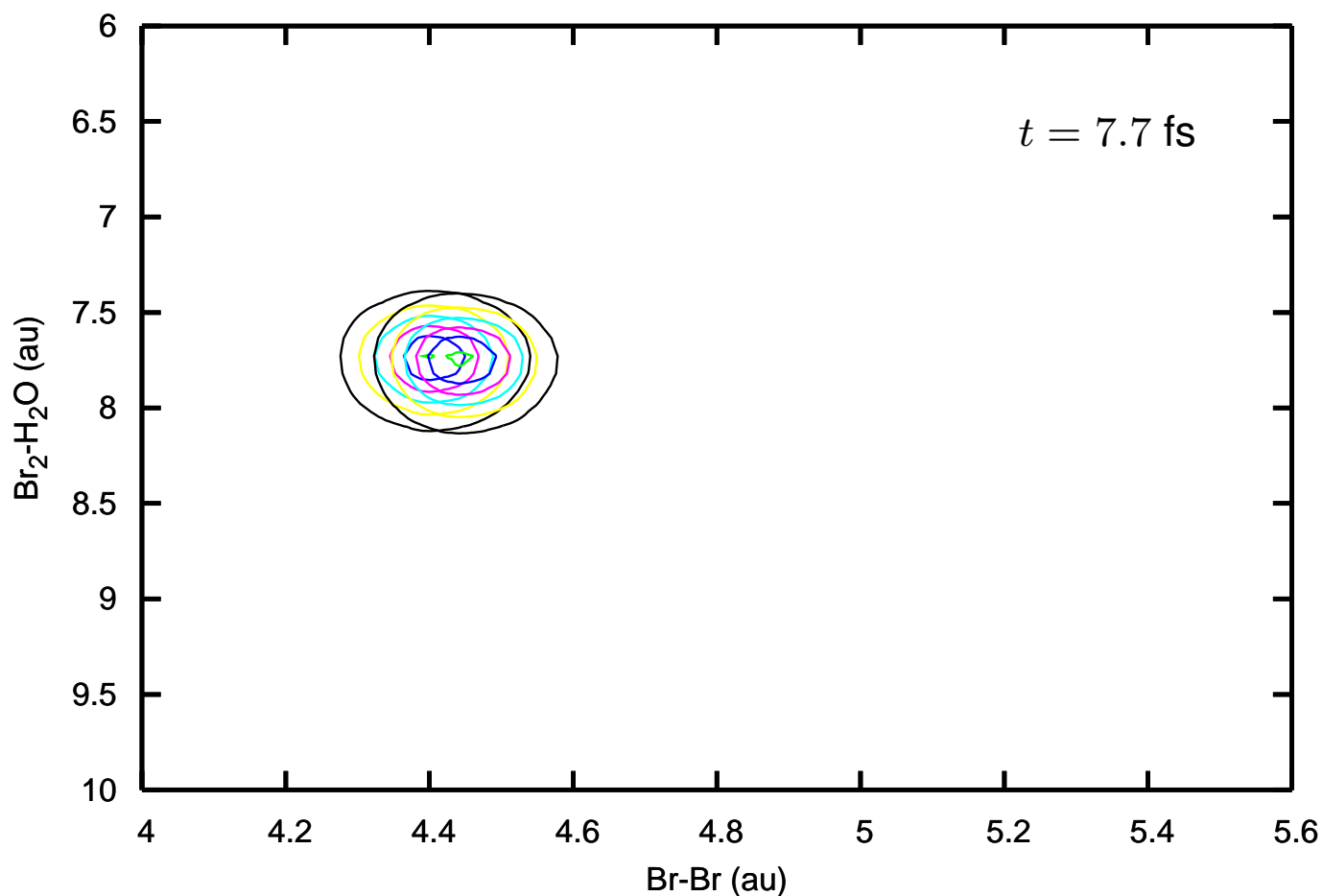
# $H_2O \cdots Br_2(B)$ dissociation: wave packet dynamics

$$I_{\text{abs}}(\mathbf{E}) \propto \int e^{-i\mathbf{E}t/\hbar} \langle \Phi(t=0) | \Phi(t) \rangle dt$$



