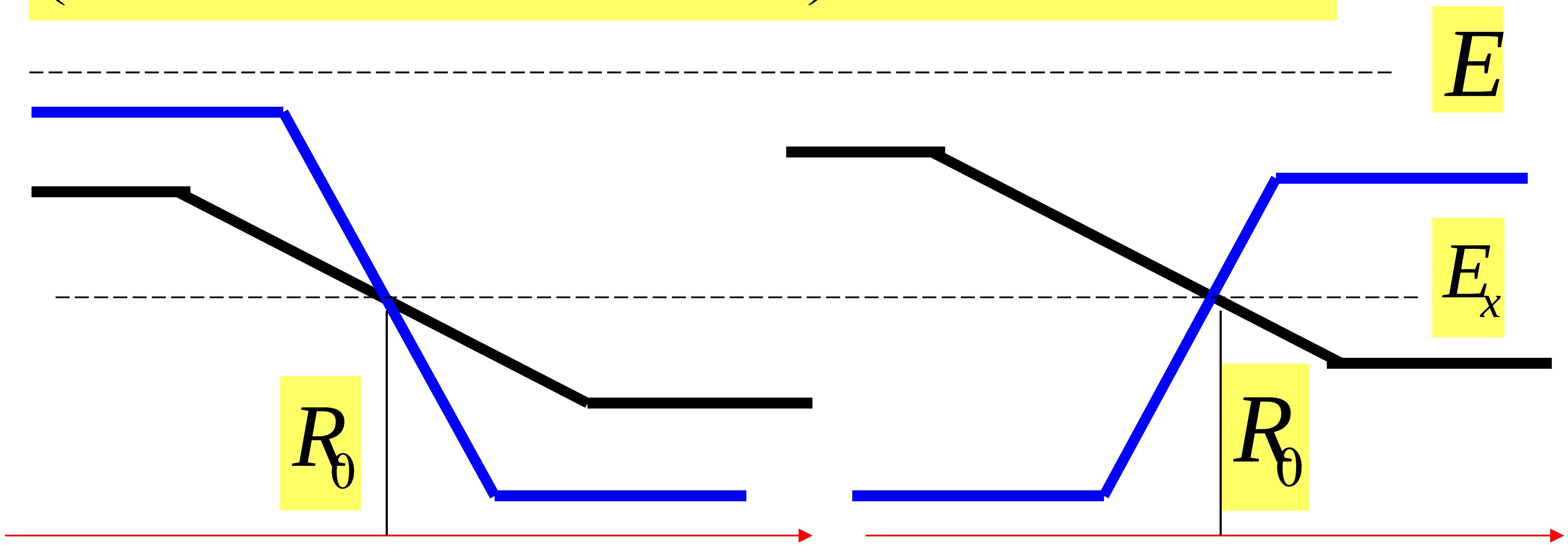
One-dimensional model

Coupled Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+\begin{bmatrix}V_{11}(R) & V_{12}(R)\\ V_{12}(R) & V_{22}(R)\end{bmatrix}\right)\begin{bmatrix}c_1(R)\\ c_2(R)\end{bmatrix}=E\begin{bmatrix}c_1(R)\\ c_2(R)\end{bmatrix}$$



same sign slope $F_1F_2>0$ opposite sign slope $F_1F_2<0$

$$V_{11}(R)=-F_1(R-R_0),\ V_{22}(R)=-F_2(R-R_0),\ V_{12}(R)=A=\text{constant}$$

Global transition probability

$$a^2 = \frac{\hbar^2}{2\mu} \frac{\sqrt{|F_1 F_2|}(F_1 - F_2)}{8A^3}$$

Effective nonadiabatic coupling

$$b^2 = (E - E_X)\frac{F_1 - F_2}{2\sqrt{|F_1 F_2|}A}$$

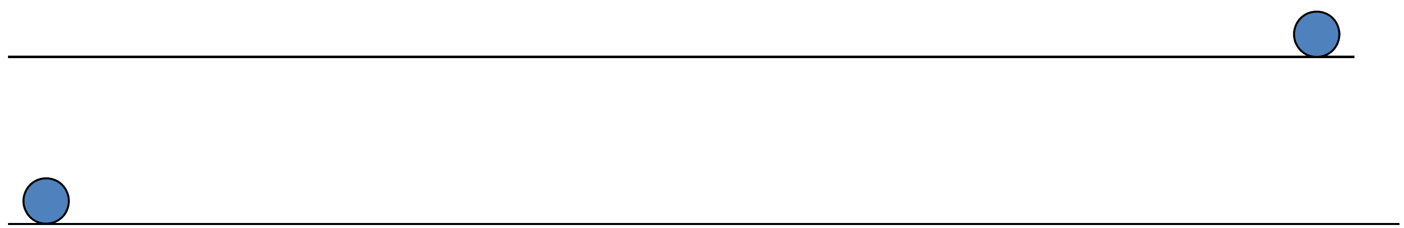
Effective collision energy

$$p = \exp\left[-\frac{\pi}{4a}\sqrt{\frac{2}{b^2 + \sqrt{b^4 + 1}}}\right]$$

$$p = \exp\left[-\frac{\pi}{4a}\sqrt{\frac{2}{b^2 + \sqrt{b^4 - 1}}}\right]$$

$$F_1 F_2 > 0$$

$$F_1 F_2 < 0$$



Section A: Diabatic case

Section B: Adiabatic case

Section C: Parallel case

Section A: Diabatic case

1. Generate two parameters (two diabatic)

Two-state diabatic potential energy surfaces

$$U_{1,2}(\mathbf{R}) = U_{1,2}(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N) = U_{1,2}(q_1, q_2, \cdots, q_{3N})$$

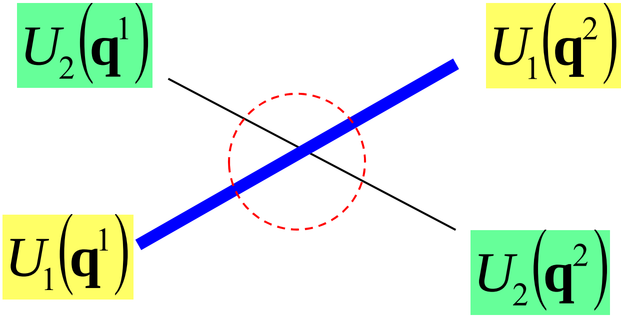
Gradient (first derivative)

$$\vec{q} = \mathbf{q} \equiv (q_1, q_2, \cdots, q_{3N})$$

$$\left(\frac{\partial U_1(\mathbf{q})}{\partial q_i}\right) \qquad \left(\frac{\partial U_2(\mathbf{q})}{\partial q_i}\right)$$

$$\begin{aligned}
\mathbf{R}_1 &= (q_1, q_2, q_3) \\
\mathbf{R}_2 &= (q_4, q_5, q_6) \\
&\cdots \\
\mathbf{R}_N &= (q_{3N-2}, q_{3N-1}, q_{3N})
\end{aligned} \longrightarrow \quad i = 1, 2, \cdots, 3N$$

