

Molecular Dynamics: Adiabatic Regime

Objective: solve the time-dependent Schrödinger Equation (TDSE) for electrons and nuclei.

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

where $\hat{H}(r, R) = \hat{T}_e(r) + V_{eN}(r, R) + V_{ee}(r) + \hat{T}_N(R) + V_{NN}(R)$

Born-Oppenheimer Approximation:

$$\Psi(r; R) \approx \chi_a(R, t) \psi_a(r; R) \quad (1)$$

Obs.: for now we are disregarding the time-dependence on the electronic part.

Substitute (1) into TDSE, multiply from left by $\psi_a^*(r; R)$, integrate over r

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \chi_a(R, t) &= \langle \psi_a | \hat{H}_{el} | \psi_a \rangle \chi_a(R, t) - \sum_n \frac{\hbar^2}{2M_n} \langle \psi_a(r; R) | \nabla_n^2 \psi_a(r; R) \chi_a(R, t) \rangle \\ &= \varepsilon_a(R) \chi_a(R, t) \\ &\quad - \sum_n \frac{\hbar^2}{2M_n} [\langle \psi_a | \psi_a \rangle \nabla_n^2 + 2 \langle \psi_a | \nabla_n \psi_a \rangle \nabla_n + \langle \psi_a | \nabla_n^2 \psi_a \rangle] \chi_a(R, t) \end{aligned}$$

Molecular Dynamics: Adiabatic Regime

$$i\hbar \frac{\partial}{\partial t} \chi_a(R, t) = \varepsilon_a(R) \chi_a(R, t) - \sum_n \frac{\hbar^2}{2M_n} [\langle \psi_a | \psi_a \rangle \nabla_n^2 + 2\langle \psi_a | \nabla_n \psi_a \rangle \nabla_n + \langle \psi_a | \nabla_n^2 \psi_a \rangle] \chi_a(R, t)$$

For systems in stationary state without magnetic fields $\psi_a(r; R) \in \mathbb{R}$;

and $\nabla_n \langle \psi_a | \psi_a \rangle = \langle \nabla_n \psi_a | \psi_a \rangle + \langle \psi_a | \nabla_n \psi_a \rangle = 0$.

Therefore $\langle \psi_a | \nabla_n \psi_a \rangle = -\langle \nabla_n \psi_a | \psi_a \rangle = 0$

$\langle \psi_a | \nabla_n^2 \psi_a \rangle \chi(R, t)$ is a small term and can be disregarded.

Thus we end up with the following TDSE for the nuclei in the PSE given by $\varepsilon_a(R)$

$$i\hbar \frac{\partial}{\partial t} \chi_a(R, t) = \varepsilon_a(R) \chi_a(R, t) - \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2 \chi_a(R, t)$$

Molecular Dynamics: Adiabatic Regime

Traditional way:

- 1) begin with a likely atomic configuration and velocities;
- 2) solve the electronic structure problem for this atomic configuration;
- 3) use the the Hellmann-Feynman theorem to calculate forces;
- 4) move the atoms according to classical equations of motion;
- 5) take new atomic coordinates, go to step (2) and continue

DFT-Energy Functional:

$$E [\{\psi_i\}, \{R_n\}, \{\alpha_\nu\}] = \sum_i \int_{\Omega} d^3r \psi_i^*(r) [-(\hbar^2/2m)\nabla^2]\psi_i(r) + U [n(r), \{R_n\}, \{\alpha_\nu\}]$$

$\{R_n\} \equiv$ nuclear positions

$\{\alpha_\nu\} \equiv$ external constraints on the system, like volume, strain, etc.

Minimization of the energy functional with respect to orbitals (subject to orthonormality constraint) leads to SCF-KS equations

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \frac{\delta U}{\delta n(r)} \right\} \psi_i(r) = \varepsilon_i \psi_i(r)$$

Solution of SCF-KS requires repeated matrix diagonalizations that scale as N^3 , rapidly growing with the size of the problem!!

Optimization by Simulated Annealing

Kirkpatrick, Gelatt, Vecchi. *Science* (1983), **220**, 671.

Regard the minimization of the KS functional as an optimization problem which can be solved by applying the concept of simulated annealing.

In this approach an objective function $O(\{\beta\})$ is minimized relative to the parameters $\{\beta\}$ with a Boltzman-type probability distribution via Monte Carlo procedure

$$\propto e^{-\frac{O(\{\beta\})}{T}}$$

In this case the objective function is the total-energy functional E and the variational parameters are the coefficients of the expansion of the KS orbitals in some convenient basis.

$$\psi_i = \sum_k C_k^i \varphi_k$$

This way diagonalization and self-consistency are achieved *simultaneously*.

Diagonalization scales as N^3 whereas this method scales as $M \log(M)$.

The method has general applicability in the context of functional minimization: in classical and quantum field theories, CI schemes, etc.

Molecular Dynamics: Car-Parrinello Method

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Unified Approach for Molecular Dynamics and Density-Functional Theory

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We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

In other words:

The Car-Parrinello Molecular Dynamics (CPMD) method is an extended MD scheme in which the electronic degrees of freedom are handled explicitly and provides for a stable atomic dynamics of real world systems in a computationally tractable way.

Molecular Dynamics: Car-Parrinello Method

Introduce the Car-Parrinello Lagrangean (disregarding external constraints):

$$\begin{aligned}\mathcal{L} &= \mathcal{K} - \mathcal{V} \\ &= \sum_j \frac{1}{2} \mu \langle \dot{\varphi}_j | \dot{\varphi}_j \rangle + \sum_n \frac{1}{2} M_n \dot{R}_n^2 - E[\{\varphi\}, \{R_n\}] + \sum_{i,j} \lambda_{ij} [\langle \varphi_i | \varphi_j \rangle - \delta_{ij}]\end{aligned}$$

subject to the condition $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ for the single-particle orbital functions:

$$n(r) = \sum_i |\varphi_i(r)|^2$$

μ is an arbitrary parameter of appropriate units.

