Nonadiabatic Quantum Molecular Dynamics (NAQMD) via Fewest-Switches Surface Hopping (FSSH)

1/6/10

[J.C. Tully, J. Chem. Phys. <u>93</u>, 1061 ('90)]

§ Mixed electron-nuclei system

Let $r = (r_1, ..., r_n)$ be the positions of n electrons of mass m, and $R = (R_1, ..., R_N)$ be those of N nuclei with masses $(M_1, ..., M_N)$ and charges $(Z_1, ..., Z_N)$. The Hamiltonian is

$$H = T_R + h(r, R) \tag{1}$$

$$T_R = \sum_{I=1}^{N} \frac{P_I^2}{2M_I} \tag{2}$$

$$h(r, R) = \sum_{i=1}^{n} \frac{P_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i, I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \tag{3}$$

§. Length-scale separation

Let us assume the separation of thermal de Broglie wave lengths

$$\Lambda_I^{ion} = \frac{\hbar}{\sqrt{2\pi M_I k_B T}} \ll \underbrace{\lambda}_{\substack{\text{length scale} \\ \text{of interest}}} \sim \Lambda^{electron} = \frac{\hbar}{\sqrt{2\pi m k_B T}} \qquad (4)$$

Note

$$\frac{\Lambda^{electron}}{\Lambda_I^{ion}} = \sqrt{1836.1 \frac{M_I}{M_{proton}}} = 42.8\,(H),\ 148\,(\underset{12.0}{C}),\ 171\,(\underset{16.0}{O}),\ 346\,(\underset{65.38}{Zn}),\ \ldots$$

thus the nucleus quantum effect is rarely effective except for protons, occationally.

At 300K,

species	$\Lambda\,(a.u.) = [Z\pi \cdot 1836.1\,(M_I/M_{proton}) \cdot 300/(11604.8 \times 27.2116)]^{-1/2}$
electron	12.94
proton	0.302
C	8.72×10^{-2} $\qquad \ll \Delta r = 0.36\,au$: MGDC mesh size
O	7.55×10^{-2} $\qquad\qquad\qquad\qquad$ for graphene
Zn	3.74×10^{-2}

(Insight: Minimum-uncertainty wave packet)

$$(\Delta x) \cdot \underbrace{(\Delta p)}_{\sim \sqrt{M_I k_B T}} = \frac{\hbar}{2}$$

$$\therefore \Delta x \sim \hbar / 2\sqrt{M_I k_B T}$$
$$\sim \Lambda_I^{ion}$$
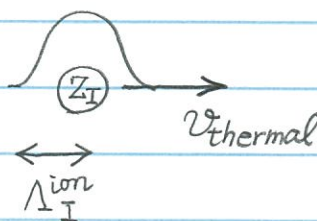
§. Born representation

Consider a set of electronic eigensolutions

$$\{\psi_k(\mathbf{r}; \mathbf{R}) \mid k = 0, 1, \ldots; @ \forall \mathbf{R}\} \tag{5}$$

for $\forall$ possible "clamped" nuclei positions $\{\mathbf{R}\}$, where

$$h(\mathbf{r}, \mathbf{R}) \, \psi_k(\mathbf{r}; \mathbf{R}) = \varepsilon_k(\mathbf{R}) \, \psi_k(\mathbf{r}; \mathbf{R}). \tag{6}$$

$\hookrightarrow$ parametric dependence

We expand the electron-nuclei wave function as

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_k \chi_k(\mathbf{R}, t) \, \psi_k(\mathbf{r}; \mathbf{R}), \tag{7}$$

where the expansion coefficients $\{\chi_k(\mathbf{R}, t)\}$ are the probability amplitudes to find the nuclei at positions $\mathbf{R}$ at time t.

Q: Is $\{\psi_k(\mathbf{r}; \mathbf{R}) \mid \forall k, \forall \mathbf{R}\}$ a complete set in the $\mathbf{r} \times \mathbf{R}$ space? In the absence of a proof, it is called the Born ansatz.