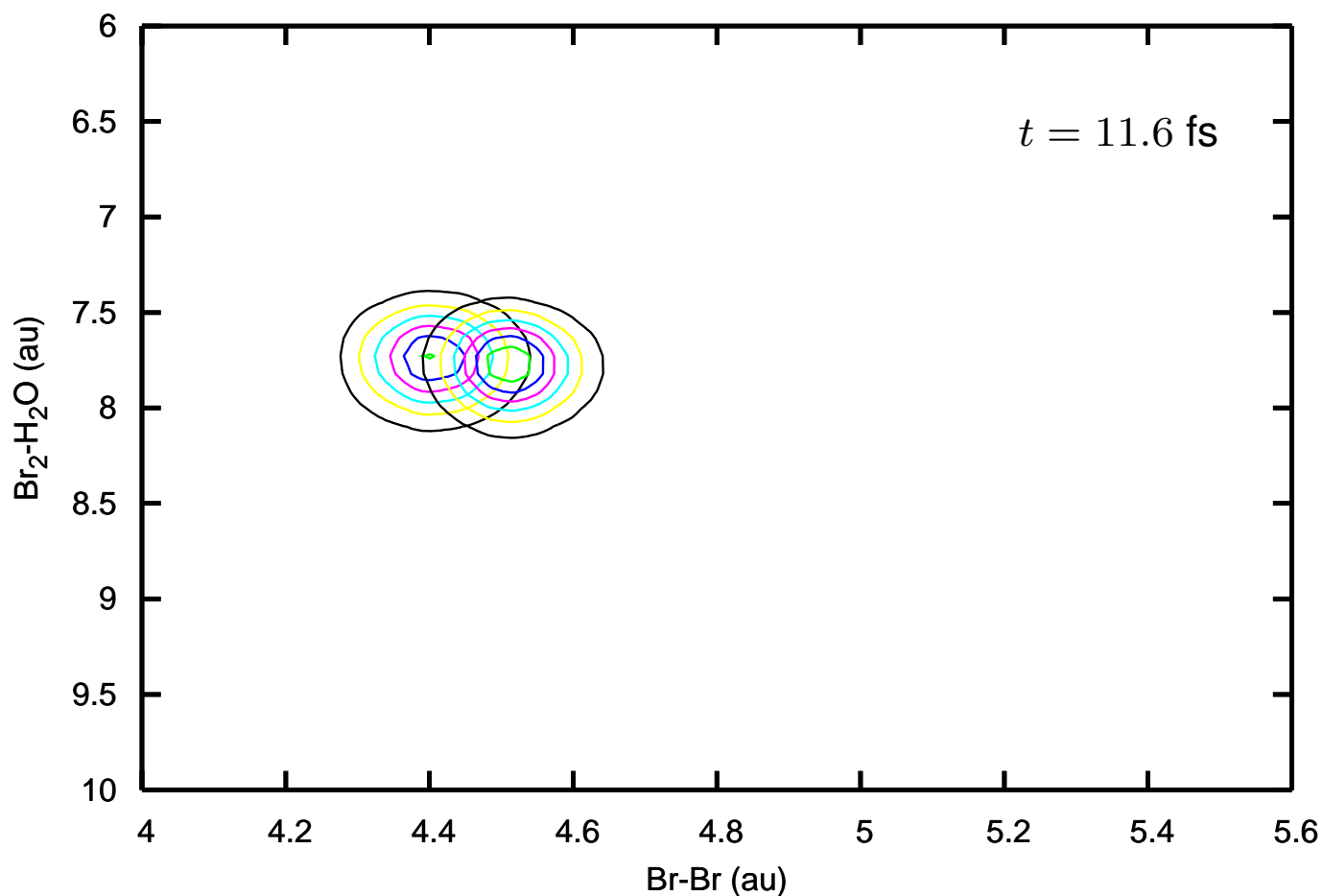
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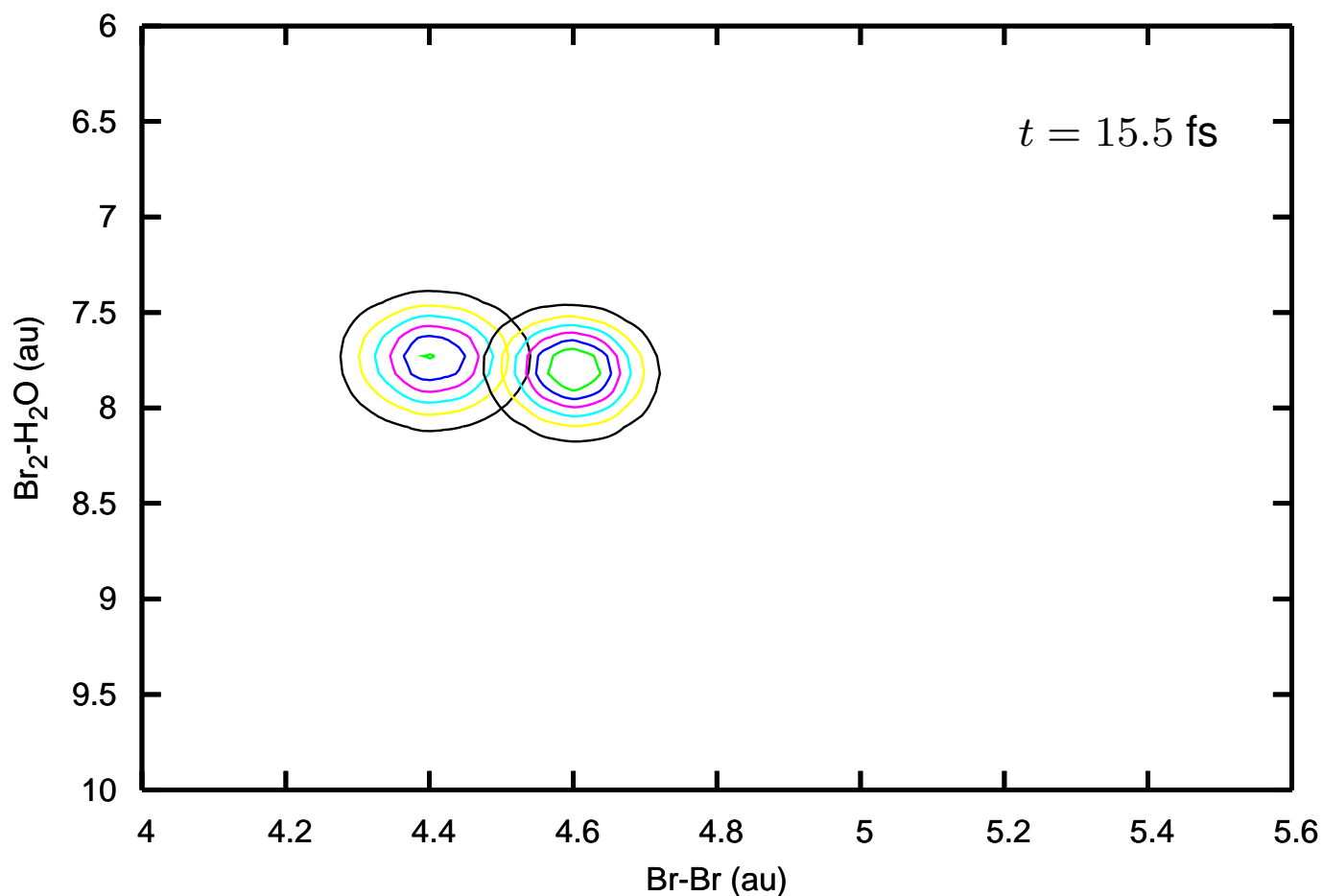
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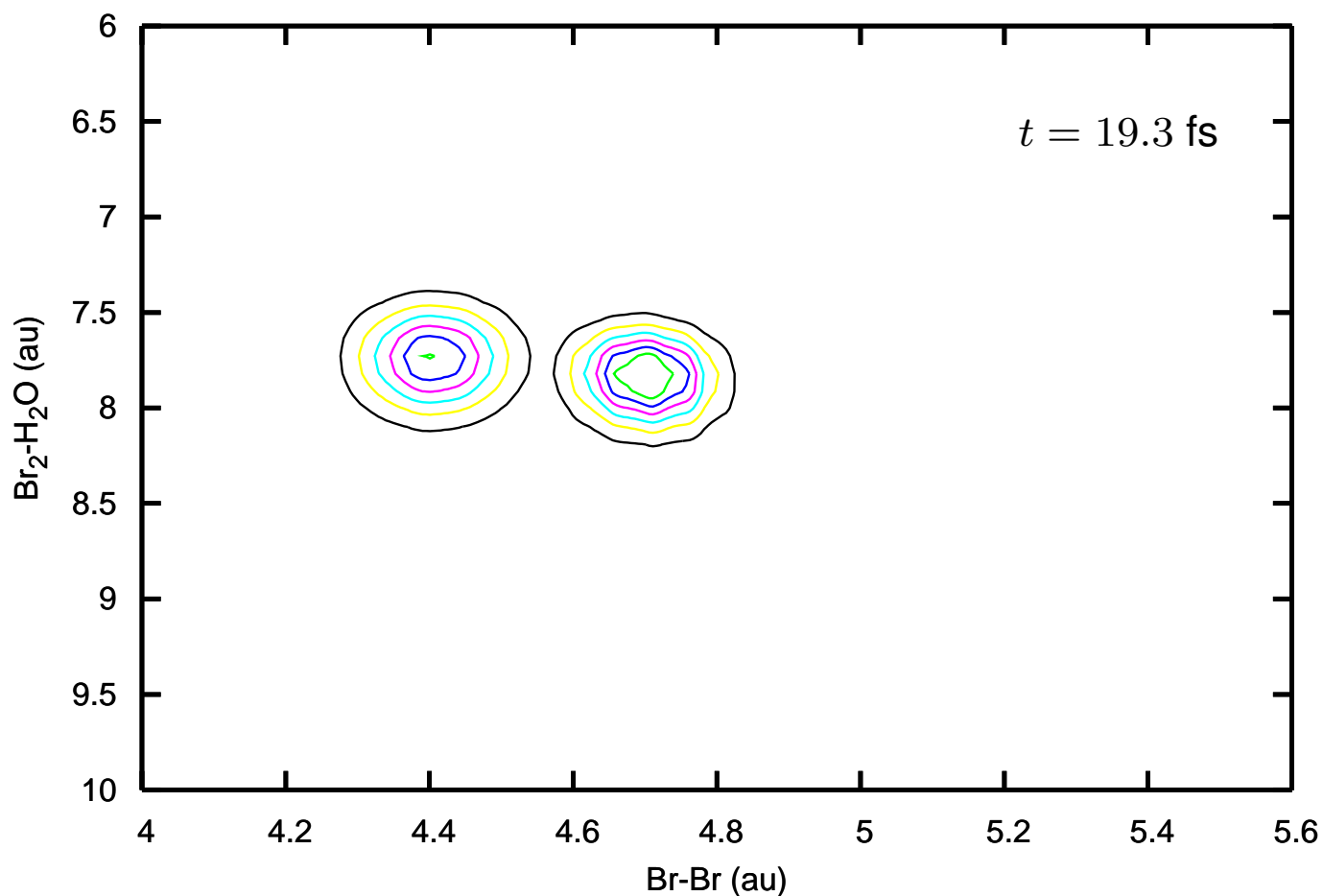
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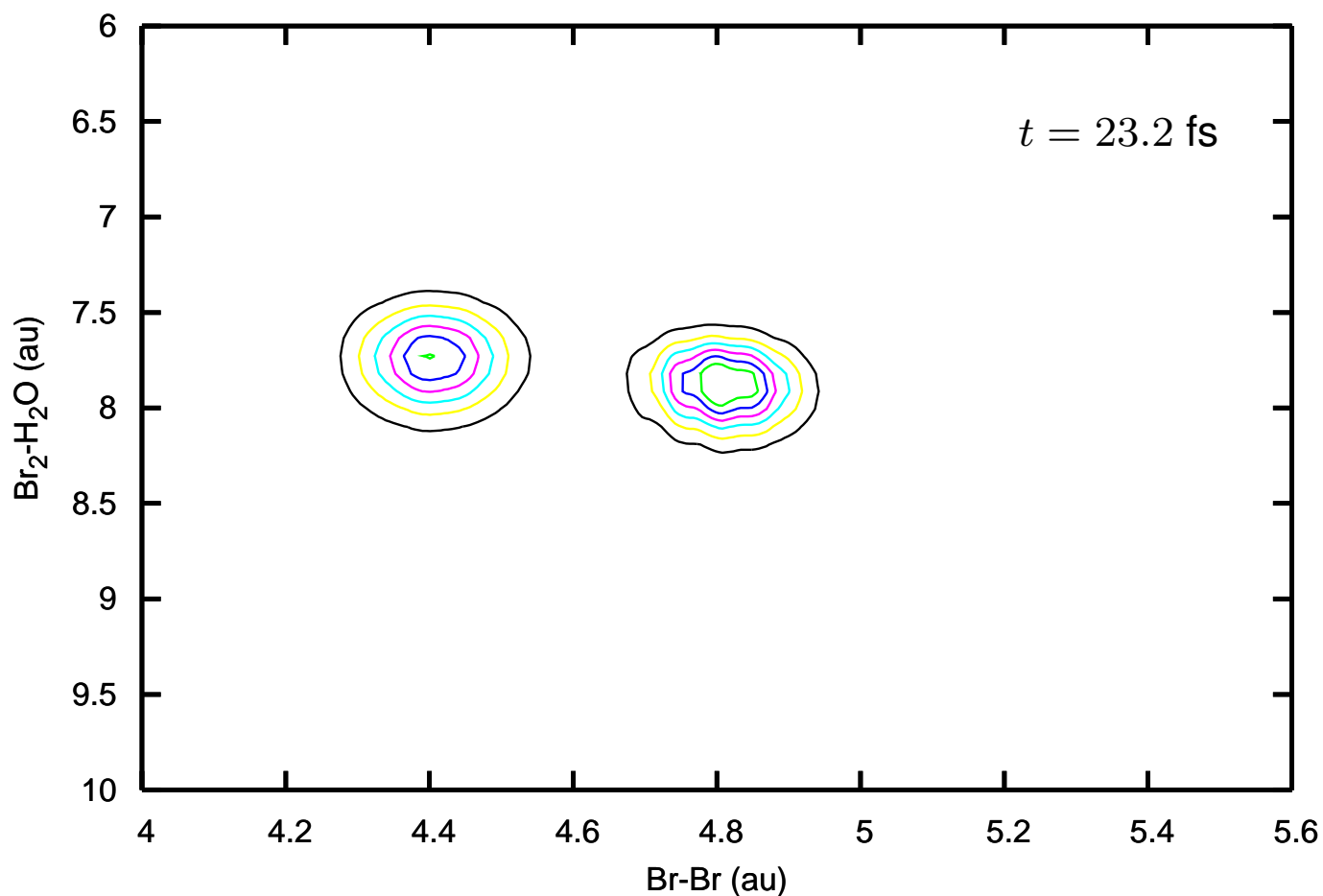
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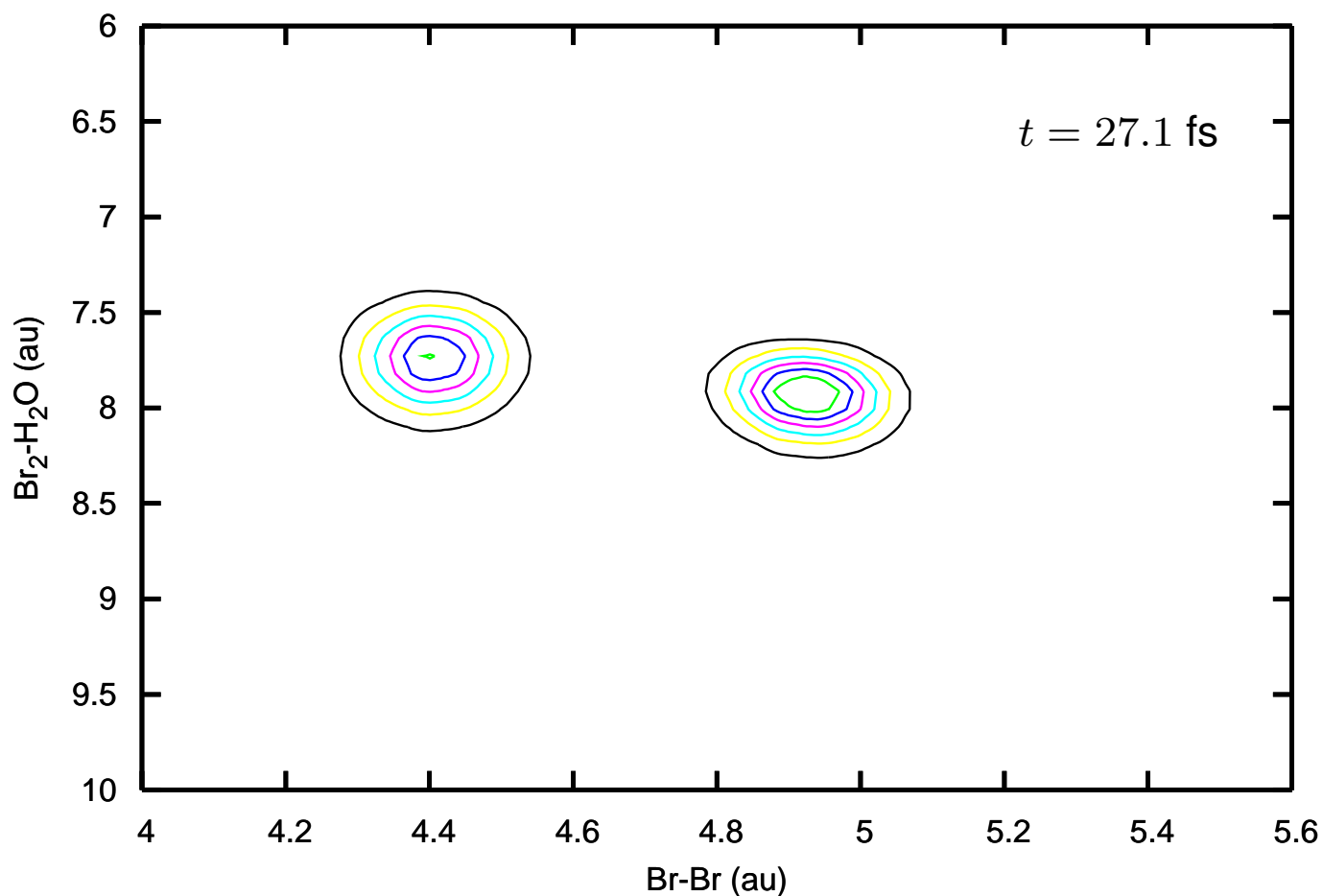