The Euler-Lagrange equations generate dynamics for the parameters:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}} = \frac{\partial \mathcal{L}}{\partial q} \quad \{q\} = \{\varphi\}, \{R_n\}$$

Molecular Dynamics: Car-Parrinello Method

Equations of motion:

$$\begin{aligned} \text{electrons} \longrightarrow \mu_j \ddot{\varphi}_j(r, t) &= -\frac{\delta E}{\delta \varphi_j^*} + \sum_i \lambda_{ij} \varphi_i \\ &= \frac{\delta \langle \varphi | \hat{H}_{el} | \varphi \rangle}{\delta \varphi_j^*} + \sum_i \lambda_{ij} \varphi_i \end{aligned}$$

more practical: in terms of the coefficients of $\varphi_i = \sum_k C_{ki} \chi_k$

$$\mu_j \ddot{C}_{kj} = -\frac{\delta E(\{C\})}{\delta C_{kj}} + \sum_i \lambda'_{ij} C_{kj}$$

$$\begin{aligned} \text{nuclei} \longrightarrow M_n \ddot{R}_n &= -\nabla_n E \\ &= \frac{-\partial \langle \varphi | \hat{H}_{el} | \varphi \rangle}{\partial R_n} \end{aligned}$$

The *nuclear dynamics has real physical* meaning whereas the dynamics associated with the parameters $\{\varphi\}$ (or C_{ki}) *is fictitious*.

The term $\frac{\delta E}{\delta \varphi_j^*}$ is calculated for fixed ion positions, unlike Hellmann-Feynman.

Molecular Dynamics: Car-Parrinello Method

Define the fictitious kinetic energy:

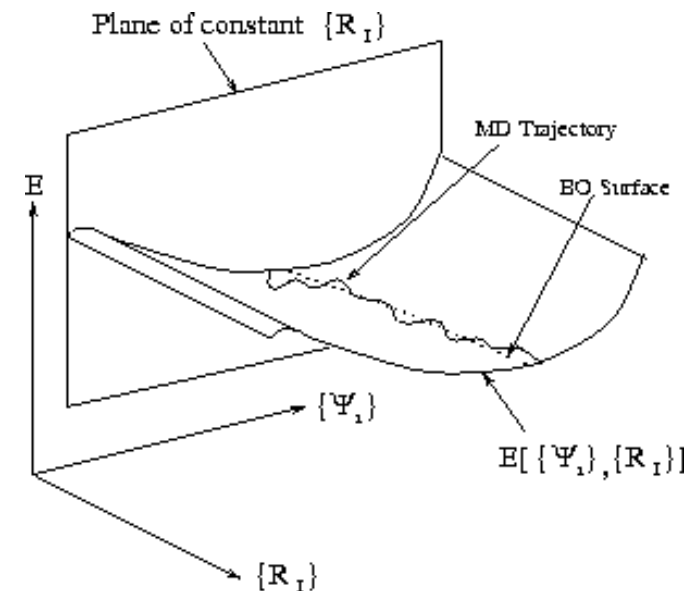
$$\mathcal{K} \equiv K_{el} + K_n = \sum_j \frac{1}{2} \mu \langle \dot{\psi}_j | \dot{\psi}_j \rangle + \sum_n \frac{1}{2} M_n \dot{R}^2$$

and the associated temperatures (T).

In the simulated annealing, by “dissipative” variation of the velocities, the temperature of the system can be slowly reduced, and for $T \rightarrow 0$ the equilibrium state of minimal E is reached.

$K_{el} \propto T_{el} \rightarrow 0$ corresponds to Born-Oppenheimer dynamics.

- If $T_{el} \neq 0$ the system is out of the BO-PES, therefore the nuclear forces calculated by Hellmann-Feynman might be wrong.
- $T_{el} \rightarrow 0$ only for very small time steps and this is not practical. Thus the criteria is $K_{el} \gg K_n$, so that electrons remain around the actual BO-PES.



Molecular Dynamics: Car-Parrinello Method

The difference between the *Car-Parrinello molecular dynamics* (for example in the code "CPMD") and Bohn-Oppenheimer molecular dynamics (implemented in "VASP", "CPMD", "CP2K", ... most DFT codes):

- Car-Parrinello dynamics is stable, ie. the constants of motion remain constant, whereas in BO-dynamics there is always a drift, which can be made smaller and smaller by increasing the accuracy of the forces (and possibly decreasing the time step).
- The time step in Car-Parrinello dynamics is shorter than in BO-dynamics, but the evaluation is faster on the computer.
- Generally it is regarded difficult to calculate metals with Car-Parrinello dynamics, at least without "tricks" (Blöchl-Parrinello thermostat on the electrons). The original Car-Parrinello dynamics does not have fractional occupation numbers.
- one can go up to some hundreds of atoms, closer to 1000. Long MD trajectories might take a while.



Quantum Dynamics: Adiabatic Regime

Car-Parrinello Dynamics

Euler-Lagrange equations: $\frac{d}{dt} \frac{d\mathcal{L}}{d\dot{q}} = \frac{\partial \mathcal{L}}{\partial q}$

Classical Lagrangean: $\mathcal{L} = T - V = \sum_n \frac{1}{2} M_n \dot{R}^2 - \varepsilon_a(R)$

$$\longrightarrow M_n \ddot{R}_n = - \frac{\partial \varepsilon_a(R)}{\partial R_n}$$

Car-Parrinello Lagrangean: $\mathcal{L} = \sum_n \frac{1}{2} M_n \dot{R}^2 - \varepsilon_a(R)$
 $+ \sum_j \frac{1}{2} \mu_j \langle \dot{\varphi}_j | \dot{\varphi}_j \rangle + \sum_{i,j} \lambda_{ij} [\langle \varphi_i | \varphi_j \rangle - \delta_{ij}]$

$$\longrightarrow M_n \ddot{R}_n = - \frac{\partial \varepsilon_a(R)}{\partial R_n}$$

$$\longrightarrow \mu_j \ddot{\varphi}_j = \frac{\delta \langle \psi_a | \hat{H}_{el} | \psi_a \rangle}{\delta \varphi_j^*} + \sum_i \lambda_{ij} \varphi_i$$

Quantum Dynamics: Nonadiabatic Regime

For the atomic-level simulation of some dynamical processes it is necessary to go beyond the Born-Oppenheimer approximation, by incorporating transitions among different potential energy surfaces:

- photoinduced processes,
- electron induced processes,
- energetic collisions,
- nonradiative relaxation in large molecules or in condensed phases,
- conical intersections,
- infrequent events,
- electron transfer, etc.