§. Quantum molecular dynamics (cf. 10/19/89)

Under the length-scale separation condition, we perform the small $\hbar$ expansion only for the nuclei (or $\hbar/\sqrt{M_I}$ expansion). To do so, we define an S-matrix

$$S = \frac{1}{\sum_k P_k(\mathbb{R})} \sum_k P_k(\mathbb{R}) \langle k\mathbb{R}| \mathcal{U}_-(t_0, t_f) \mathcal{U}_+(t_f, t_0) |k\mathbb{R}\rangle \qquad (8)$$

where $t_f \gg t \sim$ time of interest $\gg t_0$, and at time t_0, the nuclei are in the position eigenstate @ $\mathbb{R}$ and the electrons are in a mix state represented by the statistical matrix $P_k(\mathbb{R})$, where

$$|k\mathbb{R}\rangle = \underbrace{|\mathbb{R}\rangle}_{\delta(X-\mathbb{R})} \underbrace{|k; \mathbb{R}\rangle}_{\psi_k(\mathbb{r}; R)} \qquad (9)$$

$$= \Psi(\mathbb{r}, X)$$

In Eq. (8),

$$\mathcal{U}_{\pm}(t, t') = T_{\pm} \exp\left[-\frac{i}{\hbar} \int_{t'}^{t} d\tau \widetilde{H}(\tau)\right] \qquad (10)$$

where $T_{\pm}$ are the forward/backward time-ordering operators, and we have introduce an external time dependence of the Hamiltonian through

$$\widetilde{H}(\tau) = H + \sum_{i=1}^{n} \mathcal{V}(\mathbb{r}_i, t) + \sum_{I=1}^{N} V(\mathbb{R}_I, t). \qquad (11)$$

(Physical meaning of the S-matrix)

The S-matrix encodes the dynamics of the electron-nuclei system, in the sense that the expectation value of any operator $\hat{X}$ at time t, in the presence of an extra Hamiltonian term $\hat{X} F(t)$, is given by
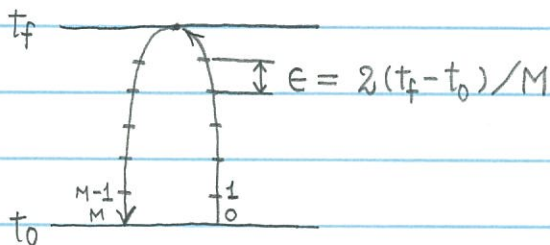
$$\langle \hat{X}(t) \rangle = \left. \frac{\delta S}{\delta F_+(t)} \right|_{F_+=F_-} = -\frac{i}{\hbar} \frac{1}{\sum_k P_k(\mathbb{R})} \sum_k P_k(\mathbb{R}) \langle k\mathbb{R}(t) | \hat{X} | k\mathbb{R}(t) \rangle \tag{12}$$

where

$$| k\mathbb{R}(t) \rangle = \mathcal{U}_+(t, t_0) | k\mathbb{R} \rangle \tag{13}$$

(Path-integral representation of the S-matrix)

We divide the closed time path $t_0 \to t_f \to t_0$ into M sections.

$\updownarrow \epsilon = 2(t_f - t_0)/M$

Then, the S-matrix can be represented by path integral as

$$S = \int_P^{\mathbb{R}(t_0) = \mathbb{R}} \mathcal{D}[\mathbb{R}(t)] \exp\left(\frac{i}{\hbar} S_0[\mathbb{R}(t)] \right) T[\mathbb{R}(t)] \tag{14}$$

where

$$\begin{cases} S_0 = \int_P dt \, \frac{M}{2} \left(\frac{d\mathbb{R}}{dt} \right)^2 \tag{15} \\[3mm] T = \frac{1}{\sum_k P_k(\mathbb{R})} \sum_k P_k(\mathbb{R}) \langle k\mathbb{R} | T_P \left[-\frac{i}{\hbar} \int_P dt \, h(\mathbb{r}, \mathbb{R}(t), t) \right] | k\mathbb{R} \rangle \tag{16} \end{cases}$$

and the functional integral along the closed time path is

$$\int_P^{R(t)=R} \mathcal{D}[R(t)] = \lim_{M \to \infty} \left(\frac{M}{2\pi i \hbar \epsilon}\right)^{3M/2} \prod_{j=1}^{M-1} \int dR_j \qquad (17)$$

The path integral path representation, Eq. (14), thus expresses the S-matrix as a superposition of multiple-path contributions.