Determine real crossing between two diabatic potential energy surfaces



Vx replace by spin-orbital coupling

$$\left[U_2(\mathbf{q}^1)-U_1(\mathbf{q}^1)\right]\left[U_2(\mathbf{q}^2)-U_1(\mathbf{q}^2)\right]<0$$

$$V_x=\frac{\left|U_1(\mathbf{q}^2)-U_2(\mathbf{q}^2)\right|}{2}$$

$$E_X=\frac{U_1(\mathbf{q}^2)+U_2(\mathbf{q}^2)}{2}$$

When it is minimum, you need evaluate a^2 and b^2

$$a^2=\frac{\hbar^2}{2m}\frac{F(F_2-F_1)}{8V_x^3}$$

$$b^2=(E-E_x)\frac{(F_2-F_1)}{2FV_x}$$

original a^2 and b^2

$$a^2b^2(old)=a^2b^2(new)$$

$$a^2=\frac{\hbar^2}{2m}\frac{(F_2-F_1)^2}{8V_x^3}$$

$$b^2=(E-E_x)\frac{1}{2V_x}$$

New definition of a^2 and b^2

Only calculate this

Two parameters for multidimensional potential energy surfaces

Vx replace by spin-orbital coupling

$$V_x = \frac{\left|U_1(\mathbf{q}^2) - U_2(\mathbf{q}^2)\right|}{2}$$

$$E_X = \frac{U_1(\mathbf{q}^2) + U_2(\mathbf{q}^2)}{2}$$

$$a^2 = \frac{\hbar^2}{2m} \frac{(F_2 - F_1)^2}{8V_x^3}$$

$$b^2 = (E - E_x)\frac{1}{2V_x}$$

$$\frac{(F_2 - F_1)^2}{m} \equiv \sum_{i=1}^{3N} \frac{(F_i^2 - F_i^1)^2}{m_i} = \sum_{\alpha=x,y,z} \sum_{i=1}^{N} \frac{(F_{i\alpha}^2 - F_{i\alpha}^1)^2}{m_i}$$

$$F_i^2 = \frac{\partial U_2(\mathbf{q}^2)}{\partial q_i}$$

$$F_i^1 = \frac{\partial U_1(\mathbf{q}^2)}{\partial q_i}$$

Replaced by

$$E = E_{//}$$

(should not use total E)

same sign slope $F_1F_2 > 0$ opposite sign slope $F_1F_2 < 0$

$$F_1F_2 = \sum_{i=1}^{3N} F_i^1\left(\mathbf{q}^2\right)F_i^2\left(\mathbf{q}^2\right)$$

Diabatic switching

$$p_{switch} = 1 - \exp\left[-\frac{\pi}{4a}\sqrt{\frac{2}{b^2 + \sqrt{b^4 + 1}}}\right]$$

$F_1F_2 > 0$

$$p_{switch} = 1 - \exp\left[-\frac{\pi}{4a}\sqrt{\frac{2}{b^2 + \sqrt{b^4 - 1}}}\right]$$

$F_1F_2 < 0$

Normalization in the following from calculation a^2

$$s_i = \frac{\left[F_i^2\left(\mathbf{q}^2\right) - F_i^1\left(\mathbf{q}^2\right)\right]\frac{1}{\sqrt{m_i}}}{\sqrt{\left(F_2 - F_1\right)^2 \frac{1}{m}}}$$

3N dimensional vector

$$\sum_{i=1}^{3N}\left(s_i\right)^2 = 1$$

$$\mathbf{n}_i = \frac{\mathbf{s}_i}{\left|\mathbf{s}_i\right|}$$

for each $\mathbf{P}_i$

Hopping direction for each (x,y,z)

$$\mathbf{n}_i^2 = 1$$

2. Define hopping direction (two diabatic)

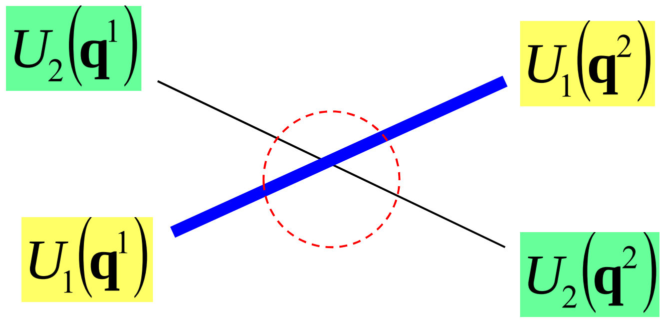
Hopping direction

$$\mathbf{n}_i = \frac{\mathbf{s}_i}{|\mathbf{s}_i|}$$

for each

$$\mathbf{n}_i^2 = 1$$

$$\mathbf{P}_i$$



Energy conservation for momentum

$$U_2(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_i^2(2)}{2m_i} = U_1(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_i^2(1)}{2m_i}$$

$$U_2(\mathbf{q}^2) + \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{P_{i\alpha}^2(2)}{2m_i} = U_1(\mathbf{q}^2) + \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{P_{i\alpha}^2(1)}{2m_i}$$

Momentum

$$\mathbf{P} = P_{x1}\vec{e}_{x1} + P_{y1}\vec{e}_{y1} + P_{z1}\vec{e}_{z1} + P_{x2}\vec{e}_{x2} + P_{y2}\vec{e}_{y2} + P_{z2}\vec{e}_{z2} + \cdots P_{xN}\vec{e}_{xN} + P_{yN}\vec{e}_{yN} + P_{zN}\vec{e}_{zN}$$

$$\mathbf{s} = s_{x1}\vec{e}_{x1} + s_{y1}\vec{e}_{y1} + s_{z1}\vec{e}_{z1} + s_{x2}\vec{e}_{x2} + s_{y2}\vec{e}_{y2} + s_{z2}\vec{e}_{z2} + \cdots s_{xN}\vec{e}_{xN} + s_{yN}\vec{e}_{yN} + s_{zN}\vec{e}_{zN}$$

For calculation of a^2 , we use normalization of total s

$$\sum_{i=1}^{N}\left(s_{ix}^2 + s_{iy}^2 + s_{iz}^2\right) = 1 \longrightarrow$$

$$\sum_{i=1}^{3N}\left(P_{i//}^2 + P_{i\perp}^2\right) = \sum_{i=1}^{3N} P_i^2$$

$$but \quad \sum_{i=1}^{3N}\left(\frac{P_{i//}^2}{m_i} + \frac{P_{i\perp}^2}{m_i}\right) \neq \sum_{i=1}^{3N}\frac{P_i^2}{m_i}$$

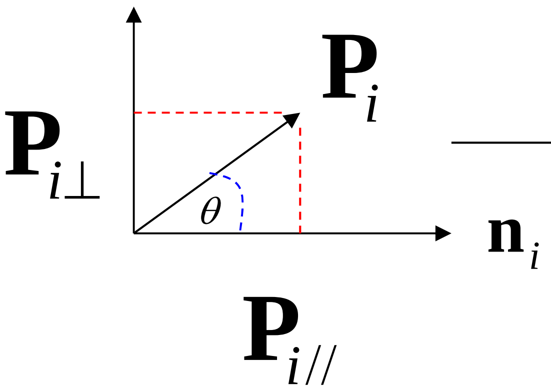
For calculating hopping direction,
we have to use normalization of each $\mathbf{s}_i$

$$\mathbf{s}_i = \left(s_{xi}, s_{iy}, s_{iz}\right)$$

Define unit vector for each $\mathbf{s}_i$

$$\mathbf{n}_i = \frac{\mathbf{s}_i}{\left|\mathbf{s}_i\right|}$$

$$\mathbf{P}_i = \mathbf{P}_{i//} + \mathbf{P}_{i\perp} \Rightarrow \begin{cases} \mathbf{P}_i^2 = \mathbf{P}_{i//}^2 + \mathbf{P}_{i\perp}^2 \\ \dfrac{\mathbf{P}_i^2}{m_i} = \dfrac{\mathbf{P}_{i//}^2 + \mathbf{P}_{i\perp}^2}{m_i} \end{cases}$$



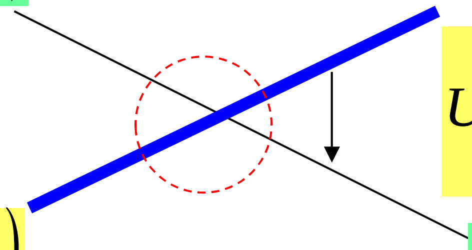
$$\boxed{\mathbf{P}_{i//} = \left(\mathbf{P}_i \cdot \mathbf{n}_i\right)\mathbf{n}_i} \rightarrow \text{Change after hopping}$$

$$\boxed{\mathbf{P}_{i\perp} = \mathbf{P}_i - \mathbf{P}_{i//}} \rightarrow \text{NO change after hopping}$$