Born-Oppenheimer (adiabatic) approximation is *inadequate* when nuclear motion evolves on more than one potential energy surface, with transitions among them.

Landau-Zener Effect

Landau-Zener problem of nonadiabatic level crossing (1932)

Consider a *two-level system*

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{V} \\ \hat{H}_0 &= E_a(\lambda)|\phi_a\rangle\langle\phi_a| + E_b(\lambda)|\phi_b\rangle\langle\phi_b| \\ \hat{V} &= V(\lambda)(|\phi_a\rangle\langle\phi_b| + |\phi_b\rangle\langle\phi_a|)\end{aligned}\quad \mathcal{H}(\lambda) = \begin{bmatrix} H_{aa}(\lambda) & V(\lambda) \\ V(\lambda) & H_{bb}(\lambda) \end{bmatrix}$$

$$E_{1,2}(\lambda) = \frac{E_a(\lambda) + E_b(\lambda)}{2} \pm \frac{1}{2} \sqrt{[E_a(\lambda) - E_b(\lambda)]^2 + 4V(\lambda)^2}$$

the parameter λ can be (reaction) coordinates $\{\mathbf{R}\}$, or time-dependent external fields $\mathbf{E}(t)$, $\mathbf{B}(t)$, etc. Let us assume $\lambda = R(t)$.

$|\phi_a\rangle$, $|\phi_b\rangle$ are called *diabatic states*

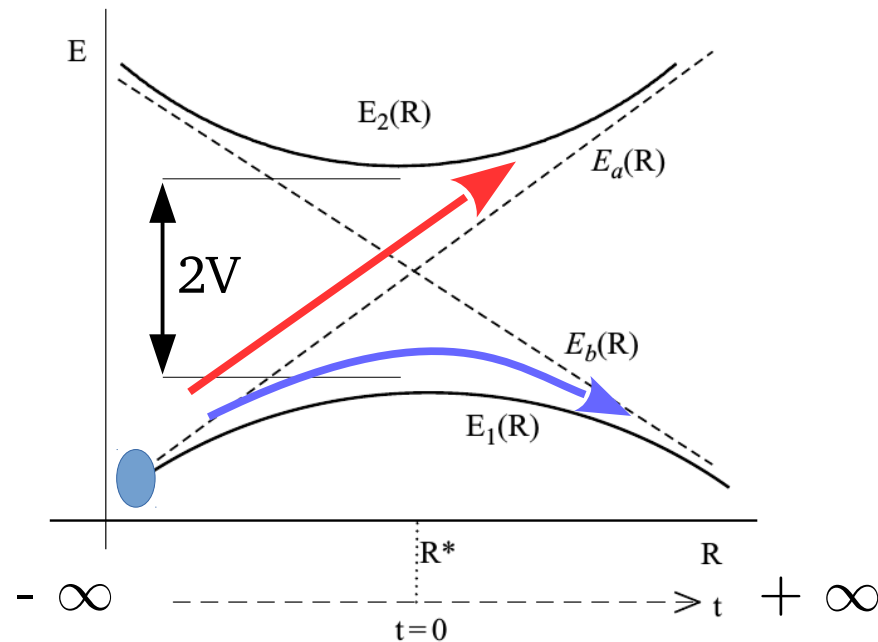
a **diabatic** electronic state is one that *does not change its physical character* as one moves along a reaction coordinate.

$|\psi_1\rangle$, $|\psi_2\rangle$ are called *adiabatic states*: $\hat{H}(R)|\psi(R)\rangle = E(R)|\psi(R)\rangle$

an **adiabatic** electronic state, i.e. the BO states, *change its physical character* as one moves along a reaction coordinate.

Landau-Zener Effect

adiabatic \times nondiabatic (or diabatic) processes in the Born-Oppenheimer sense



--- nondiabatic PES

— adiabatic PES

equivalent descriptions:

$$\begin{aligned}\Psi(R) &= C_1(R)\psi_1(R) + C_2\psi_2(R) \\ &= c_a(R)\phi_a(R) + c_b(R)\phi_b(R)\end{aligned}$$

$$|C_1(R)|^2 + |C_2(R)|^2 = |c_a(R)|^2 + |c_b(R)|^2 = 1$$

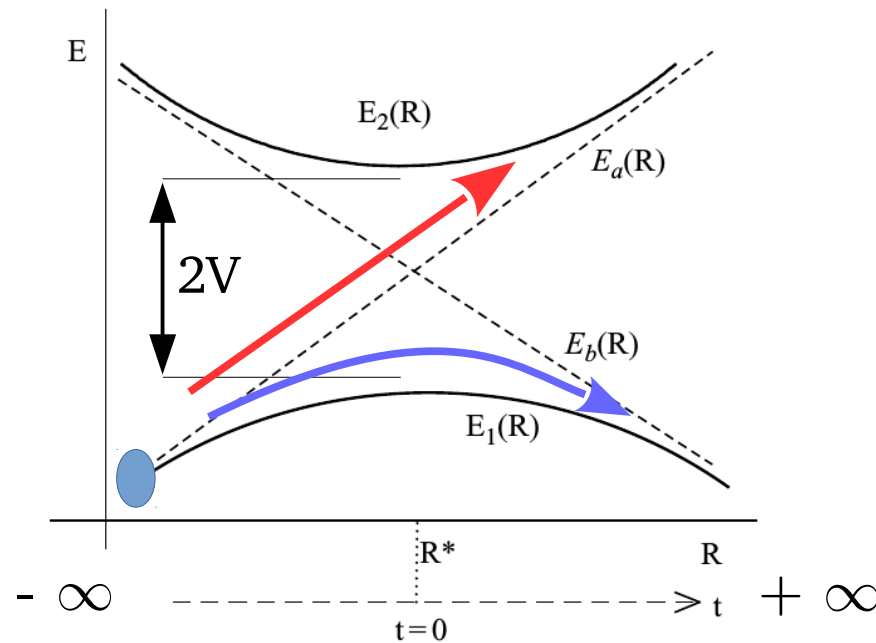
$$\text{initial state: } |C_1(R \rightarrow -\infty)|^2 = |c_a(R \rightarrow -\infty)|^2 = 1$$