(Stationary-phase approximation)

For $\hbar \to 0$, the dominant contribution to the functional integral comes from the maximum of the argument of its exponential integrand,

$$\exp\left[\frac{i}{\hbar}\left(S_0 + \underbrace{\frac{\hbar}{i} \ln T}_{\to 0}\right)\right],$$

namely its stationary point (or path),

$$\delta\left\{S_0[R(t)] + \frac{\hbar}{i} \ln T[R(t)]\right\} = 0 \qquad (18)$$

The result is

$$S \xrightarrow[\hbar \to 0]{} \exp\left(\frac{i}{\hbar} S_0[R_c(t)]\right) \qquad (19)$$

where the classical path $R_c(t)$ satisfies

$$M\ddot{R}_c(t) = -\frac{1}{\sum_k P_k(R)} \sum_k P_k(R) \langle k(t); R| \frac{\partial h(r, R_c(t), t)}{\partial R_c(t)} |k(t); R\rangle \qquad (20)$$

and

$$M = \text{diag}(M_1, \ldots, M_N) \in \mathcal{R}^{N \times N} \qquad (21)$$

The electronic dynamics is governed by the propagator

$$\mathcal{U}(t,t') = T_p \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} d\tau \; h(\mathbb{r}, \mathbb{R}_c(\tau), \tau)\right] \tag{22}$$

$\underbrace{}$ time-ordering operator on path p

and hence the electronic state is obtained by solving

$$i\hbar\frac{\partial}{\partial t}|k(t); \mathbb{R}\rangle = h(\mathbb{r}, \mathbb{R}_c(t), t)|k(t); \mathbb{R}\rangle \tag{23}$$

with the initial condition

$$|k(t=t_0); \mathbb{R}\rangle = |k; \mathbb{R}\rangle \tag{24}$$

(Ehrenfest dynamics — mean-field description)
The classical nuclei approximation to the path integral
thus amounts to a single nuclei-path, Ehrenfest dynamics:

$$\begin{cases} M\ddot{\mathbb{R}}_c(t) = -\dfrac{1}{\sum\limits_{k} P_k(\mathbb{R})} \sum\limits_{k} P_k(\mathbb{R}) \langle k(t); \mathbb{R}|\dfrac{\partial h(\mathbb{r}, \mathbb{R}_c(t), t)}{\partial \mathbb{R}_c(t)}|k(t); \mathbb{R}\rangle & (20) \\[2em] i\hbar\dfrac{\partial}{\partial t}|k(t); \mathbb{R}\rangle = h(\mathbb{r}, \mathbb{R}_c(t), t)|k(t); \mathbb{R}\rangle & (23) \end{cases}$$

The coupled classical-quantum equations, (20) & (23), describe
the nuclei moving in a "mean-field" (or self-consistly
obtained average field) over mixed states $\{|k(t); \mathbb{R}\rangle\}$.

The mean-field nature of the Ehrenfest dynamics is more
apparent from its alternative derivation by Marx & Hutter ('09).

Here, we introduce a separable approximation,

$$\Psi(\mathbb{r}, \mathbb{R}, t) \simeq \psi(\mathbb{r}, t)\, \chi(\mathbb{R}, t), \tag{25}$$

with which decoupled electron & nuclei Schrödinger equations in self-consistent potentials averaged over each other's wave functions ($\simeq$ time dependent Hartree approximation). We can then take the classical ($\hbar \to 0$) limit only of the nuclei equation to derive its single classical path.