Hopping from upper to lower potential with initio on $U_1(\mathbf{q}^1)$

$U_2(\mathbf{q}^1)$ $U_1(\mathbf{q}^2)$

$$U_2(\mathbf{q}^1)-U_1(\mathbf{q}^1)>0$$



$$U_1(\mathbf{q}^2)-U_2(\mathbf{q}^2)+\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(1)}{2m_i}=\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(2)}{2m_i}$$

$U_1(\mathbf{q}^1)$ $U_2(\mathbf{q}^2)$

After hopping

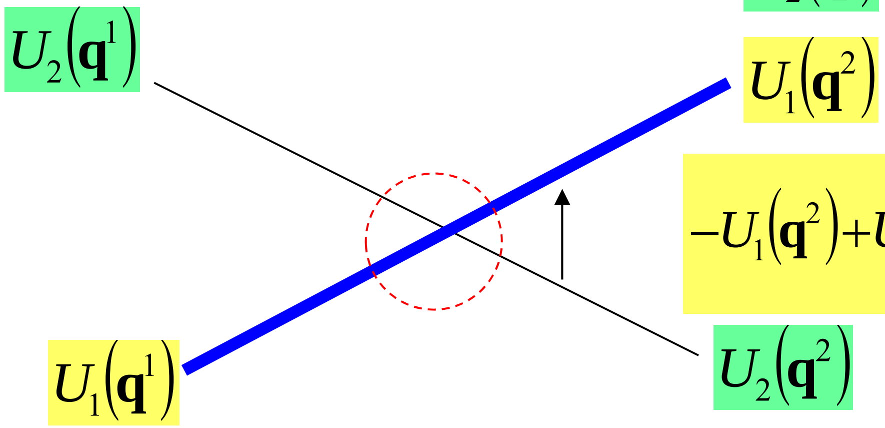
$$\mathbf{P}_{\mathbf{i}\perp}(2)=\mathbf{P}_{\mathbf{i}\perp}(1)=\mathbf{P}_{\mathbf{i}}(1)-(\mathbf{P}_{\mathbf{i}}(1)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}//}(2)=k\mathbf{P}_{\mathbf{i}//}(1)=k(\mathbf{P}_{\mathbf{i}}(1)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}}(2)=\mathbf{P}_{\mathbf{i}//}(2)+\mathbf{P}_{\mathbf{i}\perp}(2)=\mathbf{P}_{\mathbf{i}}(1)+(k-1)(\mathbf{P}_{\mathbf{i}}(1)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$k=\sqrt{1+\frac{U_1(\mathbf{q}^2)-U_2(\mathbf{q}^2)}{\sum_{i=1}^{N}\frac{\mathbf{P}_{i//}^{2}(1)}{2m_i}}}>1$$

Hopping from lower to upper potential with initio on $U_2(\mathbf{q}^1)$



$$U_2(\mathbf{q}^1) - U_1(\mathbf{q}^1) > 0$$

$$-U_1(\mathbf{q}^2) + U_2(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(2)}{2m_i} = \sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(1)}{2m_i}$$

After hopping

$$\mathbf{P}_{\mathbf{i}\perp}(1) = \mathbf{P}_{\mathbf{i}\perp}(2) = \mathbf{P}_{\mathbf{i}}(2) - (\mathbf{P}_{\mathbf{i}}(2)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}//}(1) = k\mathbf{P}_{\mathbf{i}//}(2) = k(\mathbf{P}_{\mathbf{i}}(2)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}}(1) = \mathbf{P}_{\mathbf{i}//}(1) + \mathbf{P}_{\mathbf{i}\perp}(1) = \mathbf{P}_{\mathbf{i}}(2) + (k-1)(\mathbf{P}_{\mathbf{i}}(2)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$k = \sqrt{1 - \frac{U_1(\mathbf{q}^2) - U_2(\mathbf{q}^2)}{\sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(2)}{2m_i}}} < 1$$

$$a^2 = \frac{\hbar^2}{2m}\frac{(F_2 - F_1)^2}{8V_x^3}$$

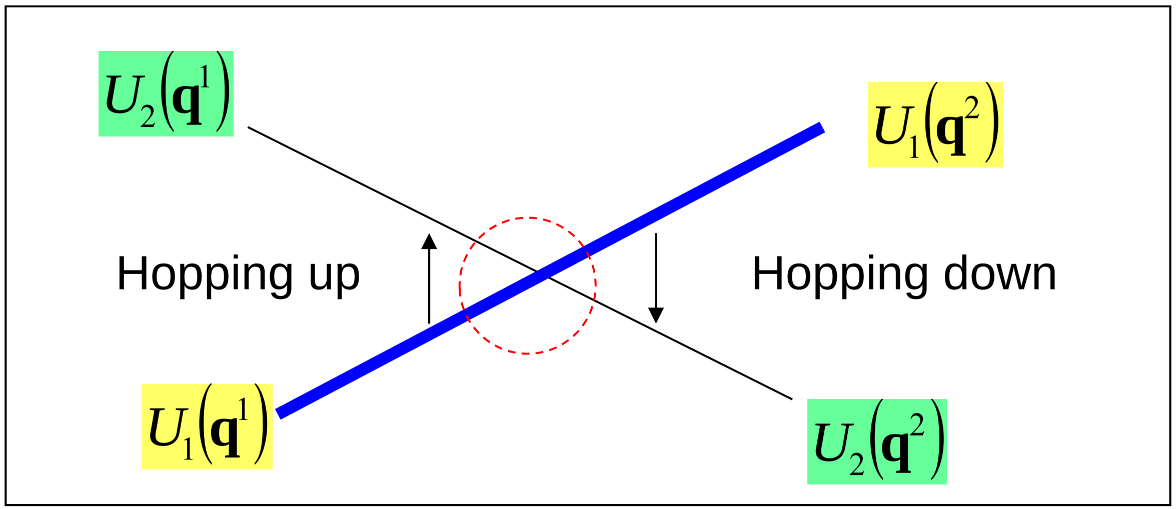
$$b^2 = (E_{//} - E_x)\frac{1}{2V_x}$$

Vx replace by spin-orbital coupling

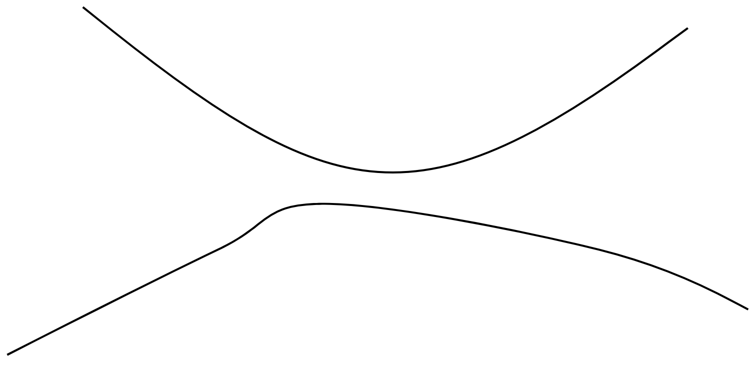
$$E_{//} = U_1(\mathbf{q}^2) + \sum_{i=1}^{N}\frac{\mathbf{P}_{i//}^{2}(1)}{2m_i} = U_2(\mathbf{q}^2) + \sum_{i=1}^{N}\frac{\mathbf{P}_{i//}^{2}(2)}{2m_i}$$

To avoid repeated hopping, after one or two time steps no hop is allowed

Not allowed



Section B: Adiabatic case



3. Generate two parameters (two adiabatic)

Two-state adiabatic potential energy surfaces

$$U_{\pm}(\mathbf{R}) = U_{\pm}(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N) = U_{\pm}(q_1, q_2, \cdots, q_{3N})$$