$$\text{adiabat probability}(P_{ad}): |C_1(R \rightarrow \infty)|^2 = |c_b(R \rightarrow \infty)|^2 \equiv P_{1 \rightarrow 1} = P_{a \rightarrow b}$$

$$\text{diabat probability}(P_{ad}): |C_2(R \rightarrow \infty)|^2 = |c_a(R \rightarrow \infty)|^2 \equiv P_{1 \rightarrow 2} = P_{a \rightarrow a}$$

Landau-Zener Effect

adiabatic \times nonadiabatic (or diabatic) processes in the Born-Oppenheimer sense



--- nonadiabatic PES

— adiabatic PES

equivalent descriptions:

$$\begin{aligned}\Psi(R) &= C_1(R)\psi_1(R) + C_2\psi_2(R) \\ &= c_a(R)\phi_a(R) + c_b(R)\phi_b(R)\end{aligned}$$

$$P_{ad} = 1 - P_{nonad} = 1 - \exp\left[-\frac{2\pi|V|^2}{\hbar\left|\frac{d}{dt}(E_a - E_b)\right|}\right], \quad \text{with } \frac{d}{dt}(E_{ab}) = \dot{\mathbf{R}} \cdot \nabla_R E_{ab}$$

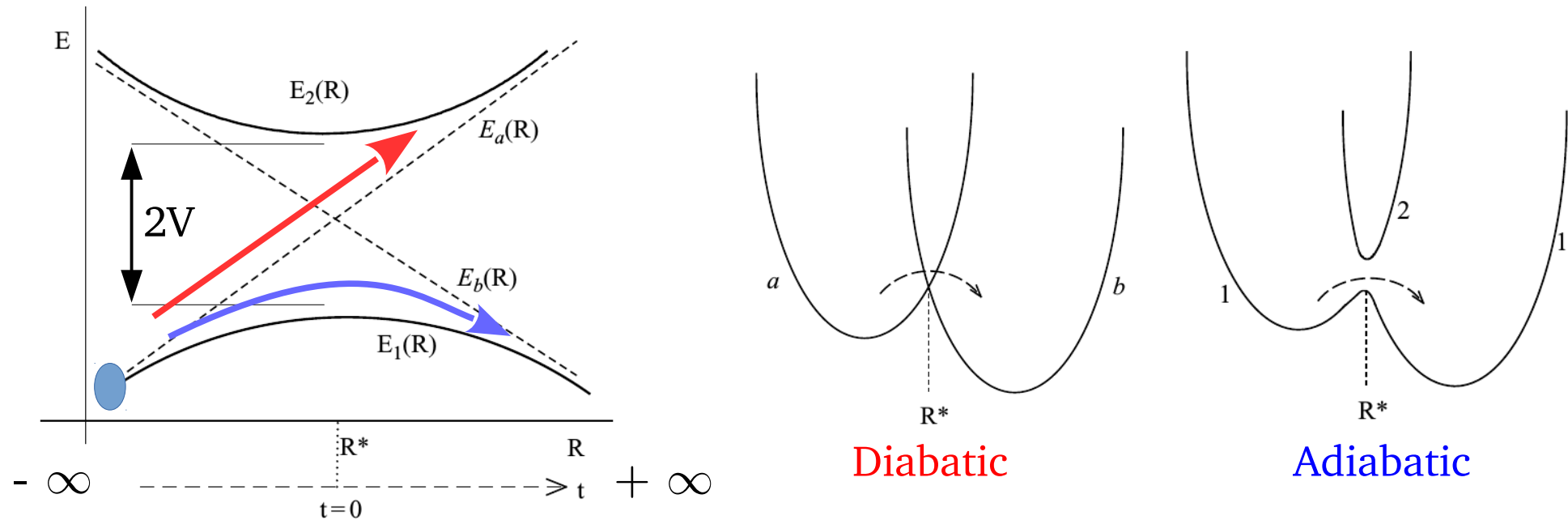
adiabatic regime: $2\pi|V|^2 \gg \hbar\dot{\mathbf{R}} \cdot \nabla_R E_{ab}$

nonadiabatic regime: $2\pi|V|^2 \ll \hbar\dot{\mathbf{R}} \cdot \nabla_R E_{ab}$

$$P_{nonad} \approx 1 - \frac{2\pi|V|^2}{\hbar|\dot{\mathbf{R}} \cdot \nabla_R E_{ab}|}$$

Landau-Zener Effect

adiabatic \times nonadiabatic (or diabatic) processes in the Born-Oppenheimer sense



$$P_{ad} = 1 - P_{nonad} = 1 - \exp \left[-\frac{2\pi|V|^2}{\hbar \left| \frac{d}{dt}(E_a - E_b) \right|} \right], \quad \text{with} \quad \frac{d}{dt}(E_{ab}) = \dot{\mathbf{R}} \cdot \nabla_R E_{ab}$$

adiabatic regime: $2\pi|V|^2 \gg \hbar \dot{\mathbf{R}} \cdot \nabla_R E_{ab}$

nonadiabatic regime: $2\pi|V|^2 \ll \hbar \dot{\mathbf{R}} \cdot \nabla_R E_{ab}$

$$P_{nonad} \approx 1 - \frac{2\pi|V|^2}{\hbar |\dot{\mathbf{R}} \cdot \nabla_R E_{ab}|}$$

Ehrenfest Dynamics

For the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{r})$$

Ehrenfest Theorem (1927):

