Toy FSSH math

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1 The Derivative of Energy

$$\begin{pmatrix} a & b \\ b & -a \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \lambda \begin{pmatrix} x \\ y \end{pmatrix}$$

$$\begin{pmatrix} a-\lambda & b \\ b & -a-\lambda \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = 0$$

$$\begin{vmatrix} a-\lambda & b \\ b & -a-\lambda \end{vmatrix} = 0$$

$$(a-\lambda)(-a-\lambda) - b^2 = 0$$

$$\lambda^2 - a^2 - b^2 = 0$$

$$\begin{cases} \lambda_1 = -\sqrt{a^2+b^2} \\ \lambda_2 = \sqrt{a^2+b^2} \end{cases}$$

We have the analytical Hamiltonian of this model system:

$$H = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$$

$$V_{11} = \begin{cases} A(1-e^{-Bx}), x > 0 \\ -A(1-e^{Bx}), x < 0 \end{cases} = sign(x)A(1-e^{-B|x|})$$

$$V_{22} = -V_{11}$$

$$V_{12} = V_{21} = Ce^{-Dx^2}$$

$$\begin{cases} A = 0.01 \\ B = 1.6 \\ C = 0.005 \\ D = 1.0 \end{cases}$$

So the eigenvalues

$$
\begin{aligned}
E_1 &= -\sqrt{V_{11}^2 + V_{12}^2} \\
E_2 &= \sqrt{V_{11}^2 + V_{12}^2}
\end{aligned}
$$

We choose E_1 as the ground state energy. Then derive it's derivative in terms of the nuclear position x:

$$
\begin{aligned}
E_1 &= -\sqrt{V_{11}^2 + V_{12}^2} \\
\text{Let } f(x) &= V_{11}^2 + V_{12}^2 = [A(1 - e^{-B|x|})]^2 + [Ce^{-Dx^2}]^2 \\
E_1(x) &= -f(x)^{\frac{1}{2}} \\
E_1'(x) &= -\frac{1}{2} f(x)^{-\frac{1}{2}} f'(x) \\
E_1'(x) &= -\frac{1}{2f(x)^{\frac{1}{2}}} f'(x) \\
E_1'(x) &= \frac{1}{2E_1(x)} f'(x) \\
f'(x) &= \left\{[A(1 - e^{-B|x|})]^2 + [Ce^{-Dx^2}]^2\right\}' \\
&= 2A^2(1 - e^{-B|x|})\frac{d}{dx}(1 - e^{-B|x|}) + C^2\frac{d}{dx}e^{-2Dx^2} \\
&= 2A^2(1 - e^{-B|x|})(-e^{-B|x|}\frac{d}{dx}(-B|x|)) + C^2 e^{-2Dx^2}\frac{d}{dx}(-2Dx^2) \\
&= sign(x)2A^2Be^{-B|x|}(1 - e^{-B|x|}) - 4C^2Dxe^{-2Dx^2} \\
\therefore\ E_1'(x) &= \frac{1}{2E_1(x)} f'(x) \\
&= \frac{1}{E_1(x)}(sign(x)A^2Be^{-B|x|}(1 - e^{-B|x|}) - 2C^2Dxe^{-2Dx^2}) \\
\text{Similarly, } E_2(x) &= \sqrt{V_{11}^2 + V_{12}^2} = f(x)^{\frac{1}{2}} \\
E_2'(x) &= \frac{1}{2f(x)^{\frac{1}{2}}} f'(x) = \frac{1}{2E_2(x)} f'(x) \\
\therefore\ E_n'(x) &= \frac{1}{E_n(x)}(sign(x)A^2Be^{-B|x|}(1 - e^{-B|x|}) - 2C^2Dxe^{-2Dx^2}
\end{aligned}
$$

2 The Evolution of Wavefunction Exapnsion Coefficients

Expand the wavefunction in nonadiabatic basis and insert it into the time-dependent Schrödinger equation:

$$|\Psi(R,t)\rangle = \sum_j c_j(t)|\phi_j(R,t)\rangle$$
$$i\hbar\frac{d}{dt}|\Psi(R,t)\rangle = H(R,t)|\Psi(R,t)\rangle$$
$$i\hbar\frac{d}{dt}\sum_j c_j(t)|\phi_j(R,t)\rangle = H(R,t)\sum_j c_j(t)|\phi_j(R,t)\rangle$$