Gradient (first derivative)

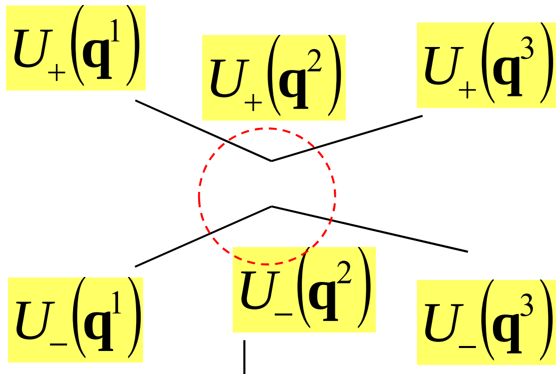
$$\vec{q} = \mathbf{q} \equiv (q_1, q_2, \cdots, q_{3N})$$

$$\left(\frac{\partial U_-(\mathbf{q})}{\partial q_i}\right) \quad \left(\frac{\partial U_+(\mathbf{q})}{\partial q_i}\right)$$

$$\mathbf{R}_1 = (q_1, q_2, q_3)$$
$$\mathbf{R}_2 = (q_4, q_5, q_6)$$
$$\cdots$$
$$\mathbf{R}_N = (q_{3N-2}, q_{3N-1}, q_{3N})$$

$$\longrightarrow \quad i = 1, 2, \cdots, 3N$$

Determine local minimum separation of potential



$$V_x = \frac{U_+(\mathbf{q}_2) - U_-(\mathbf{q}_2)}{2}$$

$$E_X = \frac{U_+(\mathbf{q}_2) + U_-(\mathbf{q}_2)}{2}$$

When it is minimum, you need evaluate a² and b²

$$a^2 = \frac{\hbar^2}{2m}\frac{F(F_2 - F_1)}{8V_x^3}$$

$$b^2 = (E - E_x)\frac{(F_2 - F_1)}{2FV_x}$$

original a² and b²

$$a^2b^2(old) = a^2b^2(new)$$

$$a^2 = \frac{\hbar^2}{2m}\frac{(F_2 - F_1)^2}{8V_x^3}$$

$$b^2 = (E - E_x)\frac{1}{2V_x}$$

New definition of a² and b²

Only calculate this

Two parameters for multidimensional potential energy surfaces

$$V_x = \frac{U_+(\mathbf{q}_2) - U_-(\mathbf{q}_2)}{2}$$

$$E_X = \frac{U_+(\mathbf{q}_2) + U_-(\mathbf{q}_2)}{2}$$

$$a^2 = \frac{\hbar^2}{2m} \frac{(F_2 - F_1)^2}{8V_x^3}$$

$$b^2 = (E - E_x)\frac{1}{2V_x}$$

$$\frac{(F_2 - F_1)^2}{m} \equiv \sum_{i=1}^{3N} \frac{(F_i^2 - F_i^1)^2}{m_i}$$

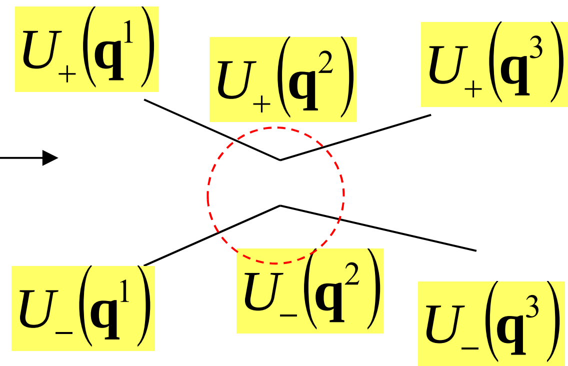
Replaced by

$$E = E_{//}$$

(should not use total E)

If $V_x \neq 0$

In order to avoid confuse of component index of vector we move point index to upper



Diabatization (derivative at q² is not useful)

$$F_i^1(\mathbf{q}) = \frac{1}{q_i^3 - q_i^1}\left[\frac{\partial U_-}{\partial q_i^3}\left(q_i - q_i^1\right) - \frac{\partial U_+}{\partial q_i^1}\left(q_i - q_i^3\right)\right] \longrightarrow F_i^1(\mathbf{q}) = \begin{cases} \dfrac{\partial U_+}{\partial q_i^1} & q_i = q_i^1 \\ \dfrac{\partial U_-}{\partial q_i^3} & q_i = q_i^3 \end{cases}$$

$$F_i^2(\mathbf{q}) = \frac{1}{q_i^3 - q_i^1}\left[\frac{\partial U_+}{\partial q_i^3}\left(q_i - q_i^1\right) - \frac{\partial U_-}{\partial q_i^1}\left(q_i - q_i^3\right)\right] \longrightarrow F_i^2(\mathbf{q}) = \begin{cases} \dfrac{\partial U_-}{\partial q_i^1} & q_i = q_i^1 \\ \dfrac{\partial U_+}{\partial q_i^3} & q_i = q_i^3 \end{cases}$$

$$\boxed{q_i^3 - q_i^1 = 0 \Rightarrow F_i^1(\mathbf{q}) = F_i^2(\mathbf{q}) = 0}$$

Mean not moving in that direction

same sign slope $F_1 F_2 > 0$ opposite sign slope $F_1 F_2 < 0$

$$F_1 F_2 = \sum_{i=1}^{3N} F_i^1(\mathbf{q}^2) F_i^2(\mathbf{q}^2)$$

$$\frac{1}{\sqrt{m_i}}\left[F_i^{\,2}\left(\mathbf{q}^2\right)-F_i^{\,1}\left(\mathbf{q}^2\right)\right]=\frac{1}{\sqrt{m_i}\left(q_i^3-q_i^1\right)}\left[\left(\frac{\partial U_+}{\partial q_i^3}-\frac{\partial U_-}{\partial q_i^3}\right)\left(q_i^2-q_i^1\right)+\left(\frac{\partial U_+}{\partial q_i^1}-\frac{\partial U_-}{\partial q_i^1}\right)\left(q_i^2-q_i^3\right)\right]$$

$$\frac{1}{\sqrt{m}}\left(F_2-F_1\right)=\max\left\{\frac{1}{\sqrt{m}}\left[\mathbf{F}^2\left(\mathbf{q}^2\right)-\mathbf{F}^1\left(\mathbf{q}^2\right)\right]\cdot\mathbf{s}\right\}$$

$\mathbf{s}$ – 3N dimensional unit vector

$\mathbf{s}$ is in the same direction of $\left(\mathbf{F}^2-\mathbf{F}^1\right)\frac{1}{\sqrt{m}}$

$$\frac{1}{m}\left(F_2-F_1\right)^2=\sum_{i=1}^{3N}\frac{1}{m_i}\left[F_i^{\,2}\left(\mathbf{q}^2\right)-F_i^{\,1}\left(\mathbf{q}^2\right)\right]\left[F_i^{\,2}\left(\mathbf{q}^2\right)-F_i^{\,1}\left(\mathbf{q}^2\right)\right]$$

Normalization in the following from calculation a^2

$$s_i = \frac{\left[F_i^2\left(\mathbf{q}^2\right) - F_i^1\left(\mathbf{q}^2\right)\right]\frac{1}{\sqrt{m_i}}}{\sqrt{\left(F_2 - F_1\right)^2 \frac{1}{m}}}$$

$$\sum_{i=1}^{3N}\left(s_i\right)^2 = 1$$

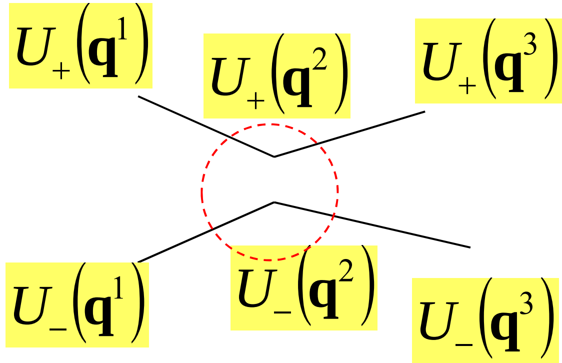
Hopping direction

$$\mathbf{n}_i = \frac{\mathbf{s}_i}{\left|\mathbf{s}_i\right|}$$

for each $\mathbf{P}_i$

$$\mathbf{n}_i^2 = 1$$

4. Define hopping direction (two adiabatic)



Hopping direction $\mathbf{n}_i = \dfrac{\mathbf{s}_i}{|\mathbf{s}_i|}$ for each $\mathbf{P}_i$