Quantum-Mechanical analogue of Newton's dynamics equation

$$m \frac{d^2}{dt^2} \langle \hat{r} \rangle = \frac{d \langle \hat{p} \rangle}{dt} = - \langle \nabla V(\hat{r}) \rangle$$

Classical Mechanics derived from Quantum Mechanics via the ansatz

$$\frac{[,]}{i\hbar} \rightarrow [,]_{Poisson}$$

due to the Heisenberg Equation of Motion

$$\frac{d\hat{A}^{(H)}}{dt} = \frac{1}{i\hbar} \left[\hat{A}^{(H)}, \hat{H} \right]$$

Ehrenfest Quantum-Classical Hybrid Methods

Assume two particles:

- the light particle with mass m and coordinates r
- the heavy particle with mass M and coordinate R

The Schrödinger equation for the particles is:

$$i\hbar \frac{\partial}{\partial t} \Psi = \left(-\frac{\hbar^2}{2m} \nabla_r^2 - \frac{\hbar^2}{2M} \nabla_R^2 + V(r, R) \right) \Psi$$

The time average of a time-independent observable is:

$$\langle A \rangle(t) = \langle \Psi | \hat{A} | \Psi \rangle = \int \Psi^*(r, R, t) \hat{A} \Psi(r, R, t) dr dR$$

The *Ehrenfest Theorem* yields operator R and P of the heavy particle :

$$\begin{aligned} \frac{d}{dt} \langle R \rangle &= \langle P \rangle / M , & \hat{P} &= -i\hbar \nabla_R \\ \frac{d}{dt} \langle P \rangle &= -\langle \nabla_R V \rangle \end{aligned}$$

with $\langle \nabla_R V \rangle = \int (\nabla_R V(r, R)) |\Psi(r, R, t)|^2 dr dR$

$\langle R \rangle$ and $\langle P \rangle$ are the position and momentum of the heavy particle wavepacket.

These purely QM equations can only be evaluated if Ψ is known.

Ehrenfest Quantum-Classical Hybrid Methods

Assuming the separable wavefunction $\Psi(r, R, t) = \phi(r, t)\chi(R, t)$

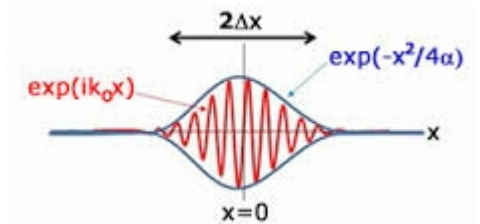
where $\phi(r, t)$ is the electronic (light particle) wavefunction

where $\chi(r, t)$ is the nuclear (heavy particle) wavefunction

In fact, $\phi(r, t)$ can be a linear combination of adiabatic orbitals $\phi = \sum_a C_a \psi_a(r; R)$

Assume now that $m \ll M$, so that χ is an approximate δ function, e.g.

$$\chi(R, t) = \frac{1}{(\epsilon(t)\sqrt{2\pi})^{2d}} \exp\left(-\frac{|R - \langle R \rangle|^2}{4\epsilon(t)^2}\right) \exp\left(i\frac{\langle P \rangle}{\hbar}R\right)$$



In the limit $\epsilon \rightarrow 0$ we have

$$\begin{aligned} \langle \nabla_R V \rangle &= \int (\nabla_R V(r, R)) |\Psi(r, R, t)|^2 dr dR \rightarrow \int \phi^*(r, t) \nabla_R V(r, \langle R \rangle) \phi(r, t) dr \\ &= \nabla_R \langle V(r, \langle R \rangle) \rangle_r \end{aligned}$$

similar but not the Hellmann-Feynman force, because ϕ is not the GS.

Ehrenfest Quantum-Classical Hybrid Methods

The equations for the Quantum-Classical Molecular Dynamics become

$$i\hbar \frac{\partial}{\partial t} \phi(r; R, t) = \left(-\frac{\hbar^2}{2m} \nabla_r^2 + V(r; R) \right) \phi(r; R, t) , \quad \text{Schrödinger Equation}$$

$$\begin{aligned} \dot{R} &= P/M , \\ \dot{P} &= -\nabla_R \langle \phi(r; R, t) | V(r, R) | \phi(r; R, t) \rangle_r , \end{aligned} \quad \text{Canonical Equations}$$

The Schrödinger equation describes the real dynamics of the quantum particle, whereas the canonical equations describe the dynamics of the “classical” particle

The approximation fails:

- if the mass M becomes small;
- if the initial variance ϵ of the heavy wavepacket is not small enough, allowing for dispersion of the wavepacket (like wavepacket in dispersive medium);
- for long time simulations the wavepacket might desintegrate;
- if the equation gets multivalued after passing a focal point (conical intersections);

Ehrenfest Quantum-Classical Hybrid Methods

Conservation of Energy:

The total energy of the full quantum system in the Ψ state is conserved

$$E(\Psi) = \left\langle \Psi(r, R) \left| -\frac{\hbar^2}{2m} \nabla_r^2 - \frac{\hbar^2}{2M} \nabla_R^2 + V(r, R) \right| \Psi(r, R) \right\rangle = \text{const}$$

The Quantum-Classical separation yields:

$$E(\Psi) = \langle \psi(r; R, t) | \hat{H}_{el}(t) | \psi(r; R, t) \rangle + \frac{P(t)^2}{2M} + \Delta E_0 + \mathcal{O}(\epsilon/L + \sqrt{m/M})$$

where L is a typical length and

$$\hat{H}_{el}(t) = -\frac{\hbar^2}{2m} \nabla_r^2 + V(\hat{r}; R(t))$$

become a time-dependent hamiltonian for the quantum system.

$\Delta E_0 = \frac{d\hbar^2}{8M\epsilon^2}$ is the self-energy of the “classical” particle.