All terms are time dependent, drop the (R,t) for now:

$$i\hbar\frac{d}{dt}\sum_j c_j|\phi_j\rangle = H\sum_j c_j|\phi_j\rangle$$
$$i\hbar\sum_j\left(\frac{d}{dt}c_j|\phi_j\rangle + c_j\frac{d}{dt}|\phi_j\rangle\right) = H\sum_j c_j|\phi_j\rangle$$
$$i\hbar\sum_j\left(\dot{c}_j|\phi_j\rangle + c_j|\dot{\phi}_j\rangle\right) = H\sum_j c_j|\phi_j\rangle$$
$$\langle\phi_k|i\hbar\sum_j\left(\dot{c}_j|\phi_j\rangle + c_j|\dot{\phi}_j\rangle\right) = \langle\phi_k|H\sum_j c_j|\phi_j\rangle$$
$$i\hbar\sum_j\left(\dot{c}_j\langle\phi_k|\phi_j\rangle + c_j\langle\phi_k|\dot{\phi}_j\rangle\right) = \sum_j c_j\langle\phi_k|H|\phi_j\rangle$$
$$i\hbar\dot{c}_k + i\hbar\sum_j c_j\langle\phi_k|\dot{\phi}_j\rangle = \sum_j c_j\langle\phi_k|H|\phi_j\rangle$$
$$\therefore\ i\hbar\dot{c}_k = \sum_j\left(\langle\phi_k|H|\phi_j\rangle - i\hbar\langle\phi_k|\dot{\phi}_j\rangle\right)c_j$$

It looks more clear in matrix form.

$$\text{Let } \bar{H}_{kj} = \langle\phi_k|H|\phi_j\rangle - i\hbar\langle\phi_k|\dot{\phi}_j\rangle$$
$$\therefore \dot{c}_k = -\frac{i}{\hbar}\sum_j \bar{H}_{kj}c_j$$
$$\begin{cases} \dot{c}_1 = -\frac{i}{\hbar}(\bar{H}_{11}c_1 + \bar{H}_{12}c_1) \\ \dot{c}_2 = -\frac{i}{\hbar}(\bar{H}_{21}c_1 + \bar{H}_{22}c_2) \end{cases}$$
$$\frac{d}{dt}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = -\frac{i}{\hbar}\begin{pmatrix} \bar{H}_{11} & \bar{H}_{12} \\ \bar{H}_{21} & \bar{H}_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$
$$\therefore \underline{|\dot{c}\rangle = -\frac{i}{\hbar}\bar{H}|c\rangle}$$
$$\text{or } \underline{i\hbar|\dot{c}\rangle = \bar{H}|c\rangle}$$
$$\text{Usually } \hbar = 1,$$
$$\therefore |\dot{c}\rangle = -i\bar{H}|c\rangle$$
$$\bar{H} = H - iW$$
$$W = \langle\phi_k|\dot{\phi}_j\rangle$$

Note, the most important thing is that $|\dot{c}\rangle = -i\bar{H}|c\rangle$, which is the time evolution of c. It requires electronic Hamiltonian H and the nonadiabatic coupling W, as discussed later.
First, let's review how generally a wavefunction evolves during a time interval t:

$$\text{Given: } H_{(t)}|\Psi(t)\rangle = i\hbar\frac{d}{dt}|\Psi(t)\rangle$$
$$\text{and: } H_{(t)} = H \text{ (which means time-independent)}$$
$$\text{Then: } |\Psi(t)\rangle = e^{-iHt/\hbar}|\Psi(t_0)\rangle$$

Proof (skip if not interested):

$$d|\Psi(t)\rangle = -\frac{i}{\hbar}H_{(t)}dt|\Psi(t)\rangle = |\Psi(t+dt)\rangle - |\Psi(t)\rangle$$
$$|\Psi(t+dt)\rangle = |\Psi(t)\rangle - \frac{i}{\hbar}H_{(t)}dt|\Psi(t)\rangle$$
$$= (I - \frac{i}{\hbar}H_{(t)}dt)|\Psi(t)\rangle$$
$$= u(t+dt, t)|\Psi(t)\rangle$$

If we want to translate forward from $t = t_0$ to $t = t_0 + T$ in N steps, each step $\Delta t = \frac{T}{N}$, and Hamiltonian H_t does not change across the time interval T:

$$\begin{aligned}
u(t, t_0) &= u[t_0 + T, t_0 + (N-1)\Delta t] \cdot u[t_0 + (N-1)\Delta t, t_0 + (N-2)\Delta t] \ldots u[t_0 + \Delta t, t_0] \\
&= (I - \frac{i}{\hbar} H_{(t_0+(N-1)\Delta t)}\Delta t)(I - \frac{i}{\hbar} H_{(t_0+(N-2)\Delta t)}\Delta t) \ldots (I - \frac{i}{\hbar} H_{(t_0)}\Delta t) \\
&\because H_{(t)} \text{is time-independent} \\
\therefore u(t, t_0) &= (I - \frac{i}{\hbar} H\Delta t)(I - \frac{i}{\hbar} H\Delta t) \ldots (I - \frac{i}{\hbar} H\Delta t) \\
&= (I - \frac{i}{\hbar} H\Delta t)^N \\
&= (I - \frac{i}{\hbar} H \frac{t - t_0}{N})^N \\
&= (I + \frac{-iH(t - t_0)/\hbar}{N})^N \\
&\text{With } \lim_{N\to\infty} (1 + \frac{a}{N})^N = e^a \\
\therefore u(t, t_0) &= e^{-iH(t-t_0)/\hbar}
\end{aligned}$$