$\mathbf{n}_i^2 = 1$

Energy conservation for momentum

$$U_+(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_i^2(+)}{2m_i} = U_-(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_i^2(-)}{2m_i}$$

$$U_+(\mathbf{q}^2) + \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{P_{i\alpha}^2(+)}{2m_i} = U_-(\mathbf{q}^2) + \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{P_{i\alpha}^2(-)}{2m_i}$$

Momentum

$$\mathbf{P} = P_{x1}\vec{e}_{x1} + P_{y1}\vec{e}_{y1} + P_{z1}\vec{e}_{z1} + P_{x2}\vec{e}_{x2} + P_{y2}\vec{e}_{y2} + P_{z2}\vec{e}_{z2} + \cdots P_{xN}\vec{e}_{xN} + P_{yN}\vec{e}_{yN} + P_{zN}\vec{e}_{zN}$$

$$\mathbf{s} = s_{x1}\vec{e}_{x1} + s_{y1}\vec{e}_{y1} + s_{z1}\vec{e}_{z1} + s_{x2}\vec{e}_{x2} + s_{y2}\vec{e}_{y2} + s_{z2}\vec{e}_{z2} + \cdots s_{xN}\vec{e}_{xN} + s_{yN}\vec{e}_{yN} + s_{zN}\vec{e}_{zN}$$

For calculation of a², we use normalization of total s

$$\sum_{i=1}^{N}\left(s_{ix}^2 + s_{iy}^2 + s_{iz}^2\right) = 1 \longrightarrow$$

$$\sum_{i=1}^{3N}\left(P_{i//}^2 + P_{i\perp}^2\right) = \sum_{i=1}^{3N} P_i^2$$

$$but \sum_{i=1}^{3N}\left(\frac{P_{i//}^2}{m_i} + \frac{P_{i\perp}^2}{m_i}\right) \neq \sum_{i=1}^{3N}\frac{P_i^2}{m_i}$$

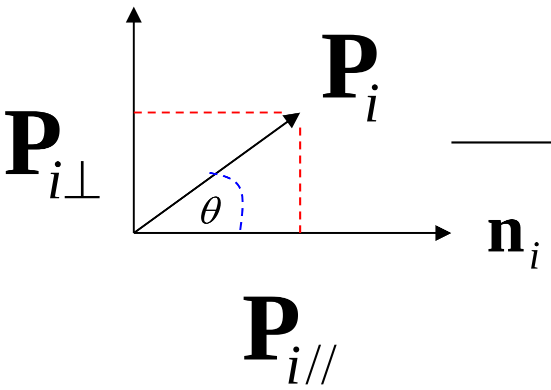
For calculating hopping direction,
we have to use normalization of each $\mathbf{s}_i$

$$\mathbf{s}_i = \left(s_{xi}, s_{iy}, s_{iz}\right)$$

Define unit vector for each $\mathbf{s}_i$

$$\mathbf{n}_i = \frac{\mathbf{s}_i}{\left|\mathbf{s}_i\right|}$$

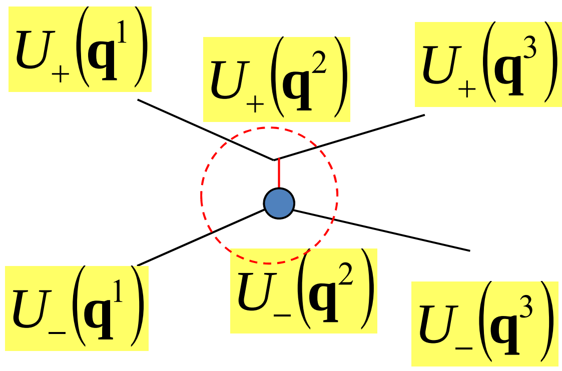
$$\mathbf{P}_i = \mathbf{P}_{i//} + \mathbf{P}_{i\perp} \Rightarrow \begin{aligned} &\mathbf{P}_i^2 = \mathbf{P}_{i//}^2 + \mathbf{P}_{i\perp}^2 \\ &\frac{\mathbf{P}_i^2}{m_i} = \frac{\mathbf{P}_{i//}^2 + \mathbf{P}_{i\perp}^2}{m_i} \end{aligned}$$



$$\boxed{\mathbf{P}_{i//} = (\mathbf{P}_i \cdot \mathbf{n}_i)\mathbf{n}_i} \rightarrow \text{Change after hopping}$$

$$\boxed{\mathbf{P}_{i\perp} = \mathbf{P}_i - \mathbf{P}_{i//}} \rightarrow \text{NO change after hopping}$$

Hopping from upper to lower potential



$$U_+(\mathbf{q}^2) - U_-(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(+)}{2m_i} = \sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(-)}{2m_i}$$

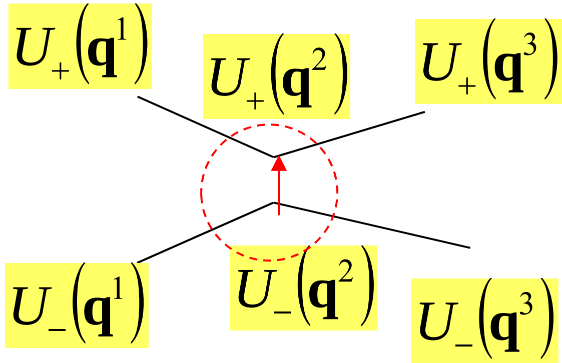
After hopping

$$\mathbf{P}_{\mathbf{i}\perp}(-) = \mathbf{P}_{\mathbf{i}\perp}(+) = \mathbf{P}_{\mathbf{i}}(+) - (\mathbf{P}_{\mathbf{i}}(+)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}//}(-) = k\mathbf{P}_{\mathbf{i}//}(+) = k(\mathbf{P}_{\mathbf{i}}(+)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}} \longrightarrow k = \sqrt{1 + \frac{U_+(\mathbf{q}^2) - U_-(\mathbf{q}^2)}{\sum_{i=1}^{N} \frac{\mathbf{P}_{i//}^{2}(+)}{2m_i}}} > 1$$

$$\mathbf{P}_{\mathbf{i}}(-) = \mathbf{P}_{\mathbf{i}//}(-) + \mathbf{P}_{\mathbf{i}\perp}(-) = \mathbf{P}_{\mathbf{i}}(+) + (k-1)(\mathbf{P}_{\mathbf{i}}(+)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

Hopping from lower to upper potential



$$-U_+(\mathbf{q}^2)+U_-(\mathbf{q}^2)+\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(-)}{2m_i}=\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(+)}{2m_i}$$

After hopping

$$b^2 \subset [0,1] \text{ and } k^2 < 0, \text{ set } k = 1$$

$$\mathbf{P}_{\mathbf{i}\perp}(+)=\mathbf{P}_{\mathbf{i}\perp}(-)=\mathbf{P}_{\mathbf{i}}(-)-(\mathbf{P}_{\mathbf{i}}(-)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}//}(+)=k\mathbf{P}_{\mathbf{i}//}(-)=k(\mathbf{P}_{\mathbf{i}}(-)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}} \longrightarrow k=\sqrt{1-\frac{U_+(\mathbf{q}^2)-U_-(\mathbf{q}^2)}{\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(-)}{2m_i}}}<1$$