The energy of the Quantum-Classical system is also conserved:

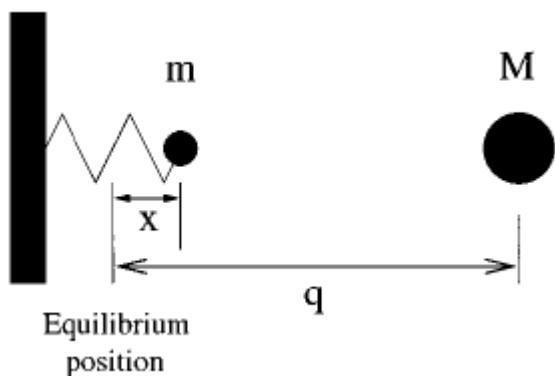
$$E_{QC} = \langle \psi(r; R, t) | \hat{H}_{el}(t) | \psi(r; R, t) \rangle + \frac{P(t)^2}{2M}$$

with the ensuing canonical equations: $\dot{R} = \frac{\partial}{\partial P} E_{QC}$ and $\dot{P} = -\frac{\partial}{\partial R} E_{QC}$

Ehrenfest Quantum-Classical MD: Example

F.A. Bornemann, P. Nettesheim, C. Schütte. J. Chem. Phys. 105, 1074 (1996)

Model system

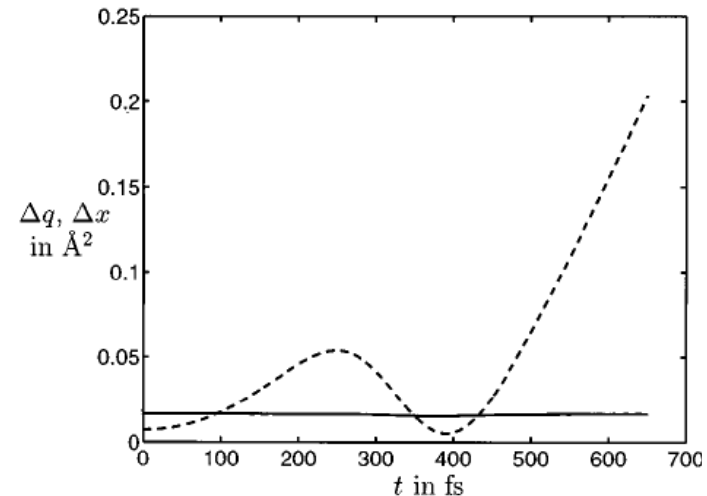
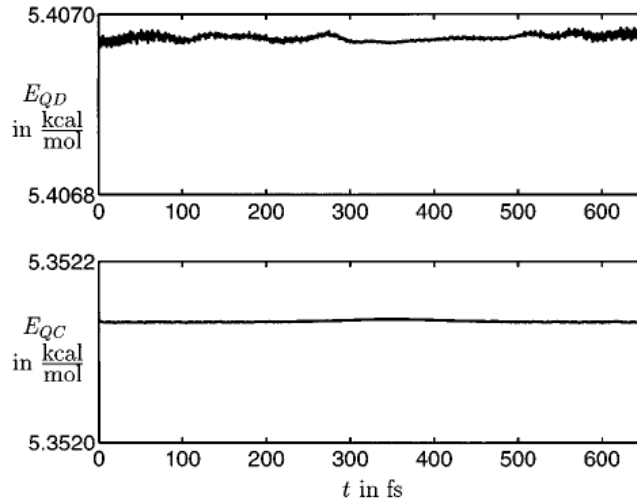
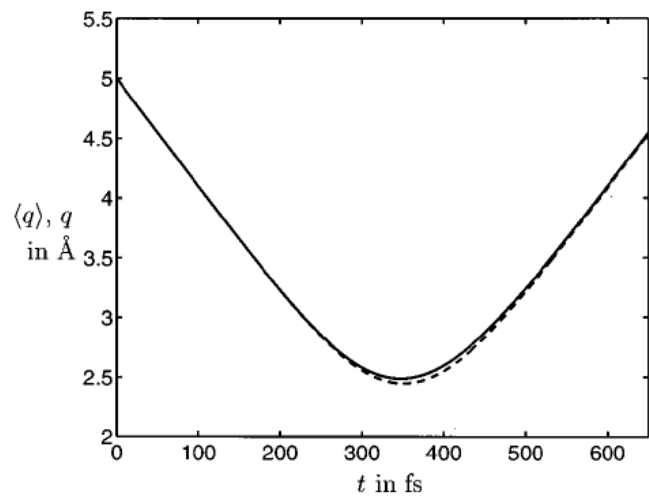


$$H = -\frac{\hbar^2}{2m} \nabla_x^2 - \frac{\hbar^2}{2M} \nabla_q^2 + \underbrace{\frac{m}{2} \omega^2 x^2 + U(|x - q|)}_{=V(x,q)}$$

$$M/m = 40 \quad U(r) = A \exp(-br) \quad \epsilon = 0.0075 \text{ \AA} \quad x/\text{ \AA} \in [-1, 0.5] \quad q/\text{ \AA} \in [1, 12]$$

--- QCMD

— QD



Ehrenfest Quantum-Classical Hybrid Methods

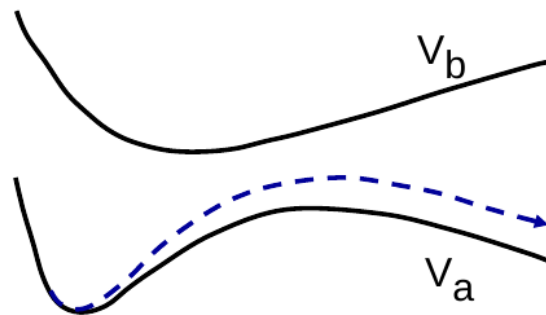
A particular case of *Time-Dependent Self-Consistent mean-field* (TDSCF) method