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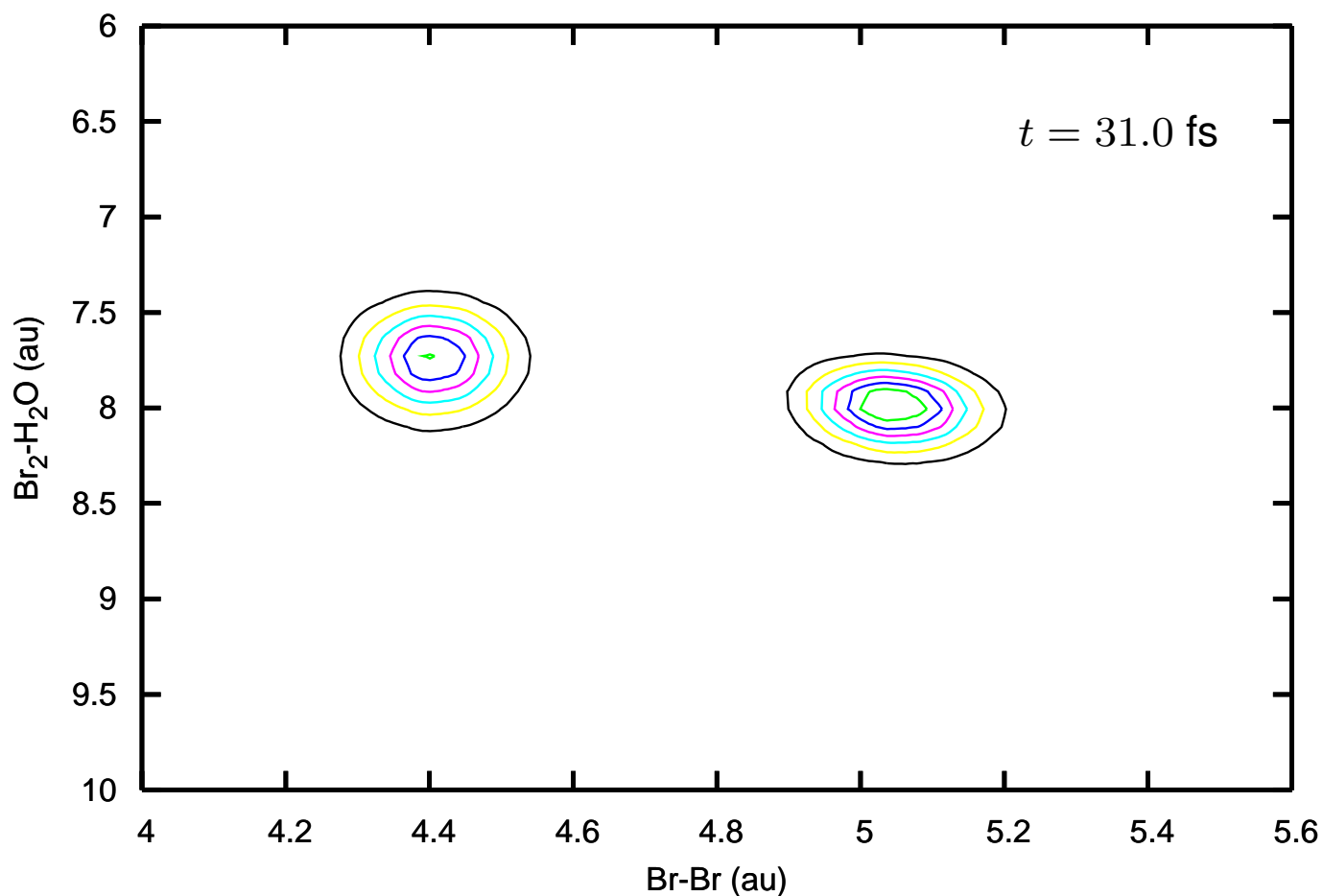
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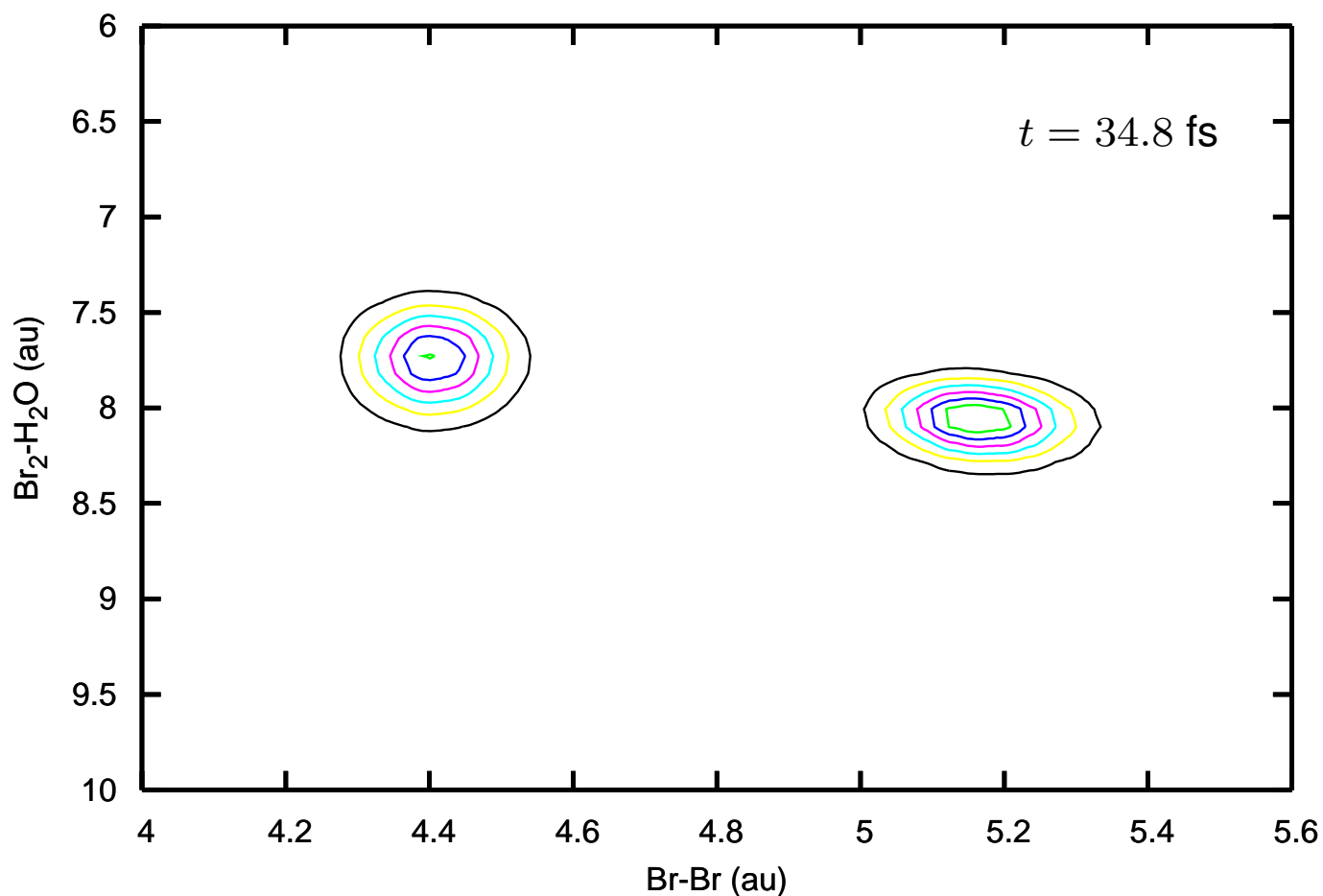
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$$I_{\text{abs}}(\mathbf{E}) \propto \int e^{-i\mathbf{E}t/\hbar} \langle \Phi(t=0) | \Phi(t) \rangle dt$$