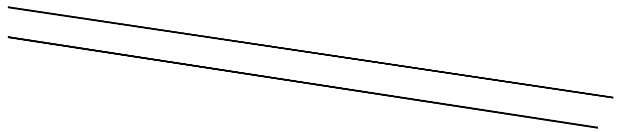
$$\mathbf{P}_{\mathbf{i}}(+)=\mathbf{P}_{\mathbf{i}//}(+)+\mathbf{P}_{\mathbf{i}\perp}(+)=\mathbf{P}_{\mathbf{i}}(-)+(k-1)(\mathbf{P}_{\mathbf{i}}(-)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$a^2 = \frac{\hbar^2}{2m}\frac{(F_2 - F_1)^2}{8V_x^3}$$

$$b^2 = (E_{//} - E_x)\frac{1}{2V_x}$$

$$E_{//} = U_-\left(\mathbf{q}^2\right) + \sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(-)}{2m_i} = U_+\left(\mathbf{q}^2\right) + \sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(+)}{2m_i}$$

Section C: Parallel case



Coupling shows in long distance region

Diabatic case
$$\begin{bmatrix} V_{11}(R) & V_{12}(R) \\ V_{12}(R) & V_{22}(R) \end{bmatrix}$$
Known

5. Generate three parameters (paralle case)

Two-state diabatic potential energy surfaces

$$U_{1,2}(\mathbf{R}) = U_{1,2}(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N) = U_{1,2}(q_1, q_2, \cdots, q_{3N})$$

$$U_{12}(\mathbf{R}) = U_{12}(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N) = U_{12}(q_1, q_2, \cdots, q_{3N})$$

Spin-orbital coupling

Gradient (first derivative)

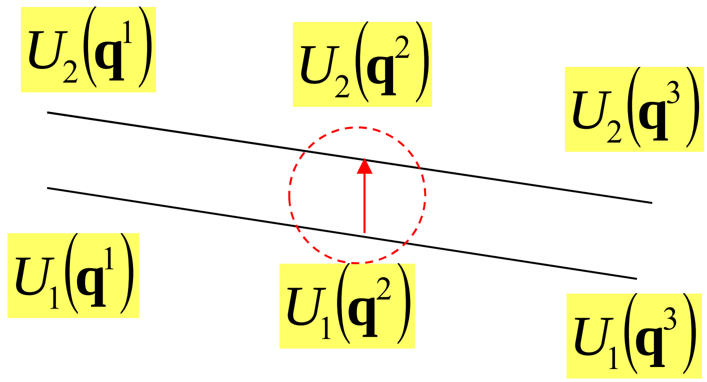
$$\vec{q} = \mathbf{q} \equiv (q_1, q_2, \cdots, q_{3N})$$

$$\left(\frac{\partial U_1(\mathbf{q})}{\partial q_i}\right) \qquad \left(\frac{\partial U_2(\mathbf{q})}{\partial q_i}\right)$$

$$\mathbf{R}_1 = (q_1, q_2, q_3)$$
$$\mathbf{R}_2 = (q_4, q_5, q_6)$$
$$\cdots$$
$$\mathbf{R}_N = (q_{3N-2}, q_{3N-1}, q_{3N})$$

$$\longrightarrow \quad i = 1, 2, \cdots, 3N$$

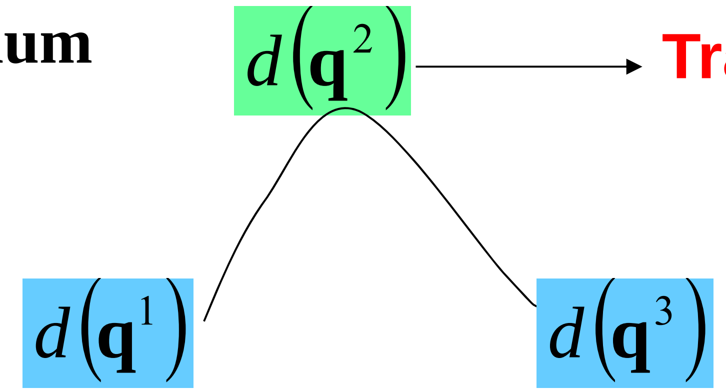
Determine transition point



$$d(\mathbf{q}^i) = \sqrt{1 + \left[\frac{2U_{12}(\mathbf{q}^i)}{U_{11}(\mathbf{q}^i) - U_{22}(\mathbf{q}^i)} \right]^2}$$

Spin-orbital coupling

Find local maximum (one parameter)



Transition point

The other two parameters

$$F_i^2 = \frac{\partial U_2(\mathbf{q}^2)}{\partial q_i} \qquad F_i^1 = \frac{\partial U_1(\mathbf{q}^2)}{\partial q_i}$$

$$\frac{(F_2+F_1)^2}{m} \equiv \sum_{i=1}^{3N} \frac{(F_i^2+F_i^1)^2}{m_i} = \sum_{\alpha=x,y,z} \sum_{i=1}^{N} \frac{(F_{i\alpha}^2+F_{i\alpha}^1)^2}{m_i}$$

Vx replace by spin-orbital coupling

$$V_x = \frac{\left|U_1(\mathbf{q}^2) - U_2(\mathbf{q}^2)\right|}{2}$$

$$E_X = \frac{U_1(\mathbf{q}^2) + U_2(\mathbf{q}^2)}{2}$$

$$a^2 = \frac{\hbar^2}{2m}\frac{(F_2+F_1)^2}{8V_x^3}\frac{1}{4}$$

$$b^2 = (E - E_x)\frac{1}{2V_x}$$

Replaced by

$$E = E_{//}$$

(should not use total E)

The diabatic switching probability

$$\delta = \frac{\pi}{8a}\sqrt{\frac{2}{b^2 + \sqrt{b^4+1}}}$$

Diabatic switching

$$p_{switch} = 1 - \frac{e^{2\left(d^2-1\right)\delta} - 1}{e^{2d^2\delta} - 1}$$

Note in numerical calculation $e^{2d^2\delta}$ may too big

Set up if $d^2\delta > 6$

$$p_{switch} = 1 - e^{-2\delta}$$

Generate random number 0<x<1

$$p_{switch} > x \longrightarrow \text{hop}$$

Normalization in the following from calculation a^2

$$s_i = \frac{\left[F_i^2\left(\mathbf{q}^2\right) + F_i^1\left(\mathbf{q}^2\right)\right]\frac{1}{\sqrt{m_i}}}{\sqrt{\left(F_2 + F_1\right)^2 \frac{1}{m}}}$$

$$\sum_{i=1}^{3N} \left(s_i\right)^2 = 1$$

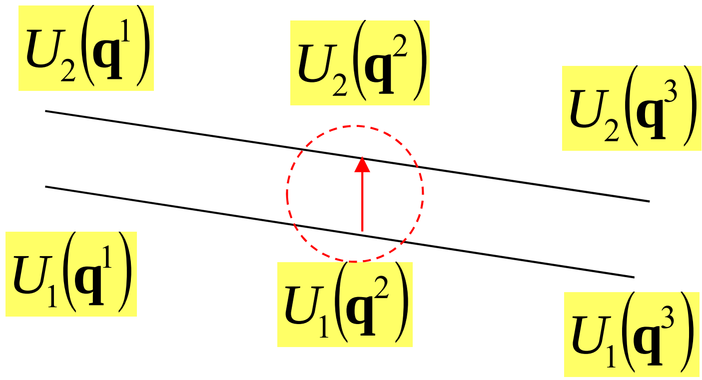
Hopping direction $$\mathbf{n}_i = \frac{\mathbf{s}_i}{\left|\mathbf{s}_i\right|}$$ for each $\mathbf{P}_i$

$$\mathbf{n}_i^2 = 1$$

6. Define hopping direction (two parallel)

Hopping direction $\mathbf{n}_i = \dfrac{\mathbf{s}_i}{|\mathbf{s}_i|}$ for each $\mathbf{P}_i$