Ehrenfest Quantum-Classical Hybrid Methods

The classical dynamics evolves in an average PES

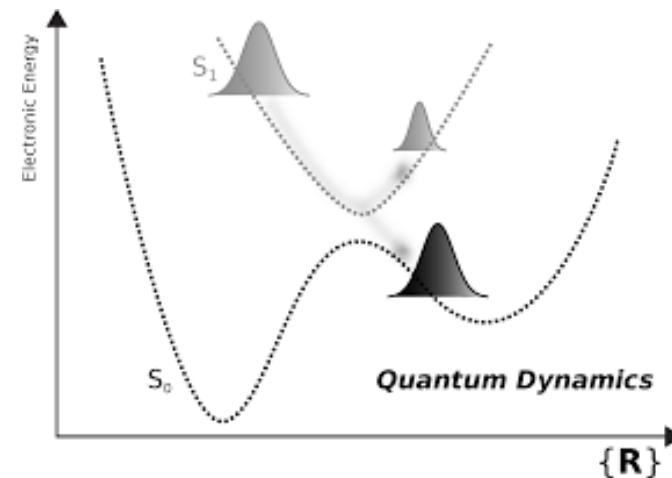
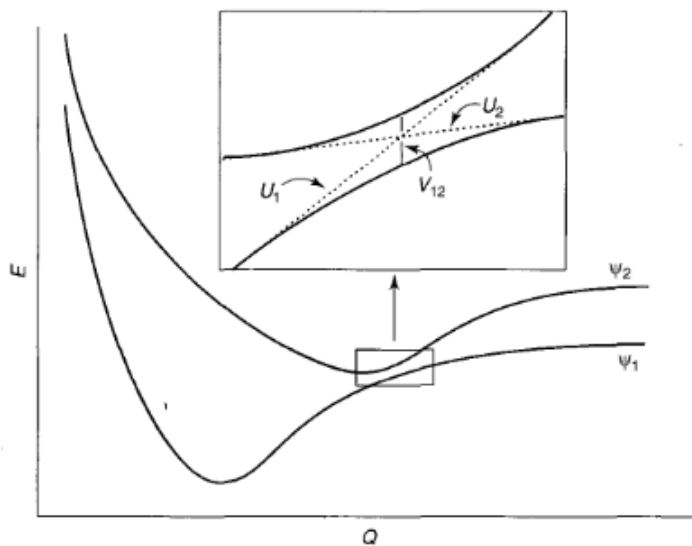
$$M \frac{d}{dt^2} R = -\nabla_R \langle \phi(r; R, t) | V(r, R) | \phi(r; R, t) \rangle_r$$

$\phi(r, t)$ can be a linear combination of adiabatic orbitals $\phi = \sum_a C_a \psi_a(r; R, t)$

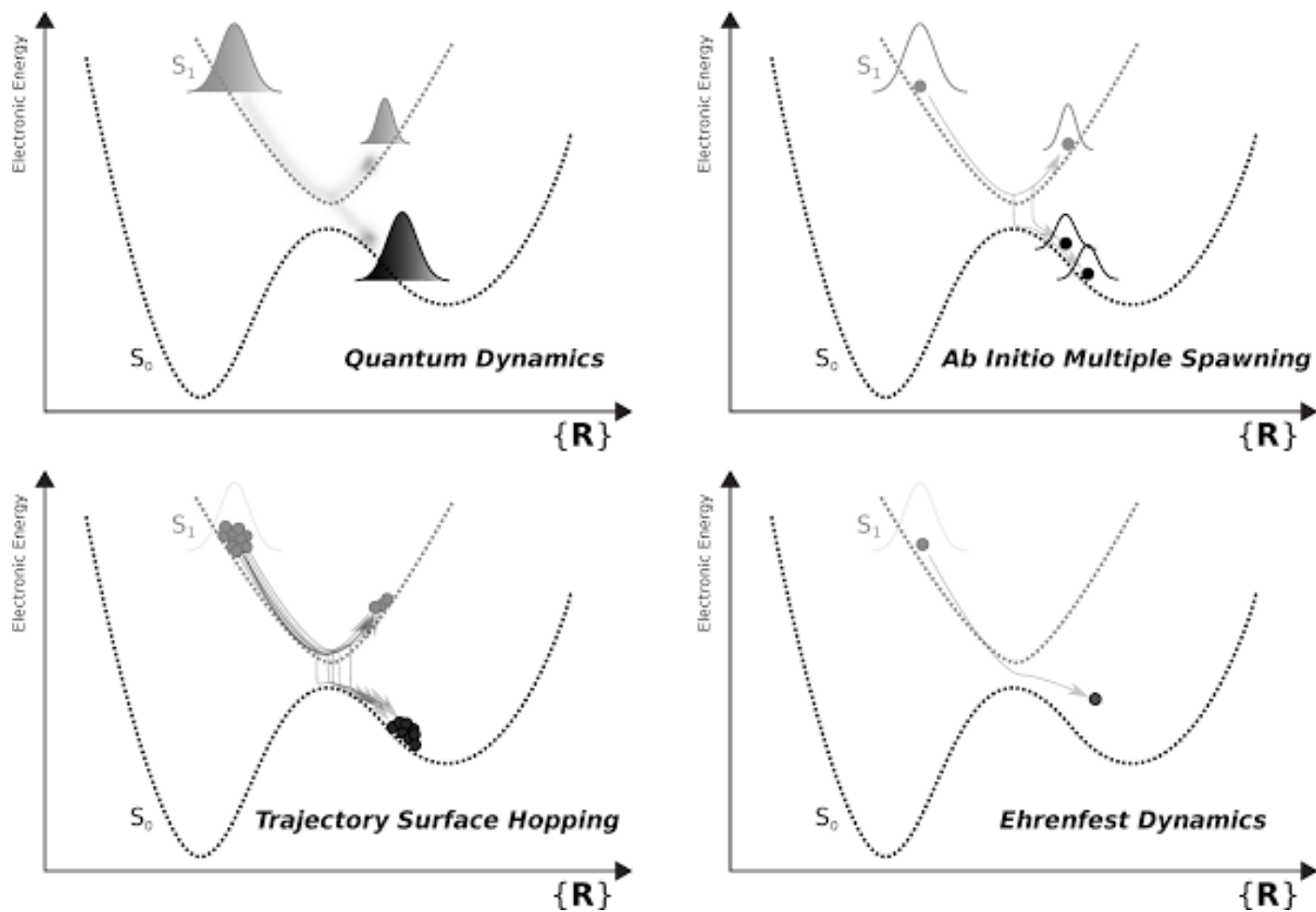


Classical trajectory

But the real quantum system splits at the PES intersection



Alternatives at this crossing point



Surface Hopping Hybrid Method

John C. Tully:

Mixed Quantum-Classical dynamics: mean-field and surface-hopping, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, World Scientific.