# *Quantum dynamics with wave packets*

- 😊 can calculate any observable (in principle)
- 😊 a variety of methods for propagating: gaussian wave packets, basis set expansion, grid expansion, SOD, split operator, Chebyshev, FFT,...
- 😊 MCTDH!
- 😞 size limitation
- 😞 time limitation

## *Part III*

### *Mixed Quantum-Classical Molecular Dynamics*

- Introduction: molecular dynamics, need for mixed methods
- Classical trajectory methods
- Mean field methods
- Surface hopping methods
- Example: dissociative ionization of a rare gas cluster



# *Size Problem in Quantum Molecular Dynamics*

$$\Psi(q_1, q_2, \dots, q_n, t)$$

$n$ -coordinate wave packet, grid with 10 points/coordinate :

$10^n$  points

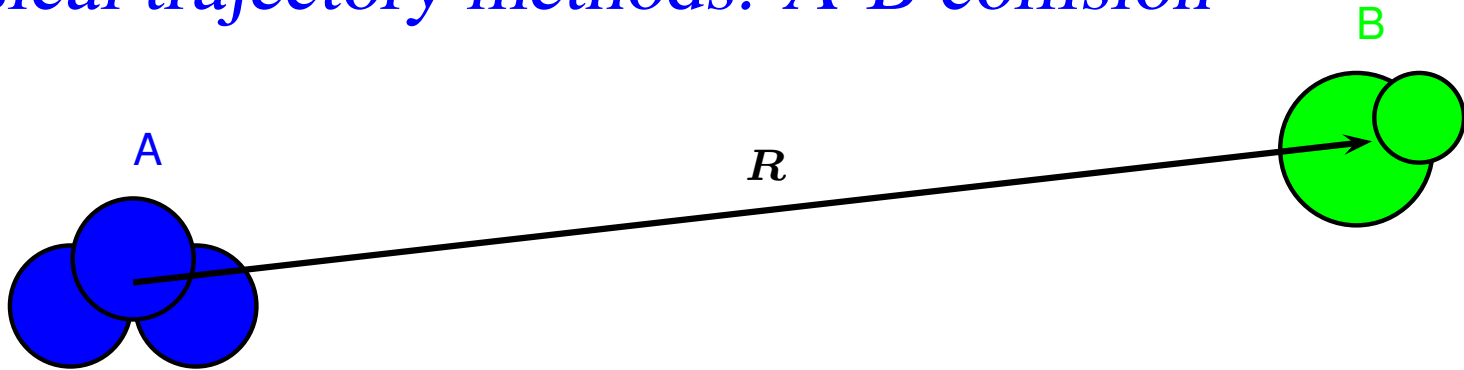
8 B / point (double precision)  $\rightarrow 8 \times 10^n$  bytes for the grid:

8 MB for  $n = 6$ ,

8 GB for  $n = 9$

...

# Classical trajectory methods: A-B collision



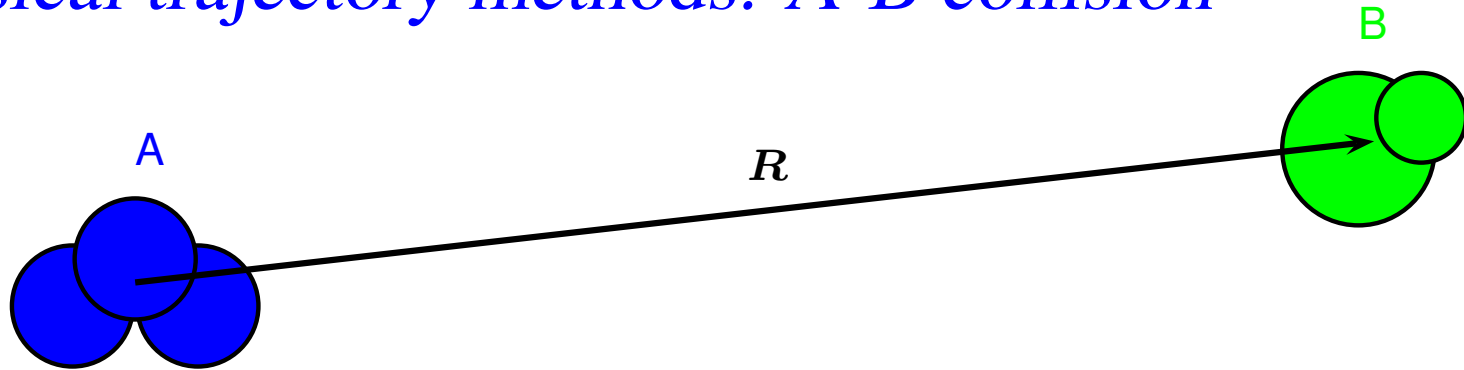
$$i\hbar \frac{\partial \Psi(\mathbf{r}, \mathbf{R})}{\partial t} = H \Psi(\mathbf{r}, \mathbf{R})$$

with  $H = \frac{P_R^2}{2m} + H_0(\mathbf{r}, \mathbf{R})$  and  $H_0(\mathbf{r}, \mathbf{R}) = T_{\mathbf{r}} + V(\mathbf{r}, \mathbf{R})$

$\mathbf{R}$  collision coordinate, with reduced mass  $m = M_A M_B / (M_A + M_B)$

$\mathbf{r}$  internal degree(s) of freedom

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$\mathbf{R}$  collision coordinate, with reduced mass  $m = M_A M_B / (M_A + M_B)$

$\mathbf{r}$  internal degree(s) of freedom

**Classical trajectory approximation:**  $\mathbf{R} \rightarrow \mathcal{R}(t)$  classical degree of freedom

$$i\hbar \frac{\partial \Psi(\mathbf{r}, \mathcal{R}(t), t)}{\partial t} = H_0(\mathbf{r}, \mathcal{R}(t)) \Psi(\mathbf{r}, \mathcal{R}(t), t)$$

$\mathcal{R}(t)$  classical trajectory determined *a priori*

$\mathbf{r}$  **quantum** degree of freedom

# Classical trajectory: basis set expansion

$$i\hbar \frac{\partial \Psi(\mathbf{r}, \mathcal{R}(t), t)}{\partial t} = H_0(\mathbf{r}, \mathcal{R}(t)) \Psi(\mathbf{r}, \mathcal{R}(t), t)$$

Expand  $\Psi(\mathbf{r}, \mathcal{R}(t), t)$  in  $\{\phi_k(\mathbf{r}; \mathcal{R}(t))\}$  (adiabatic, diabatic, or neither):

$$\Psi(\mathbf{r}, \mathcal{R}(t), t) = \sum_k c_k(t) \phi_k(\mathbf{r}; \mathcal{R}(t))$$

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$$i\hbar \sum_k \frac{\partial}{\partial t} [c_k(t) \phi_k(\mathbf{r}; \mathcal{R}(t))] = H_0 \sum_k c_k(t) \phi_k(\mathbf{r}; \mathcal{R}(t))$$

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$$\langle \phi_j | : \quad i\hbar \sum_k \frac{\partial}{\partial t} [c_k(t) \phi_k(\mathbf{r}; \mathcal{R}(t))] = H_0 \sum_k c_k(t) \phi_k(\mathbf{r}; \mathcal{R}(t))$$

$$i\hbar \frac{\partial c_j}{\partial t} = \sum_k \left( \langle \phi_j | H_0 | \phi_k \rangle - i\hbar \langle \phi_j | \frac{\partial \phi_k}{\partial t} \rangle \right) c_k(t)$$

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$$\text{notation: } \begin{cases} \langle \phi_j | \partial \phi_k / \partial t \rangle & = & \langle \phi_j | \partial \phi_k / \partial \mathbf{R} \rangle \cdot \dot{\mathbf{R}} & = & \mathcal{T}_{jk}(t) \cdot \dot{\mathbf{R}} \\ \langle \phi_j | H_0 | \phi_k \rangle & = & H_{jk}^0 \end{cases}$$

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$$i\hbar \frac{\partial c_j}{\partial t} = \sum_k \left( H_{jk}^0(t) - i\hbar \mathcal{T}_{jk}(t) \cdot \dot{\mathbf{R}}(t) \right) c_k(t)$$



# Classical trajectory: different basis sets

Introducing

$$c_j(t) = d_j(t) e^{-\frac{i}{\hbar} \int_{t_0}^t H_{jj}^0(t') dt'}$$

$$i\hbar \frac{\partial d_j}{\partial t} = \sum_{k \neq j} \left( H_{jk}^0(t) - i\hbar \mathcal{T}_{jk} \cdot \dot{\mathbf{R}}(t) \right) e^{-\frac{i}{\hbar} \int_{t_0}^t [H_{kk}^0(t') - H_{jj}^0(t')] dt'} d_k(t)$$

- adiabatic basis set:  $H_{jk}^0 = U_j^{(a)} \delta_{jk}$

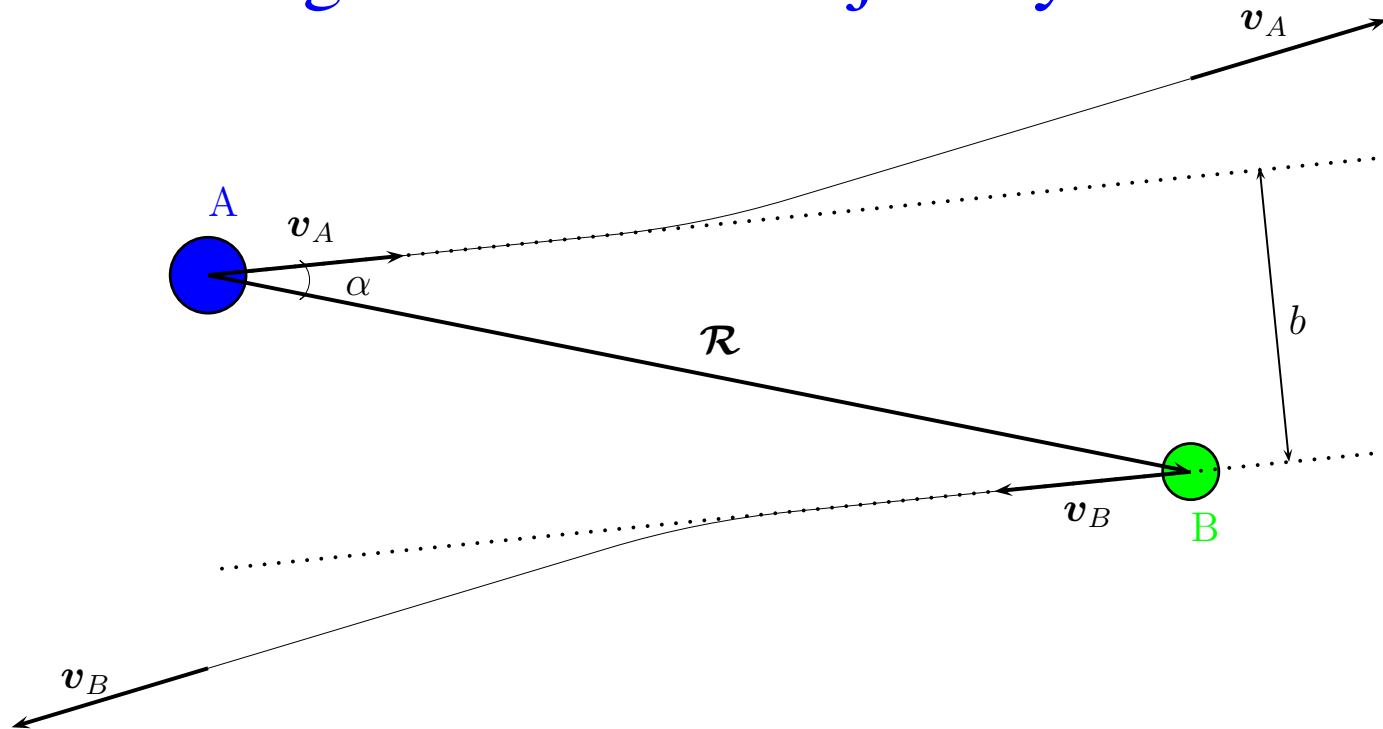
$$\frac{\partial d_j^{(a)}}{\partial t} = - \sum_{k \neq j} \mathcal{T}_{jk} \cdot \dot{\mathbf{R}}(t) e^{-\frac{i}{\hbar} \int_{t_0}^t [U_k^{(a)}(t') - U_j^{(a)}(t')] dt'} d_k^{(a)}(t)$$