§. Adiabatic dynamics

Consider the time-dependent Schrödinger equation for electrons, Eq. (23) (in the absence of external time dependence $V(\mathbb{r}, t)$),

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbb{r}, t) = h(\mathbb{r}, \underbrace{\mathbb{R}(t)}_{}) \psi(\mathbb{r}, t) \tag{26}$$

Single classical path
(we omit subscript c for simplicity)

Expand the wave function in terms of the Born adiabatic basis

$$\psi(\mathbb{r}, t) = \sum_k C_k(t)\, \psi_k(\mathbb{r}; \mathbb{R}(t)) \tag{27}$$

Substituting Eq. (27) in (26),

$$(\text{lhs}) = \sum_k \left[i\hbar \dot{C}_k(t)\, \psi_k(\mathbb{r}; \mathbb{R}(t)) + i\hbar C_k(t)\, \dot{\mathbb{R}}(t) \cdot \frac{\partial}{\partial \mathbb{R}(t)}\, \psi_k(\mathbb{r}; \mathbb{R}(t)) \right]$$

$$(\text{rhs}) = \sum_k C_k(t)\, \underbrace{h(\mathbb{r}, \mathbb{R}(t))\, \psi_k(\mathbb{r}; \mathbb{R}(t))}_{}$$

$$E_k(\mathbb{R}(t))\, \psi_k(\mathbb{r}; \mathbb{R}(t)) \;\; (\odot \text{ Eq. (6)})$$

$$\int d\mathbf{r}\, \psi_k^*(\mathbf{r}; \mathbf{R}(t)) \times (\text{above})$$

$$i\hbar \dot{C}_k(t) + i\hbar \sum_\ell C_\ell(t) \dot{\mathbf{R}}(t) \cdot \underbrace{\int d\mathbf{r}\, \psi_k^*(\mathbf{r}; \mathbf{R}(t)) \frac{\partial}{\partial \mathbf{R}} \psi_\ell(\mathbf{r}; \mathbf{R})}_{\equiv \mathbf{d}_{k\ell}(\mathbf{R}(t))}$$

$$= E_k(\mathbf{R}(t)) C_k(t)$$

In summary, the electrons dynamically follows the single nuclei path as

$$\boxed{\begin{aligned} i\hbar \dot{C}_k(t) &= E_k(\mathbf{R}(t)) C_k(t) - i\hbar \dot{\mathbf{R}}(t) \cdot \sum_\ell \mathbf{d}_{k\ell}(\mathbf{R}(t)) C_\ell(t) \qquad (28)\\[1em] \text{where the} &\text{ nonadiabatic coupling vector is defined as}\\[0.5em] \mathbf{d}_{k\ell}(\mathbf{R}) &\equiv \int d\mathbf{r}\, \psi_k^*(\mathbf{r}; \mathbf{R}) \frac{\partial}{\partial \mathbf{R}} \psi_\ell(\mathbf{r}; \mathbf{R}) = \langle k; \mathbf{R} | \frac{\partial}{\partial \mathbf{R}} | \ell; \mathbf{R} \rangle \qquad (29) \end{aligned}}$$

$$-\frac{i}{\hbar} \times \text{Eq. (28)}$$

Note that

$$\dot{C}_k = -\frac{i}{\hbar} E_k C_k - \dot{\mathbf{R}} \cdot \sum_\ell \mathbf{d}_{k\ell} C_\ell$$

$$\mathbf{d}_{k\ell}^* = -\mathbf{d}_{\ell k}$$

$$= \sum_\ell \left(-\frac{i}{\hbar} \delta_{k\ell} E_\ell - \underbrace{\langle k | \dot{\mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{R}} | \ell \rangle}_{\langle k | \frac{d}{dt} | \ell \rangle} \right) C_\ell \qquad (30)$$

and especially

$$= -\sum_\ell \left(i \delta_{k\ell} \omega_\ell + \underbrace{\langle k | \frac{d}{dt} | \ell \rangle}_{\equiv d_{k\ell}} \right) C_\ell \qquad (31)$$