$\mathbf{n}_i^2 = 1$

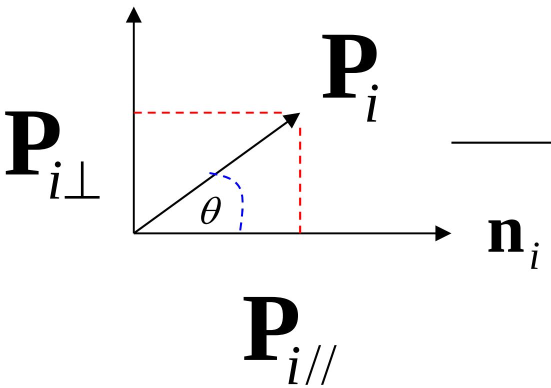


Energy conservation for momentum

$$U_2(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_i^2(2)}{2m_i} = U_1(\mathbf{q}^2) + \sum_{i=1}^{N} \frac{\mathbf{P}_i^2(1)}{2m_i}$$

$$U_2(\mathbf{q}^2) + \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{P_{i\alpha}^2(2)}{2m_i} = U_1(\mathbf{q}^2) + \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{P_{i\alpha}^2(1)}{2m_i}$$

$$\mathbf{P}_i = \mathbf{P}_{i//} + \mathbf{P}_{i\perp} \Rightarrow \begin{cases} \mathbf{P}_i^2 = \mathbf{P}_{i//}^2 + \mathbf{P}_{i\perp}^2 \\ \dfrac{\mathbf{P}_i^2}{m_i} = \dfrac{\mathbf{P}_{i//}^2 + \mathbf{P}_{i\perp}^2}{m_i} \end{cases}$$



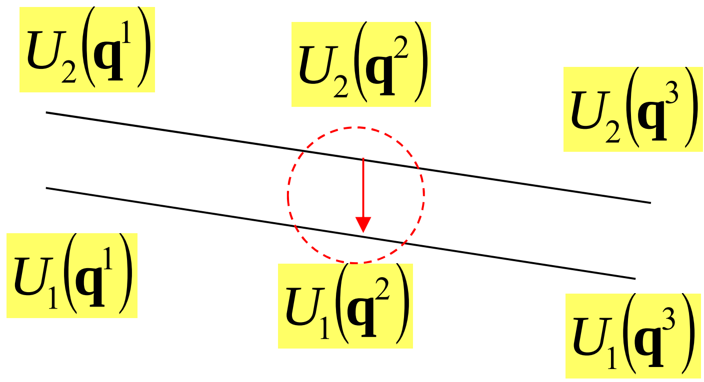
$$\boxed{\mathbf{P}_{i//} = \left(\mathbf{P}_i \cdot \mathbf{n}_i\right)\mathbf{n}_i}$$

Change after hopping

$$\boxed{\mathbf{P}_{i\perp} = \mathbf{P}_i - \mathbf{P}_{i//}}$$

NO change after hopping

Hopping from upper to lower potential



$$U_2\left(\mathbf{q}^2\right) - U_1\left(\mathbf{q}^2\right) + \sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(2)}{2m_i} = \sum_{i=1}^{N} \frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(1)}{2m_i}$$

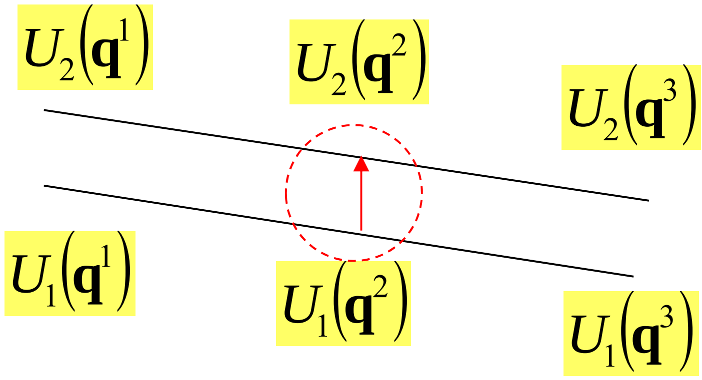
After hopping

$$\mathbf{P}_{\mathbf{i}\perp}(1) = \mathbf{P}_{\mathbf{i}\perp}(2) = \mathbf{P}_{\mathbf{i}}(2) - \left(\mathbf{P}_{\mathbf{i}}(2)\cdot\mathbf{n}_{\mathbf{i}}\right)\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}//}(1) = k\mathbf{P}_{\mathbf{i}//}(2) = k\left(\mathbf{P}_{\mathbf{i}}(2)\cdot\mathbf{n}_{\mathbf{i}}\right)\mathbf{n}_{\mathbf{i}} \longrightarrow k = \sqrt{1 + \frac{U_2\left(\mathbf{q}^2\right) - U_1\left(\mathbf{q}^2\right)}{\sum_{i=1}^{N} \frac{\mathbf{P}_{i//}^{2}(2)}{2m_i}}} > 1$$

$$\mathbf{P}_{\mathbf{i}}(1) = \mathbf{P}_{\mathbf{i}//}(1) + \mathbf{P}_{\mathbf{i}\perp}(1) = \mathbf{P}_{\mathbf{i}}(2) + (k-1)\left(\mathbf{P}_{\mathbf{i}}(2)\cdot\mathbf{n}_{\mathbf{i}}\right)\mathbf{n}_{\mathbf{i}}$$

Hopping from lower to upper potential



$$-U_2(\mathbf{q}^2)+U_1(\mathbf{q}^2)+\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(1)}{2m_i}=\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(2)}{2m_i}$$

After hopping

$$\mathbf{P}_{\mathbf{i}\perp}(2)=\mathbf{P}_{\mathbf{i}\perp}(1)=\mathbf{P}_{\mathbf{i}}(1)-(\mathbf{P}_{\mathbf{i}}(1)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$\mathbf{P}_{\mathbf{i}//}(2)=k\mathbf{P}_{\mathbf{i}//}(1)=k(\mathbf{P}_{\mathbf{i}}(1)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}} \longrightarrow k=\sqrt{1-\frac{U_2(\mathbf{q}^2)-U_1(\mathbf{q}^2)}{\sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i}//}^{\mathbf{2}}(1)}{2m_i}}}<1$$

$$\mathbf{P}_{\mathbf{i}}(2)=\mathbf{P}_{\mathbf{i}//}(2)+\mathbf{P}_{\mathbf{i}\perp}(2)=\mathbf{P}_{\mathbf{i}}(1)+(k-1)(\mathbf{P}_{\mathbf{i}}(1)\cdot\mathbf{n}_{\mathbf{i}})\mathbf{n}_{\mathbf{i}}$$

$$a^2 = \frac{\hbar^2}{2m}\frac{(F_2 + F_1)^2}{8V_x^3}$$

$$b^2 = (E_{//} - E_x)\frac{1}{2V_x}$$

$$E_{//} = U_1\left(\mathbf{q}^2\right) + \sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i//}}^{\mathbf{2}}\left(1\right)}{2m_i} = U_2\left(\mathbf{q}^2\right) + \sum_{i=1}^{N}\frac{\mathbf{P}_{\mathbf{i//}}^{\mathbf{2}}\left(2\right)}{2m_i}$$

Constrained molecular dynamics

$$\boxed{H(q,p,\lambda)=\sum_{i}^{3N}\frac{P_i^2}{2m_i}+V(q)+\sum_{k}^{N_C}\lambda_k g_k(q)}$$