- diabatic basis sets:  $\mathcal{T}_{jk} = 0 : \exists$  an infinite number!

$$i\hbar \frac{\partial d_j^{(d)}}{\partial t} = \sum_{k \neq j} U_{jk}^{(d)}(t) e^{-\frac{i}{\hbar} \int_{t_0}^t [U_{kk}^{(d)}(t') - U_{jj}^{(d)}(t')] dt'} d_k^{(d)}(t)$$

- quasi-diabatic basis sets

# Choosing the classical trajectory

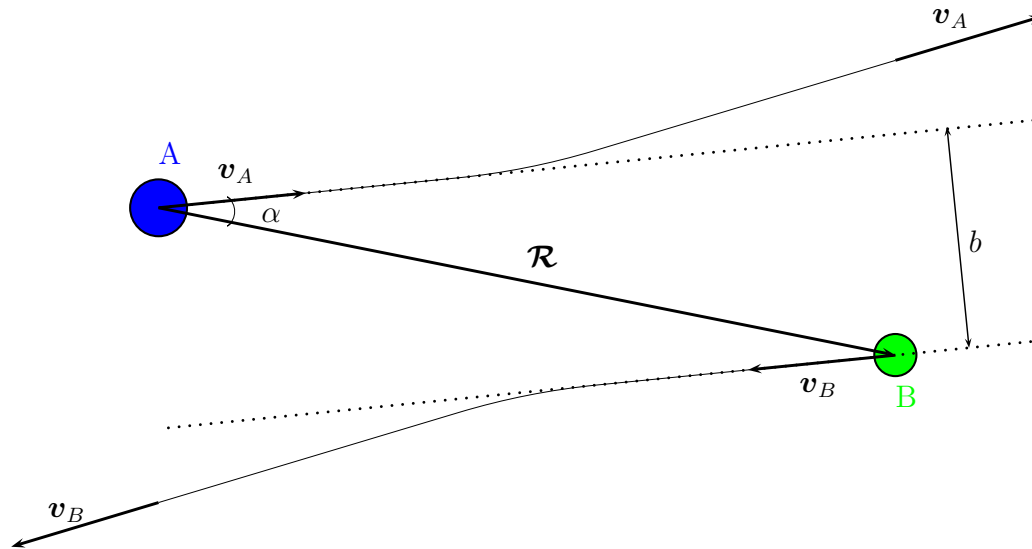


$$\mathbf{v}_A = \mathbf{V}_A - \mathbf{V}_G = \frac{M_B}{M} (\mathbf{V}_A - \mathbf{V}_B) = -\frac{M_B}{M} \mathbf{v}$$

$$\mathbf{v}_B = \mathbf{V}_B - \mathbf{V}_G = -\frac{M_A}{M} (\mathbf{V}_A - \mathbf{V}_B) = \frac{M_A}{M} \mathbf{v}$$

with  $M = M_A + M_B$  and  $\mathbf{v} = \dot{\mathcal{R}} = (\mathbf{V}_B - \mathbf{V}_A)$

## Choosing the classical trajectory II



$$\mathbf{L} = \mathbf{R} \times \mathbf{P}_{\mathcal{R}} = \mathbf{R} \times m\mathbf{v} \quad \text{with} \quad m = M_A M_B / (M_A + M_B)$$

$$L = m\mathcal{R}v \sin \alpha = m v b = m \mathcal{R}^2 \dot{\theta} \quad \text{with} \quad \mathcal{R}(\mathcal{R}, \theta) \text{ polar coordinates}$$

$$\text{total energy} \quad E = \frac{1}{2} m \dot{\mathcal{R}}^2 + \frac{1}{2} m \mathcal{R}^2 \dot{\theta}^2 + \bar{V}(\mathcal{R}) \quad \bar{V}(\mathcal{R}) \text{ trajectory potential}$$

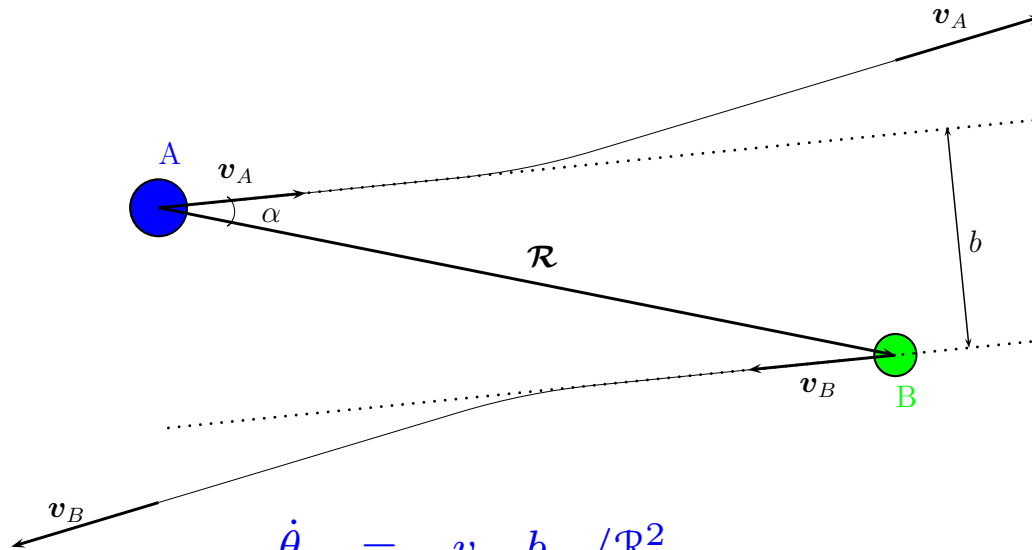
$$\text{for } \mathcal{R} \rightarrow \infty \quad E = \frac{1}{2} m v_{\infty}^2; \quad L = m v_{\infty} b_{\infty}$$

Equations of motion:

$$\dot{\theta} = v_{\infty} b_{\infty} / \mathcal{R}^2$$

$$\dot{\mathcal{R}} = \pm v_{\infty} \left[ 1 - \frac{b_{\infty}^2}{\mathcal{R}^2} - \frac{\bar{V}(\mathcal{R})}{E} \right]^{1/2}$$

# Choosing the classical trajectory III



$$\dot{\theta} = v_{\infty} b_{\infty} / \mathcal{R}^2$$

$$\dot{\mathcal{R}} = \pm v_{\infty} \left[ 1 - \frac{b_{\infty}^2}{\mathcal{R}^2} - \frac{\overline{V}(\mathcal{R})}{E} \right]^{1/2}$$

Special case: free motion or “elastic collision”:  $\overline{V}(\mathcal{R}) = 0$  hence  $v = v_{\infty}$

$$\mathcal{R}(t) = [b_{\infty}^2 + v_{\infty}^2 t^2]^{1/2}$$

$$\theta(t) = \text{Arctan}(v_{\infty} t / b_{\infty}) + \pi/2$$

*Rectilinear or impact parameter method.* For head-on collisions ( $b = 0$ ):

$$\mathcal{R} = v_{\infty} |t|$$

# Classical trajectory solution

Knowing  $\mathcal{R}(t)$ , solve for  $d_j(t)$

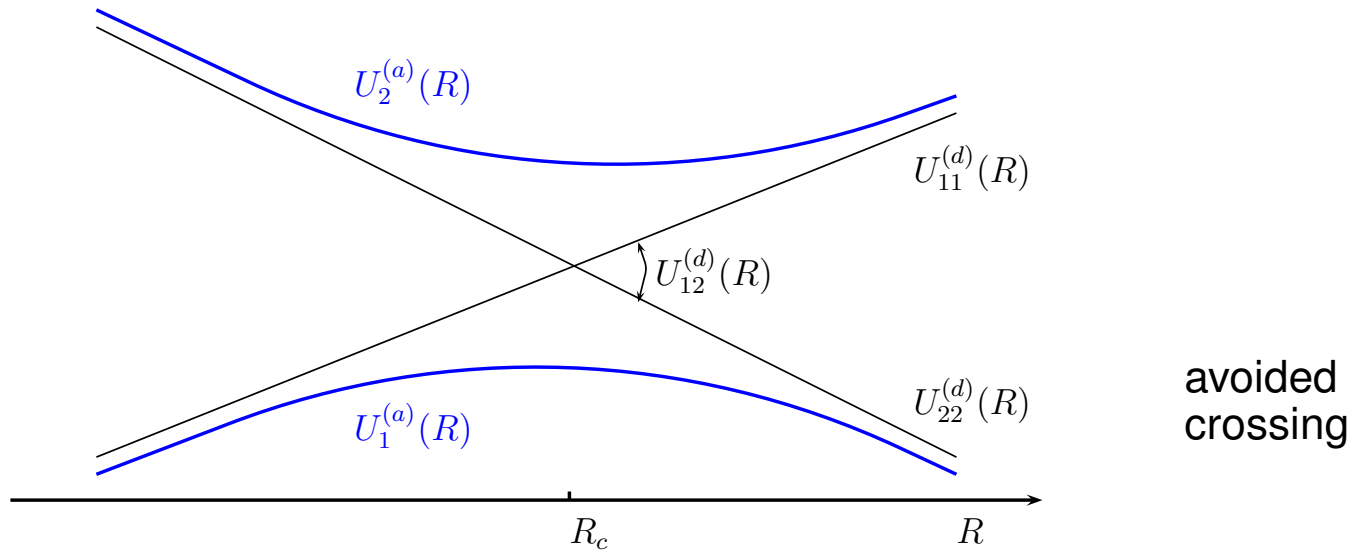
$$i\hbar \frac{\partial d_j}{\partial t} = \sum_{k \neq j} \left( H_{jk}^0(t) - i\hbar \mathcal{T}_{jk} \cdot \dot{\mathcal{R}}(t) \right) e^{-\frac{i}{\hbar} \int_{t_0}^t [H_{kk}^0(t') - H_{jj}^0(t')] dt'} d_k(t)$$

analytically, using perturbation theory, or numerically.