Therefore, the expansion coefficients c evolves as:

$$\begin{aligned}
\text{Known: } i\hbar|\dot{c}\rangle &= \bar{H}|c\rangle \\
\bar{H} &= H - iW \\
\text{which means } \bar{H} &\text{ is the effective Hamiltonian of } c \\
\therefore c(t + dt) &= u(t + dt, t)c(t) \\
u(t + dt, t) &= e^{-i\bar{H}dt/\hbar} = Ve^{-i\bar{E}dt/\hbar}V^T \\
\text{where } \bar{H} &= V\bar{E}V^T
\end{aligned}$$

$W = \langle \phi_k | \dot{\phi}_j \rangle$ is the nonadiabatic coupling.

$$\begin{aligned}
W &= \langle \phi_k | \dot{\phi}_j \rangle \\
&= \langle \phi_k | \frac{d\phi_j}{dt} \rangle \\
&= \langle \phi_k | \frac{dR}{dt} \frac{d\phi_j}{dR} \rangle \\
&= \frac{dR}{dt} \langle \phi_k | \frac{d\phi_j}{dR} \rangle \\
&= \dot{R} \cdot \tau_{kj},
\end{aligned}$$

where $\dot{R}$ is the nuclear velocity, τ_{kj} is the derivative coupling. Here is derivation of the derivative coupling τ, let $x = R$ for simplicity:

$$
\begin{aligned}
H|\phi_n\rangle &= E_n|\phi_n\rangle \\
\frac{d}{dx}H|\phi_n\rangle &= \frac{d}{dx}E_n|\phi_n\rangle \\
\frac{dH}{dx}|\phi_n\rangle + H|\frac{d\phi_n}{dx}\rangle &= \frac{dE_n}{dx}|\phi_n\rangle + E_n|\frac{d\phi_n}{dx}\rangle \\
\text{when } m \neq n : \\
\langle\phi_m|\frac{dH}{dx}|\phi_n\rangle + \langle\phi_m|H|\frac{d\phi_n}{dx}\rangle &= \frac{dE_n}{dx}\langle\phi_m|\phi_n\rangle + E_n\langle\phi_m|\frac{d\phi_n}{dx}\rangle \\
\langle\phi_m|\frac{dH}{dx}|\phi_n\rangle + E_m\langle\phi_m|\frac{d\phi_n}{dx}\rangle &= 0 + E_n\langle\phi_m|\frac{d\phi_n}{dx}\rangle \\
\tau_{mn} = \langle\phi_m|\frac{d\phi_n}{dx}\rangle &= \frac{\langle\phi_m|\frac{dH}{dx}|\phi_n\rangle}{E_n - E_m}
\end{aligned}
$$

$$
\begin{aligned}
\text{when } m = n : \\
\frac{d\langle\phi_n|\phi_n\rangle}{dx} &= 0 \\
\langle\dot{\phi}_n|\phi_n\rangle + \langle\phi_n|\dot{\phi}_n\rangle &= 0 \\
\therefore \langle\phi_n|\dot{\phi}_n\rangle &= 0
\end{aligned}
$$

As to matrix derivative $\frac{dH}{dx}$,

$$
\begin{aligned}
H &= \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \\
\frac{dH}{dx} &= \begin{pmatrix} \frac{d}{dx}V_{11} & \frac{d}{dx}V_{12} \\ \frac{d}{dx}V_{21} & \frac{d}{dx}V_{22} \end{pmatrix} \\
\therefore V'_{11} &= ABe^{-B|x|} \\
V'_{22} &= -V'_{11} \\
V'_{12} = V'_{21} &= -2CDxe^{-Dx^2}
\end{aligned}
$$

Hopping probability from state k to n during the time interval Δt is

$$
\begin{aligned}
p_{k->n} &= \frac{b_{nk}\Delta t}{a_{kk}} \\
b_{nk} &= \frac{2}{\hbar}Im\,(a_{kn}V_{nk}) - 2Re\left(a_{nk}\dot{R}\cdot\tau_{kn}\right) \\
a_{nk} &= c_k c_n^*
\end{aligned}
$$

If in diabatic basis, $|\phi_n\rangle$ is time-independent, so the *Re* part is 0; If in adiabatic basis, the Hamiltonian is diagonal ($V_{nk} = 0$), so the *Im* part is 0. We use adiabatic basis $|\phi_n\rangle$, which is the eigenket of electronic Hamiltonian H.