$$\mathbf{d}_{kk} = 0$$

☺

$$\frac{\partial}{\partial \mathbf{R}} \underbrace{\langle \psi_\ell(\mathbf{r}); \mathbf{R} | \psi_k(\mathbf{r}); \mathbf{R} \rangle}_{\delta_{\ell k} (\odot \text{ orthonormality})} = 0$$

$$(\text{lhs}) = \int d\mathbf{r} \left\{ \left[\frac{\partial}{\partial \mathbf{R}} \psi_\ell^*(\mathbf{r};\mathbf{R}) \right] \psi_k(\mathbf{r};\mathbf{R}) + \psi_\ell^*(\mathbf{r};\mathbf{R}) \frac{\partial}{\partial \mathbf{R}} \psi_k(\mathbf{r};\mathbf{R}) \right\}$$

$$= \underbrace{\left[\int d\mathbf{r}\, \psi_k^*(\mathbf{r};\mathbf{R}) \frac{\partial}{\partial \mathbf{R}} \psi_\ell(\mathbf{r};\mathbf{R}) \right]^*}_{d_{k\ell}^*} + d_{\ell k}$$

$$\therefore \quad d_{k\ell}^* + d_{\ell k} = 0$$

Setting $k = \ell$ in the above

$$\text{Re } d_{kk} = 0$$

In fact, in a nonmagnetic system, the adiabatic electronic wave function $\psi_k(\mathbf{r};\mathbf{R})$ can be made real always, in which case,

$$d_{kk} = 0. \quad //$$

Suppose that $C_k(t) = \delta_{k,k_0}$ at $t = 0$ (pure adiabatic state), and $\dot{\mathbf{R}}(t) \sim 0$, then the electronic state remains at state k_0.

$\downarrow$

Adiabatic approximation

§. Validity of the adiabatic approximation (cf. 10/18/89)

Substitute the Born adiabatic representation of the electron-nuclei wave function, Eq.(7), to the electron-nuclei Schrödinger equation (in the absence of external time dependence),

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = H\Psi(\mathbf{r},\mathbf{R},t) \tag{32}$$

Then, we obtain

$$\left[i\hbar\frac{\partial}{\partial t} + \sum_{I=1}^{N}\frac{\hbar^2}{2M_I}\nabla_I^2 - \epsilon_k(\mathbf{R}) - T_{kk}(\mathbf{R})\right]\chi_k(\mathbf{R},t)$$

$$= \sum_{k'(\neq k)} T_{kk'}(\mathbf{R})\chi_{k'}(\mathbf{R},t) \tag{33}$$

where

$$T_{kk'}(\mathbf{R}) = \sum_{I=1}^{N}\langle k;\mathbf{R}|\frac{\hbar}{i}\nabla_I|k;\mathbf{R}\rangle\cdot\frac{\hbar}{iM_I}\nabla_I - \sum_{I=1}^{N}\langle k;\mathbf{R}|\frac{\hbar^2\nabla_I^2}{2M_I}|k';\mathbf{R}\rangle \tag{34}$$

If we set $T_{kk'}=0$ in Eq.(33), we obtain a single nuclei motion in the presence of the potential surface $\epsilon_k(\mathbf{R})$, the adiabatic dynamics.

(Validity of dropping $T_{kk'}$)

Let

$$\chi_k(\mathbf{R},t) = \zeta_k(\mathbf{R},t)\exp\left[-i\epsilon_k(\mathbf{R})t/\hbar\right] \tag{35}$$

and assume $\zeta_k(\mathbf{R},t=0) = \delta_{k,l}C(\mathbf{R})$. Then, for $k\neq l$

$$|\zeta_k(\mathbf{R},t)|^2 = 4\left|\frac{T_{kl}(\mathbf{R})}{\epsilon_k(\mathbf{R})-\epsilon_l(\mathbf{R})}\right|^2\sin^2\left(\frac{\epsilon_l(\mathbf{R})-\epsilon_k(t)}{\hbar}t\right)|C(\mathbf{R})|^2 \tag{36}$$

Dropping it is valid for $T_{kl}(\mathbf{R})\sim k_BT \ll \epsilon_k(\mathbf{R})-\epsilon_l(\mathbf{R})$. Namely, near a level-crossing point (or conical intersection, the adiabatic dynamics becomes invalid.