Using initial conditions  $d_k(t \rightarrow -\infty) = \delta_{j,k}$ ,

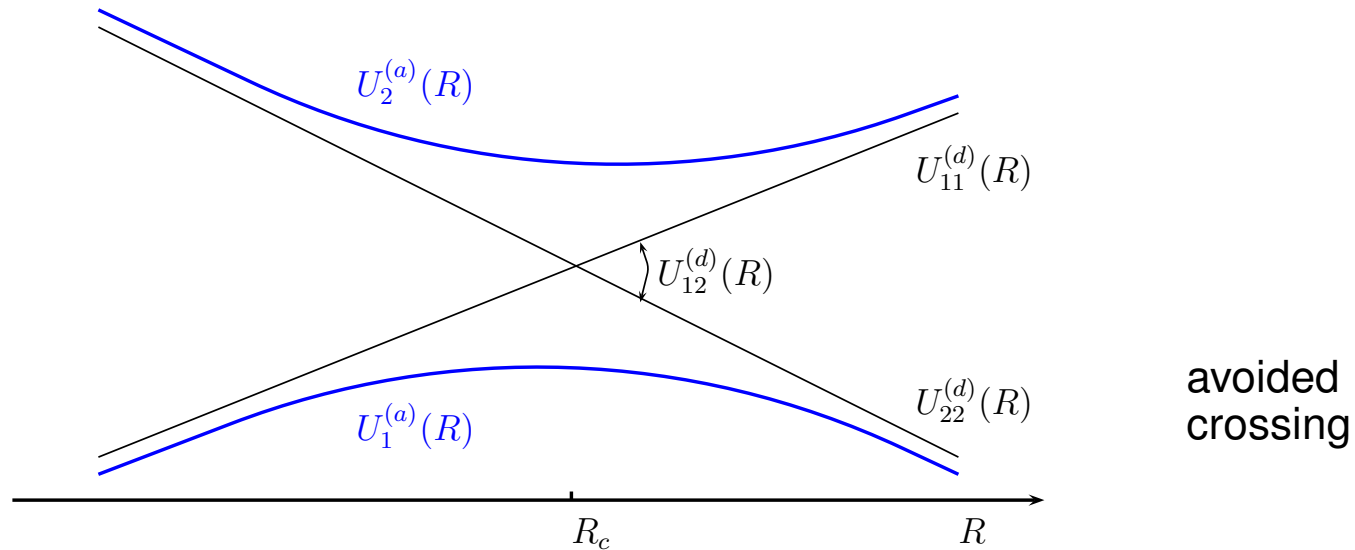
$$P_{j \rightarrow k} = |d_k(\infty)|^2$$

# Landau-Zener model



$$P_{1 \rightarrow 2}^{(d)} = 1 - e^{-2\pi\delta} \quad \text{with} \quad \delta = \frac{V_0^2}{\hbar v |F_1 - F_2|}$$

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$$P_{1 \rightarrow 2}^{(d)} = 1 - e^{-2\pi\delta} \quad \text{with} \quad \delta = \frac{V_0^2}{\hbar v |F_1 - F_2|}$$

- adiabatic passage :  $v \ll V_0^2 / |F_1 - F_2|$     hence  $\delta \gg 1$ :  $P_{1 \rightarrow 2}^{(d)} = 1$
- diabatic passage :  $v \gg V_0^2 / |F_1 - F_2|$     hence  $\delta \simeq 0$ :  $P_{1 \rightarrow 2}^{(d)} = 0$

## *Classical trajectory method: validity*

- ☺ describes transitions between quantum states due to classical motion
- ☹ NOT the influence of quantum transitions on the classical motion
- Valid if classical kinetic energy  $\gg$  quantum transition energies

Other ways of including auto-consistent energy exchange between quantum and classical:

- Mean field methods
- Trajectory surface hopping methods



# Mean field methods: quantum

Mean field = Time-dependent Hartree (TDH) = Time-dependent self-consistent field (TDSCF) = Hemiquantal = ...

$$H = T_R + T_r + V(r, R) \quad \text{with} \quad T_R = -\frac{\hbar^2}{2m} \nabla_R^2 \quad \text{and} \quad T_r = -\frac{\hbar^2}{2\mu} \nabla_r^2$$

Write the overall time-dependent wave function as:

$$\Psi(r, R, t) = \phi(r, t) F(R, t) e^{\frac{i}{\hbar} \int_0^t E_r(t') dt'}$$

$$\text{with} \quad \int |\phi(r, t)|^2 dr = \int |F(R, t)|^2 dR = 1 \quad \forall t$$

and  $E_r(t)$  arbitrary phase factor (to be fixed later)

# Quantum mean field methods: equations

$$\Psi(r, R, t) = \phi(r, t) F(R, t) e^{\frac{i}{\hbar} \int_0^t E_r(t') dt'}$$

$$i\hbar \frac{\partial \Psi(r, R, t)}{\partial t} = H \Psi(r, R, t) \quad \text{with} \quad H = T_R + T_r + V(r, R) :$$

$$i\hbar \left( \frac{\partial \phi}{\partial t} F + \phi \frac{\partial F}{\partial t} + \frac{i}{\hbar} E_r(t) \phi F \right) = H(r, R) \phi F$$

Left multiply by  $\langle F |$  (and integrate over  $R$ ) gives the equation for  $\phi(r, t)$ :

$$i\hbar \frac{\partial \phi}{\partial t} = \langle F | H | F \rangle_R \phi - i\hbar \left\langle F \left| \frac{\partial F}{\partial t} \right. \right\rangle_R \phi + E_r(t) \phi$$

Left multiply by  $\langle \phi |$  (and integrate over  $r$ ) gives the equation for  $F(R, t)$ :

$$i\hbar \frac{\partial F}{\partial t} = \langle \phi | H | \phi \rangle_r F - i\hbar \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right. \right\rangle_r F + E_r(t) F$$

Left multiply by  $\langle \phi | \langle F |$  (and integrate over both  $r$  and  $R$ ) gives :

$$i\hbar \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right. \right\rangle_r + i\hbar \left\langle F \left| \frac{\partial F}{\partial t} \right. \right\rangle_R - E_r(t) = \langle \langle \phi F | H | F \phi \rangle \rangle_{rR} = E$$

# Quantum mean field methods: usual phase choice

$$\begin{aligned}\Psi(r, R, t) &= \phi(r, t) F(R, t) e^{\frac{i}{\hbar} \int_0^t E_r(t') dt'} \\ i\hbar \frac{\partial \phi}{\partial t} &= \langle F|H|F \rangle_R \phi - i\hbar \left\langle F \left| \frac{\partial F}{\partial t} \right. \right\rangle_R \phi + E_r(t) \phi \\ i\hbar \frac{\partial F}{\partial t} &= \langle \phi|H|\phi \rangle_r F - i\hbar \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right. \right\rangle_r F + E_r(t) F\end{aligned}$$

Usual phase choice for (MC)TDH for instance (equivalent coordinates):

$$\left\langle F \left| \frac{\partial F}{\partial t} \right. \right\rangle_R = \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right. \right\rangle_r = 0, \quad \text{hence} \quad E_r(t) = -E \quad \text{and:}$$

$$\begin{aligned}\Psi(r, R, t) &= \phi(r, t) F(R, t) e^{-\frac{iEt}{\hbar}} \\ i\hbar \frac{\partial \phi}{\partial t} &= \left( \langle F|H|F \rangle_R \phi - E \right) \phi \\ i\hbar \frac{\partial F}{\partial t} &= \left( \langle \phi|H|\phi \rangle_r F - E \right) F\end{aligned}$$

Here  $r$  fast,  $R$  slow, we make a different choice:

$$i\hbar \left\langle F \left| \frac{\partial F}{\partial t} \right. \right\rangle_R = E; \quad i\hbar \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right. \right\rangle_r = E_r(t); \quad \text{and}$$

$$E_r(t) = \langle \langle \phi F | H_0 | F \phi \rangle \rangle \quad \text{with} \quad H_0(r; R) = -\frac{\hbar^2}{2\mu} \nabla_r^2 + V(r, R)$$

## Quantum mean field methods: phase choice (II)

$$\begin{aligned}\Psi(r, R, t) &= \phi(r, t) F(R, t) e^{\frac{i}{\hbar} \int_0^t E_r(t') dt'} \\ i\hbar \frac{\partial \phi}{\partial t} &= \langle F | H | F \rangle_R \phi - i\hbar \left\langle F \left| \frac{\partial F}{\partial t} \right\rangle_R \phi + E_r(t) \phi \\ i\hbar \frac{\partial F}{\partial t} &= \langle \phi | H | \phi \rangle_r F - i\hbar \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right\rangle_r F + E_r(t) F\end{aligned}$$

For this system (slow  $R$ , fast  $r$ ) we choose

$$\begin{aligned}i\hbar \left\langle F \left| \frac{\partial F}{\partial t} \right\rangle_R &= E; \quad i\hbar \left\langle \phi \left| \frac{\partial \phi}{\partial t} \right\rangle_r = E_r(t); \quad \text{and} \\ E_r(t) &= \langle \langle \phi F | H_0 | F \phi \rangle \rangle \quad \text{with} \quad H_0(r; R) = -\frac{\hbar^2}{2\mu} \nabla_r^2 + V(r, R)\end{aligned}$$

which gives the equations for  $\phi(r)$  and  $F(R)$ :

$$\begin{aligned}i\hbar \frac{\partial \phi}{\partial t} &= -\frac{\hbar^2}{2\mu} \frac{\partial^2 \phi}{\partial r^2} + \langle F | V(r, R) | F \rangle_R \phi \\ i\hbar \frac{\partial F}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 F}{\partial R^2} + \langle \phi | H_0 | \phi \rangle_r F\end{aligned}$$

# Mixed quantum-classical Mean field method

Treat  $R$  as a classical:  $R \rightarrow \mathcal{R}(t)$ ,  $F(R, t) = \delta (R - \mathcal{R}(t))$

Classical trajectories  $\mathcal{R}(t)$  determined by

$$\left\{ \begin{array}{l} \mathcal{R}(t = 0) \quad ; \quad \mathcal{P}(t = 0) \quad (\text{initial conditions}) \\ \dot{\mathcal{R}}(t) \quad = \quad \frac{1}{m} \mathcal{P}(t) \\ \dot{\mathcal{P}}(t) \quad = \quad -\nabla_{\mathcal{R}} \left( \langle \phi | H_0 | \phi \rangle_r \right) = -\frac{\partial \langle \phi | V(r, \mathcal{R}) | \phi \rangle_r}{\partial \mathcal{R}} \end{array} \right.$$