Multi-configuration description may offer an improvement over mean-field Ehrenfest dynamics.

Take into account the nonseparable wavefunction

$$\Psi(r, R, t) = \sum_a \chi_a(R, t) \psi_a(r, R)$$

where $\psi_a(r; R)$ is an **adiabatic** basis function, and substitute into the TDSE

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \chi_b(R, t) &= - \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2 \chi_b(R, t) + \varepsilon_b(R) \chi_b(R, t) \\ &- \sum_{a,n} \frac{\hbar^2}{2M_n} [2\langle \psi_b | \nabla_n \psi_a \rangle \nabla_n + \langle \psi_b | \nabla_n^2 \psi_a \rangle] \chi_a(R, t) \end{aligned}$$

the integral of $|\chi_a(R, t)|^2 dR$ is the population of quantum state i at time t .

Surface Hopping Hybrid Method

The nonadiabatic TDSE for the nuclear degrees of freedom:

$$i\hbar \frac{\partial}{\partial t} \chi_b(R, t) = - \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2 \chi_b(R, t) + \varepsilon_b(R) \chi_b(R, t) - \sum_{a,n} \frac{\hbar^2}{2M_n} [2\langle \psi_b | \nabla_n \psi_a \rangle \nabla_n + \langle \psi_b | \nabla_n^2 \psi_a \rangle] \chi_a(R, t)$$

$$i\hbar \frac{\partial}{\partial t} \chi_b(R, t) = - \sum_n \frac{\hbar^2}{2M_n} \nabla_n^2 \chi_b(R, t) + \varepsilon_b(R) \chi_b(R, t) - \sum_{a \neq b, n} \frac{\hbar^2}{M_n} \mathbf{d}_{ab}^n \chi_a(R, t) + \sum_{a,n} \frac{\hbar^2}{2M_n} \mathbf{D}_{ab}^n \chi_a(R, t)$$

\mathbf{d}_{ab}^n is the nonadiabatic coupling matrix.

\mathbf{D}_{ab}^n is a small correction term.

Take a classical limit for the nuclear degrees of freedom (no rigorous recipe).

Surface Hopping Hybrid Method

1) an *ensemble* of nuclei evolve on a single PES:

$$M_n \frac{d^2}{dt^2} \mathbf{R}_n = -\nabla_n \langle \psi_a | H_{el} | \psi_a \rangle$$

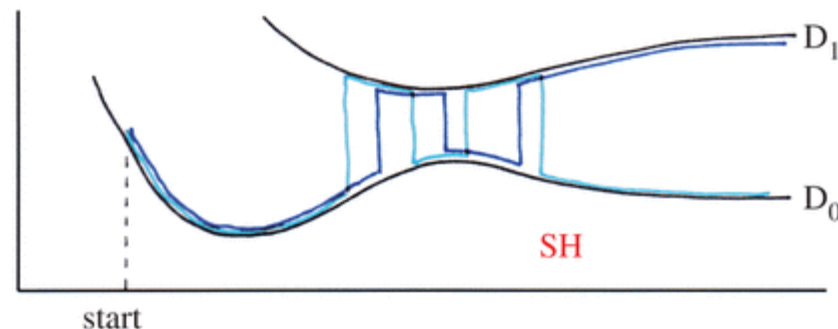
2) the time-varying amplitude of each adiabatic state are computed on-the-fly as:

$$i\hbar \dot{c}_a(t) = c_a(t) \varepsilon_a(\mathbf{R}) - i\hbar \sum_{bn} c_b(t) \dot{\mathbf{R}}_n \cdot \mathbf{d}_{ab}^n$$

3) the trajectories are governed by Hellmann-Feynman forces of a particular quantum state, except for occasional instantaneous switches amongst the PSE's.

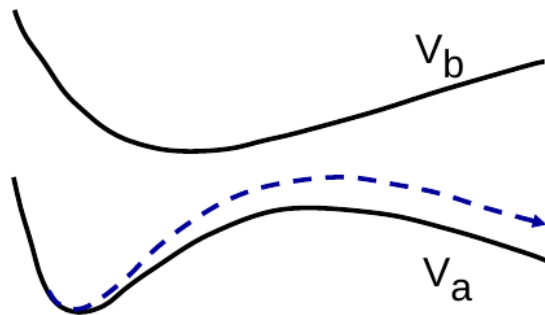
4) if the switch is made, energy is conserved by re-setting the nuclear velocity in the direction of the nonadiabatic coupling vector, \mathbf{d}_{ab}

5) Stochastic hops between states occur with probability based on how $|c_a(t)|^2$ are changing with time.

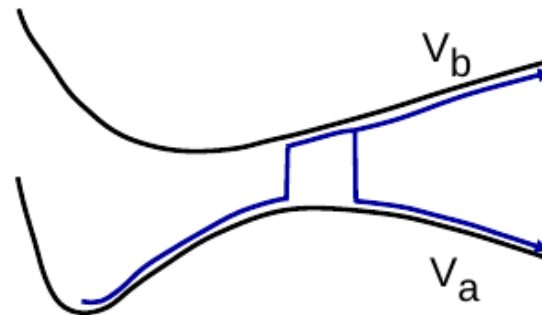


Surface Hopping Hybrid Method

Differences between mean-field Ehrenfest (MFE) and Surface Hopping (SH):



MF Ehrenfest



Surface Hopping

- SH is computationally more demanding than MFE because the former requires the calculation of an ensemble of trajectories;
- SH is capable of describing state-specific pathways in scattering processes, something that is beyond the scope of the Ehrenfest method;
- phase coherence and quantum interference effects are included in (SH) through the complex amplitudes, $c_j(t)$;
- SH can satisfy microscopic reversibility, though most do not. However, in general, deviations from microscopic reversibility are quantitatively much less severe than for MFE.
- These methods are complementary, both have limitations, and **neither is universally superior** to the other.