In fact, near a conical intersection, the length-scale separation (or $\hbar/\sqrt{M_I}$ expansion), which leads to the single-nuclei-path Ehrenfest dynamics, may not apply ($\leftarrow$ to be checked), and the nuclei dynamics may inherently involve multiple nuclei paths.

§. Surface-hopping approach

① Approximate a multipath-involving transition event as an instantaneous transition sandwitched by two single-path trajectories (where the adiabatic approximation holds).
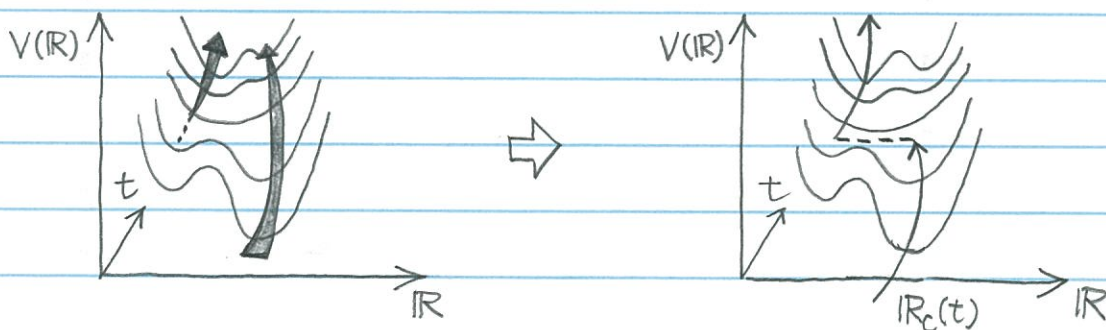
② The quantum uncertainty (or multipath probability) is dealt with an ensemble of classical paths with instantaneous nonadiabatic branches.

§. Fewest-switches surface hopping
(Density matrix)

For stochastic simulation involving inter-path transitions,
we introduce a density matrix,

$$a_{k\ell}(t) \equiv C_k(t) C_\ell^*(t) \tag{37}$$

such that the diagonal matrix element,

$$a_{kk}(t) = |C_k(t)|^2 = P_k(t), \tag{38}$$

is the probability to find the system in state k at time t.

From Eq. (28) and its complex conjugate, the equation of motion
for the density matrix is

$$i\hbar \dot{a}_{k\ell}(t) = i\hbar (\dot{C}_k C_\ell^* + C_k \dot{C}_\ell^*)$$

$$= [\mathcal{E}_k C_k - i\hbar \dot{\mathbb{R}} \cdot \sum_{k'} d_{kk'} C_{k'}] C_\ell^*$$

$$+ C_k [-\mathcal{E}_\ell C_\ell^* - i\hbar \dot{\mathbb{R}} \cdot \sum_{k'} \underbrace{d_{\ell k'}^* C_{k'}^*}_{-d_{k'\ell}} (\because \text{Eq. (30)})$$

$$\therefore i\hbar \dot{a}_{k\ell} = (\mathcal{E}_k - \mathcal{E}_\ell) a_{k\ell} - i\hbar \dot{\mathbb{R}} \cdot \sum_{k'} (d_{kk'} a_{k'\ell} - a_{kk'} d_{k'\ell}) \tag{39}$$