Quantum motion determined by

$$i\hbar \frac{\partial \phi(r, t)}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \phi(r, t)}{\partial r^2} + V(r, \mathcal{R}(t)) \phi(r, t)$$

Total energy

$$E = \frac{\mathcal{P}^2}{2m} + \langle \phi | H_0(r, \mathcal{R}(t)) | \phi \rangle_r$$

# Energy conservation

$$E = \frac{\mathcal{P}^2}{2m} + \langle \phi | H_0(r, \mathcal{R}(t)) | \phi \rangle_r$$
$$\frac{\partial E}{\partial t} = \frac{\mathcal{P}}{m} \dot{\mathcal{P}} + \frac{\partial}{\partial t} \left( \langle \phi(r, t) | H_0(r, \mathcal{R}(t)) | \phi(r, t) \rangle_r \right)$$

$$\frac{\partial}{\partial t} \left( \langle \phi(r, t) | H_0(r, \mathcal{R}(t)) | \phi(r, t) \rangle_r \right) = \left\langle \phi(r, t) \left| \frac{\partial H_0(r, \mathcal{R}(t))}{\partial t} \right| \phi(r, t) \right\rangle_r$$
$$+ \left\langle \frac{\partial \phi(r, t)}{\partial t} \left| H_0(r, \mathcal{R}(t)) \right| \phi(r, t) \right\rangle_r + \left\langle \phi(r, t) \left| H_0(r, \mathcal{R}(t)) \right| \frac{\partial \phi(r, t)}{\partial t} \right\rangle_r$$

$$\frac{\partial H_0(r, \mathcal{R}(t))}{\partial t} = \frac{\partial H_0}{\partial \mathcal{R}} \frac{\partial \mathcal{R}}{\partial t} = \frac{\partial V(r, \mathcal{R})}{\partial \mathcal{R}} \dot{\mathcal{R}}$$

$$\frac{\partial E}{\partial t} = \frac{\mathcal{P}}{m} \dot{\mathcal{P}} + \dot{\mathcal{R}} \left\langle \phi(r, t) \left| \frac{\partial V(r, \mathcal{R})}{\partial \mathcal{R}} \right| \phi(r, t) \right\rangle_r = 0$$

## Mean field: Strong and weak points

- ☺ describes transitions between quantum states due to classical motion
- ☺ AND the influence of quantum transitions on the classical motion
- ☺ relatively simple to implement
- ☺ total energy conserved
- ☺ total angular momentum conserved (dynamics deriving from a potential)
- ☺ no dependence on the choice of a basis set for  $\phi(r, t)$  propagation
- ☹ quantum-classical energy exchanges are averaged
- if  $\langle \chi_1 | V(r, \mathcal{R}) | \chi_1 \rangle_r$  and  $\langle \chi_2 | V(r, \mathcal{R}) | \chi_2 \rangle_r$  are very different, validity of the dynamics??? (small probability or dissociative channels)
- ☹ problem with micro-reversibility, e.g. near an avoided crossing:  $V_1(R)$  before and  $(1 - P)V_1 + PV_2$  for  $R$  after the crossing ( $P = P_{1 \rightarrow 2}$ ): but inverting the trajectory does not give back  $P_1$ .

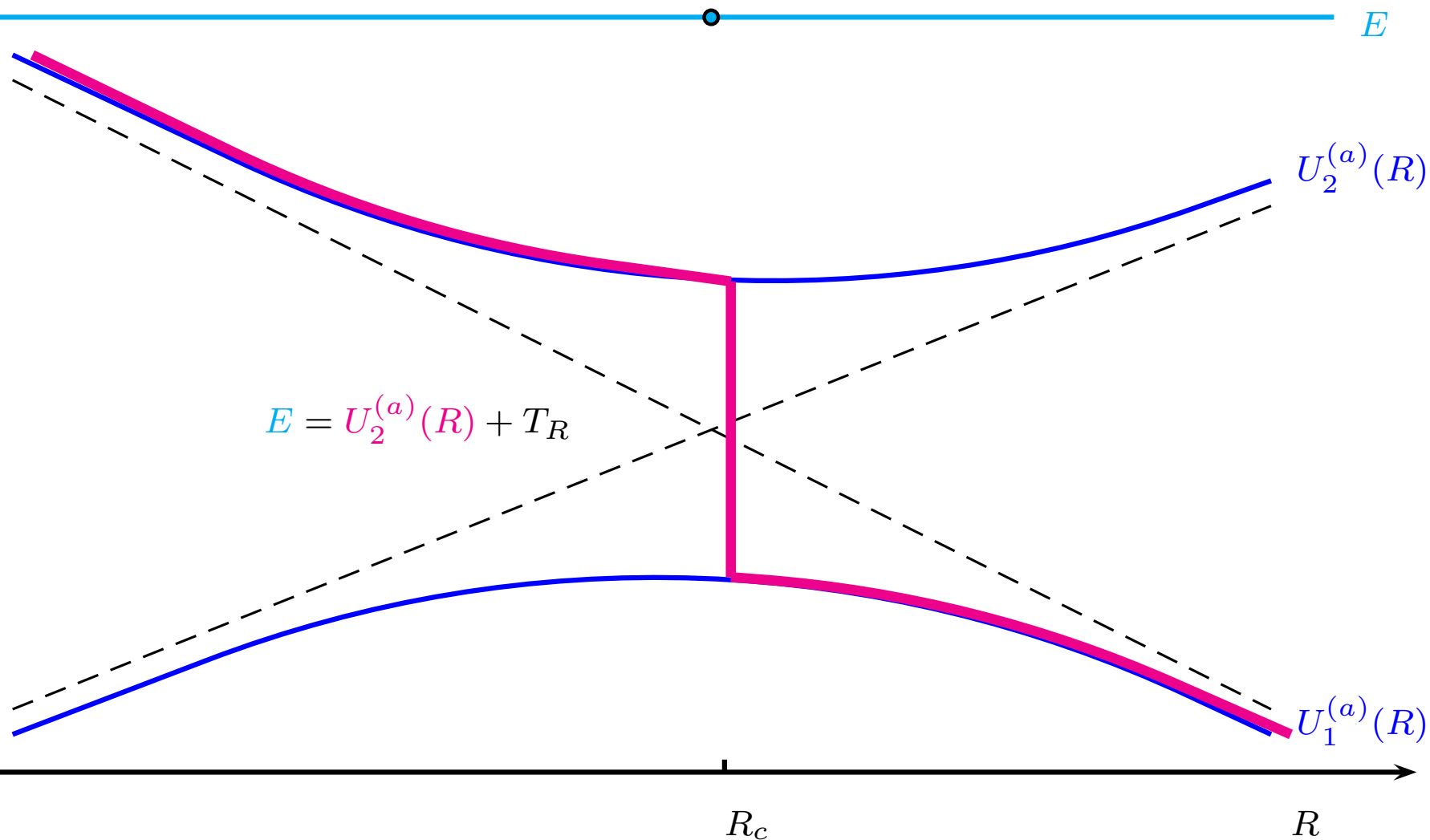
Good method for similar states, especially at high kinetic energy / energy difference between quantum states.

# Trajectory surface hopping (TSH) methods: principle

- Classical coordinates evolve on 1 PES at a time (1 quantum state)
- Transitions = “hops” between surfaces at times
- adjust classical momenta (velocities) to account for difference in potential energy at a hop:  $\vec{h}$
- methods differ by
  - times for hops
  - probabilities for hops  $P_{j \rightarrow k}(t)$
  - choice of  $\vec{h}$  to adjust momenta (velocities) at a hop
  - how to sum up trajectories (ants or anteatater)

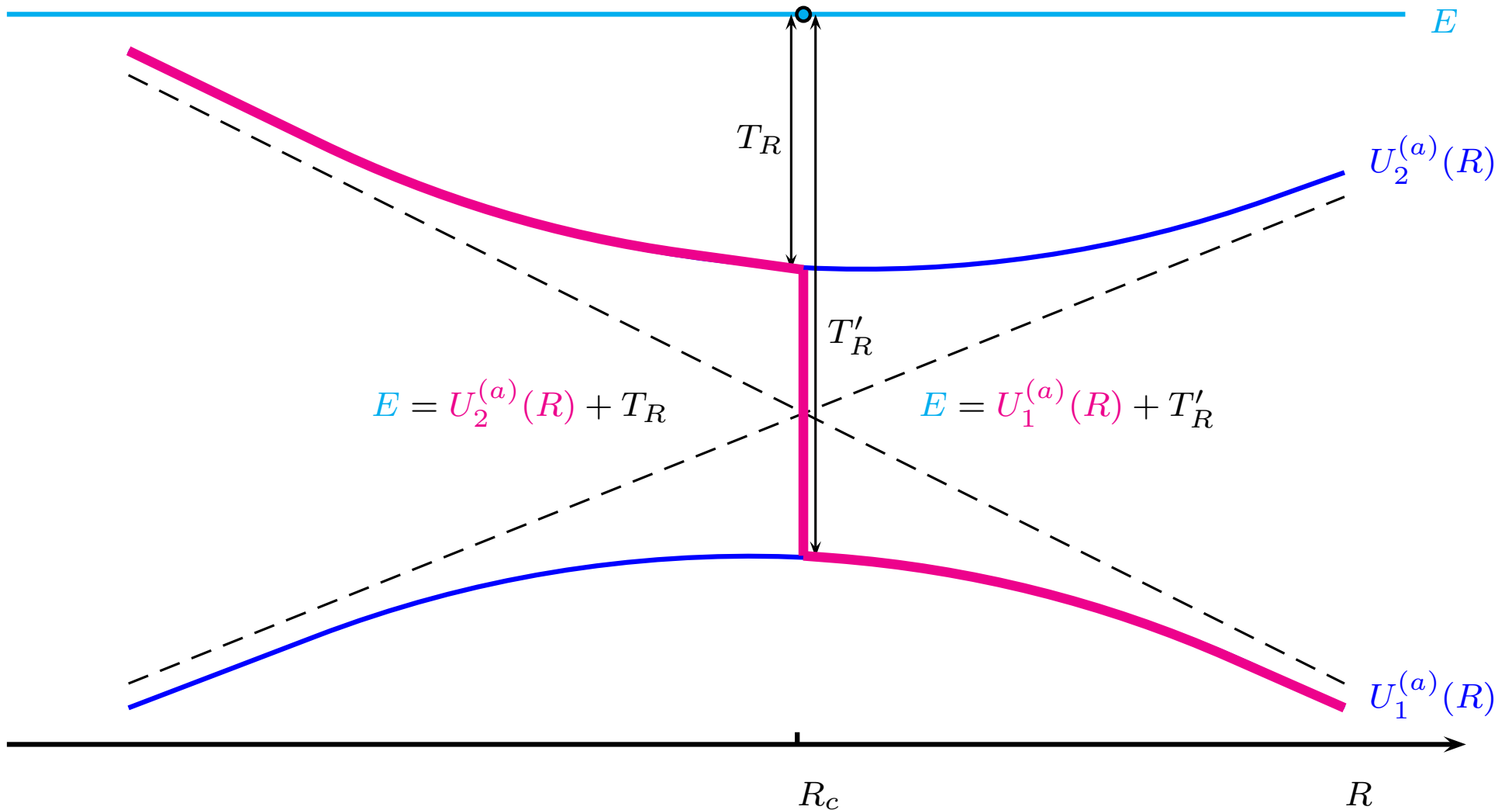


# A simple example of TSH

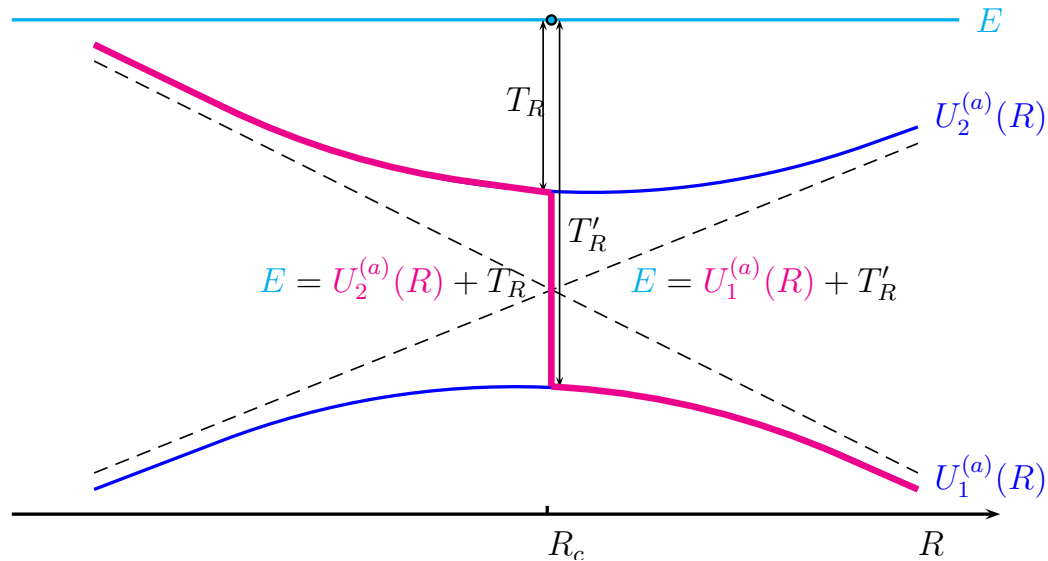




# A simple example of TSH



## TSH: a simple example II



Hopping probability  
= Landau-Zener  
at the avoided crossing

$$E = \frac{1}{2m} \left( \mathcal{P}_R^{(2)} \right)^2 + U_2^{(a)}(R_c) = \frac{1}{2m} \left( \mathcal{P}_R^{(1)} \right)^2 + U_1^{(a)}(R_c)$$

$$\left( \mathcal{P}_R^{(1)} \right)^2 = \left( \mathcal{P}_R^{(2)} \right)^2 + 2m \left( U_2^{(a)}(R_c) - U_1^{(a)}(R_c) \right)$$

- if  $\left( U_2^{(a)}(R_c) - U_1^{(a)}(R_c) \right) > 0$  all the hops are allowed
- if  $\left( U_2^{(a)}(R_c) - U_1^{(a)}(R_c) \right) < 0$ , some can give  $\left( \mathcal{P}_R^{(1)} \right)^2 < 0$ : *forbidden hops*

# MDQT method (Tully)

“fewest switches” or “molecular dynamics with quantum transitions” method (Tully, 1990)

$$H = T_R + H_0(\mathbf{r}, \mathbf{R}) \quad \mathbf{r} \text{ quantum,} \quad \mathbf{R} = \mathcal{R}(t) \text{ classical}$$

Notation:

$$H_{jk}^0(\mathbf{R}) = \langle \phi_j(\mathbf{r}; \mathbf{R}) | H_0(\mathbf{r}, \mathbf{R}) | \phi_k(\mathbf{r}; \mathbf{R}) \rangle_{\mathbf{r}}$$
$$(\mathcal{T}_{jk})_{\alpha} = \left\langle \phi_j \left| \frac{\partial}{\partial R_{\alpha}} \right| \phi_k \right\rangle_{\mathbf{r}} \quad \alpha = 1, N_c : \quad \mathcal{T}_{jk}(\mathbf{R}) = \langle \phi_j(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} | \phi_k(\mathbf{r}; \mathbf{R}) \rangle_{\mathbf{r}}$$

Expand  $\psi(\mathbf{r}, t)$  in a basis set  $\phi$  (cf. classical trajectory method):

$$\psi(\mathbf{r}, t) = \sum_l c_l(t) \phi_l(\mathbf{r}; \mathcal{R}(t))$$

Reporting in the  $t$ -dependent Schrödinger equation gives:

$$\dot{c}_k = \sum_l c_l \left( -\frac{i}{\hbar} H_{kl}^0 - \dot{\mathcal{R}} \cdot \mathcal{T}_{kl} \right)$$

Define density matrix coefficients:

$$a_{jk}(t) = c_j(t) c_k^*(t)$$

$$\dot{a}_{jk} = \sum_l \left\{ a_{lk} \left( -\frac{i}{\hbar} H_{jl}^0 - \dot{\mathcal{R}} \cdot \mathcal{T}_{jl} \right) + a_{jl} \left( \frac{i}{\hbar} H_{kl}^{0*} - \dot{\mathcal{R}} \cdot \mathcal{T}_{kl}^* \right) \right\}.$$

## MDQT method (Tully) II

$P_j(t) = a_{jj}(t) = |c_{jj}(t)|^2$  population of quantum state  $j$ :

$$\frac{dP_j}{dt} = \dot{a}_{jj} = \sum_{l \neq j} B_{jl} \quad \text{with} \quad B_{jl} = \frac{2}{\hbar} \Im m \left( a_{jl}^* H_{jl}^0 \right) - 2 \Re e \left( a_{jl}^* \dot{\mathbf{R}} \cdot \mathcal{T}_{jl} \right)$$

( $\phi$  real hence  $\mathcal{T}_{jj} = 0$ )

$B_{jl}$  is interpreted as the probability for switching from  $j$  to  $l$  per unit of time:

$$P_{j \rightarrow l}(t) = \frac{-\Delta t B_{jl}}{a_{jj}}$$

## MDQT: implementation

Initial conditions:  $\mathcal{R}_\alpha(t=0)$ ,  $\mathcal{P}_\alpha(t=0)$ ,  $c_k(t=0)$ , initial quantum state  $j_0$  for  $\mathcal{R}(t)$

At each time step, solve:

$$\begin{cases} \dot{\mathcal{R}}_\alpha(t) &= \frac{1}{M_\alpha} \mathcal{P}_\alpha(t) \\ \dot{\mathcal{P}}_\alpha(t) &= -\nabla_{\mathcal{R}_\alpha} H_{jj}^0(\mathcal{R}) \end{cases} \quad \alpha = 1, N_c$$

and

$$\dot{c}_k = \sum_l c_l \left( -\frac{i}{\hbar} H_{kl}^0 - \dot{\mathcal{R}} \cdot \mathcal{T}_{kl} \right)$$

Calculate  $P_{j \rightarrow k}(t)$  for all  $k$  and compare to random number  $r$ :

if  $P_{j \rightarrow 1}(t) > r$ , hop to 1; if  $P_{j \rightarrow 1}(t) < r < P_{j \rightarrow 1}(t) + P_{j \rightarrow 2}(t)$ , switch to 2;...

If there is a hop, adjust all the momenta so that total energy is conserved, using vector  $\mathbf{h}$

$$\mathcal{P}^k - \mathcal{P}^j = \gamma \mathbf{h}$$

and determine  $\gamma$  using energy conservation:

$$U_j(\mathbf{R}) + \sum_{\alpha=1}^N \frac{1}{2M_\alpha} (\mathcal{P}_\alpha^j)^2 = U_k(\mathbf{R}) + \sum_{\alpha=1}^N \frac{1}{2M_\alpha} (\mathcal{P}_\alpha^k + \gamma h_\alpha)^2$$

In Tully's initial paper,  $\mathbf{h} = \mathcal{T}_{jk}$  for a hop from  $j$  to  $k$ . Other possibilities have been tested.

REPEAT for A NUMBER of TRAJECTORIES

## MDQT Strong and weak points

- ☺ describes transitions between quantum states due to classical motion
- ☺ AND the influence of quantum transitions on the classical motion
- ☺ relatively simple to implement
- ☺ total energy conserved
- ☺ total angular momentum conserved when working in internal coordinates
- ☺ no problem handling very different potentials, weak probabilities
- ☹ because of forbidden hops,  $P_{class}(j) \neq |c_j|^2$  ( $P_{class}(j)$  is then used).
- ☹ the results can depend on the basis set used (same reason)
- ☹ Non adiabatic couplings are often difficult to treat numerically
- ☹ total angular momentum not conserved in cartesian coordinates in the standard ( $\vec{h} = \mathcal{T}_{jk}$ ) version (conserved when using  $\vec{h} = \nabla V_j - \nabla V_k$ )

Good method in general, very flexible, but to be handled with care when quantum coherence is important.



## A few (basic) references

- **Classical trajectory method :**

J.B. Delos, W.R. Thorson et S.K. Knudson, «*Semiclassical theory of inelastic collisions. I. Classical picture and semiclassical formulation*», Physical Review A, vol. **6**, pages 709-720 (1972).

- **Mean field method:**

- The best introduction is given in pages 8-9 of the (very big!) review paper on MCTDH :

M.H. Beckle, A. Jäckle, G.A. Worth et H.D. Meyer, «*The multiconfiguration time-dependent Hartree (MCTDH) method: A highly efficient algorithm for propagating wavepackets*», Physics Reports, vol. **324**, pages 1-105 (2000).

- A short (historical) presentation :

R.B. Gerber, V. Buch et M.A. Ratner, «*Time-dependent self-consistent field approximation for intramolecular energy transfer. I. Formulation and application to dissociation of van der Waals molecules*», Journal of Chemical Physics vol. **77**, pages 3022-3030 (1982).

- **Tully's surface hopping trajectory by Tully himself :**

J.C. Tully, «*Molecular dynamics with electronic transitions*», Journal of Chemical Physics, vol. **93**, pages 1061-1071 (1990).