For the diagonal element (probability),

$$\cancel{i\hbar} \dot{P}_k = \cancel{i\hbar} \dot{a}_{kk} = -\cancel{i\hbar} \dot{\mathbb{R}} \cdot \sum_{k'} (d_{kk'} a_{k'k} - \underbrace{a_{kk'} d_{k'k}}_{-a_{kk'}^* d_{kk'}^*} (\because \text{Eq. (30)})$$

$$\underbrace{d_{kk'} a_{k'k} + (d_{kk'} a_{k'k})^*}_{} = 2 \text{Re} (d_{kk'} a_{k'k})$$

$$\therefore \quad \dot{P_k} = \dot{\mathbf{R}} \cdot \sum_{k'(\neq k)} 2 \, \mathrm{Re}\,(\mathbf{d}_{kk'} a_{k'k}) \tag{40}$$

$$\qquad\qquad\qquad \smile (\because \mathbf{d}_{kk} = 0, \ \text{Eq. (31)}\,)$$

$$= \sum_{k'(\neq k)} b_{kk'} \tag{41}$$

where the transition matrix is

$$b_{kk'} = 2\dot{\mathbf{R}} \cdot \mathrm{Re}\,(\mathbf{d}_{kk'} a_{k'k}) \tag{42}$$

Note

$$b_{kk'} = 2\dot{\mathbf{R}} \cdot \mathrm{Re}\,(\underbrace{\mathbf{d}_{kk'} a_{k'k}}_{-\mathbf{d}^{*}_{k'k}\, a^{*}_{k'k}}) = -2\dot{\mathbf{R}} \cdot \underbrace{\mathrm{Re}\,(\mathbf{d}_{k'k} a_{kk'})^{*}}_{= \,\mathrm{Re}\,(\mathbf{d}_{k'k} a_{kk'})} = -b_{k'k}$$

$$\therefore \quad b_{kk'} = -b_{k'k} \quad (\Pi_{kk'} P_{k'} = -\Pi_{k'k} P_k) \tag{43}$$

For a pair of states, we only consider transitions toward
the probability-increasing state (not vice versa), i.e.,
minimal switching to maintain the correct ensemble population.
$\qquad\qquad\qquad\qquad \nwarrow \simeq$ Metropolis algorithm

During Δt_{MD} ($\sim$ 1 fs),

$$\Delta P_{k'} = \sum_{k(\neq k')} \Delta t_{MD}\, b_{k'k} = \sum_{k(\neq k')} \Pi_{k' \leftarrow k}\, P_k \tag{44}$$

where the (conditional) transition probability is

$$\Pi_{k' \leftarrow k} = \frac{\Delta t_{MD}\, b_{k'k}}{P_k} = 2\Delta t_{MD}\, \dot{\mathbf{R}} \cdot \frac{\mathrm{Re}\,(\mathbf{d}_{k'k} a_{kk'})}{a_{kk}} \tag{45}$$

(FSSH algorithm)

Let

$$\widetilde{\Pi}_{k' \leftarrow k} = \max\left(0, \Pi_{k' \leftarrow k}\right) = \max\left(0, 2\Delta t_{MD} \, \dot{\vec{R}} \cdot \frac{Re\left(d_{k'k} \, a_{k'k}\right)}{a_{kk}}\right) \quad (46)$$

and the system is on the k-th adiabatic state.
Order the other $(k' \neq k)$ states in descending order of
transition probability, $\widetilde{\Pi}_{1 \leftarrow k} > \widetilde{\Pi}_{2 \leftarrow k} > \cdots$, and define
an accumulated transition probability,

$$\Lambda_{k' \leftarrow k} = \sum_{\ell=1}^{k'} \widetilde{\Pi}_{k' \leftarrow k} \quad (47)$$

Then, generate a uniform random number, $rnd \in [0,1]$,
and make a transition to destination k' such tat

$$\Lambda_{k'-1 \leftarrow k} \leq rnd() < \Lambda_{k' \leftarrow k} \quad (48)$$

(Here, we define $\Lambda_{0 \leftarrow k} = 0$.)

$\widetilde{\Pi}_{1 \leftarrow k}$	$\widetilde{\Pi}_{2 \leftarrow k}$	$\widetilde{\Pi}_{3 \leftarrow k}$

0 $rnd()$