Constrained Hamiltonian canonical equations

$$\boxed{\begin{cases}\dot{q}_i=\dfrac{\partial H(q,p,\lambda)}{\partial p_i}=H_{q_i}(q,p,\lambda)=\dfrac{p_i}{m_i}\\[2ex] \dot{p}_i=-\dfrac{\partial H(q,p,\lambda)}{\partial q_i}=f_i^{uc}+f_i^{c}=-\dfrac{\partial V(q)}{\partial q_i}-\displaystyle\sum_{k}^{N_C}\lambda_k\dfrac{\partial g_k(q)}{\partial q_i}\\[2ex] g_k(q)=0\\[2ex] \dot{g}_k(q)=0\Rightarrow\displaystyle\sum_{i}\dfrac{\partial g_k(q)}{\partial q_i}\dot{q}_i=\sum_{i}\dfrac{\partial g_k(q)}{\partial q_i}\dfrac{p_i}{m_i}=0\end{cases}}$$

The most simple case for on-the-fly trajectory

At time t_i, force is treated as constant until t_{i+1}

$$U(t)=U(q_1,q_2,\ldots,q_M)=U(q_{10},q_{20},\ldots,q_{M0})+\sum_{i=1}^{M}\left(\frac{\partial U}{\partial q_i}\right)_{q=q_0}(q_i-q_{i0})$$

$$m\frac{d^2q}{dt^2}=F$$

$$F=-\frac{\partial U}{\partial q}$$

$$q(t)=\frac{F}{2m}t^2+C_1t+C_2$$
$$p(t)=m\dot{q}(t)=Ft+C_1m$$

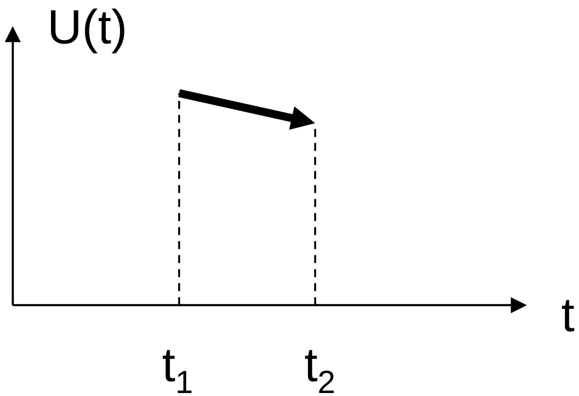
$$q_0=q(t_0)=\frac{F}{2m}t_0^{\ 2}+C_1t_0+C_2$$
$$p_0=p(t_0)=Ft_0+C_1m$$

$$C_1=\frac{p_0-Ft_0}{m}$$
$$C_2=\frac{F}{m}t_0^{\ 2}+q_0-\frac{p_0t_0}{m}$$

Finally

$$q(t)-q(t_0)=\frac{F}{2m}(t-t_0)^2+\frac{p(t_0)(t-t_0)}{m}$$
$$p(t)-p(t_0)=F(t-t_0)$$

Coding



For each $q_i(t), p_i(t)$

Force at t

$$F_i(q_0) = -\left(\frac{\partial U}{\partial q_i}\right)_{q=q_0}$$

$$q_i(t_2) - q_i(t_1) = \frac{F_i(q_1)}{2m_i}(t_2 - t_1)^2 + \frac{p_i(t_1)(t_2 - t_1)}{m_i}$$

$$p_i(t_2) - p_i(t_1) = F_i(q_1)(t_2 - t_1)$$

All coordinates and momentum evolutes from t_1 to t_2 according the above

Next step $t_2 \longrightarrow t_3$, using above again

RATTLE

Use average force (for better)

~0.5fs

$$q_i = \left(q_1(t_1), q_2(t_1), \ldots, \mathrm{q}_{3n}(t_1)\right)$$

$$\Delta t = t_2 - t_1$$

$$q_i(t_2) - q_i(t_1) = \frac{F_i^c\left(q_i^1\right) + F_i^{uc}\left(q_i^1\right)}{2m_i}(t_2 - t_1)^2 + \frac{p_i(t_1)(t_2 - t_1)}{m_i}$$

$$q_2 = \left(q_1(t_2), q_2(t_2), \ldots, \mathrm{q}_{3n}(t_2)\right)$$

$$p_i(t_2) - p_i(t_1) = \left[\frac{F_i(q_i^1) + F_i(q_i^2)}{2}\right](t_2 - t_1)$$

Leap-Frog method
macromolecules,
15:1528, 1544, 1982.
RATTLE
J. Comput. Phys.
52, 24, 1983.

$$F_i(q_i^j) = F_i^{uc}(q_i^j) + F_i^c(q_i^j) = -\frac{\partial V(q_i^j)}{\partial q_i^j} - \sum_k^{Nc} \lambda_k \frac{\partial g_k(q_i^j)}{\partial q_i^j}$$

Powell's Dog Leg method

- These non-linear constrained equations $g_k\ (t)$ are best solved using **Powell's Dog Leg method** (works with combinations of the Gauss-Newton and the steepest descent directions)[1, 2]. This method involves computing the **Jacobian** of the vector of constraint equation.

1) K. Madsen, H. B. Nielsen, O. Tingleff, Methods For Non-linear Least Squares Problems 2nd Edition, 2004, Informatics and Mathematical Modelling Technical University of Denmark
http://www2.imm.dtu.dk/pubdb/views/edoc_download.php/3215/pdf/imm3215.pdf

2) M.J.D. Powell (1970): A Hybrid Method for Non-Linear Equations. In P. Rabinowitz(ed): *Numerical Methods for Non-Linear Algebraic Equations*, Gordon and Breach. pp 87ff.

Jacobian matrices

$$J_g = \begin{bmatrix} \dfrac{\partial g_1}{\partial \lambda_1} & \dfrac{\partial g_1}{\partial \lambda_2} & \cdots & \dfrac{\partial g_1}{\partial \lambda_{N_C}} \\ \dfrac{\partial g_2}{\partial \lambda_1} & \dfrac{\partial g_2}{\partial \lambda_2} & \cdots & \dfrac{\partial g_2}{\partial \lambda_{N_C}} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \dfrac{\partial g_{N_C}}{\partial \lambda_1} & \dfrac{\partial g_{N_C}}{\partial \lambda_2} & \cdots & \dfrac{\partial g_{N_C}}{\partial \lambda_{N_C}} \end{bmatrix} \qquad J_{\dot{g}} = \begin{bmatrix} \dfrac{\partial \dot{g}_1}{\partial \xi_1} & \dfrac{\partial \dot{g}_1}{\partial \xi_2} & \cdots & \dfrac{\partial \dot{g}_1}{\partial \xi_{N_C}} \\ \dfrac{\partial \dot{g}_2}{\partial \xi_1} & \dfrac{\partial \dot{g}_2}{\partial \xi_2} & \cdots & \dfrac{\partial \dot{g}_2}{\partial \xi_{N_C}} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \dfrac{\partial \dot{g}_{N_C}}{\partial \xi_1} & \dfrac{\partial \dot{g}_{N_C}}{\partial \xi_2} & \cdots & \dfrac{\partial \dot{g}_{N_C}}{\partial \xi_{N_C}} \end{bmatrix}$$

Powell's Dog Leg method

- with combinations of the Gauss–Newton and the steepest descent directions.
- a) Gauss–Newton step: $\boxed{(J(x)^T J(x))h_{gn} = -J(x)^T g(x)}$
- b) steepest descent direction: $\boxed{h_{sd} = -J(x)^T g(x)}$

  the step should be αh_{sd}

$$\boxed{g(x+\alpha h_{sd}) \approx g(x) + \alpha J(x) h_{sd} \Rightarrow \alpha = -\frac{h_{sd}{}^T J(x)^T g(x)}{\| J(x) h_{sd} \|^2}}$$

- The name ***Dog Leg*** is taken from golf: The fairway at a "dog-leg hole"(曲形球道) has a shape as the line from **x** (the tee point) via the end point of **a** to the end point of $\mathbf{h}_{dl}$ (the hole). **Powell is a keen golfer!**

Powell's Dog Leg method

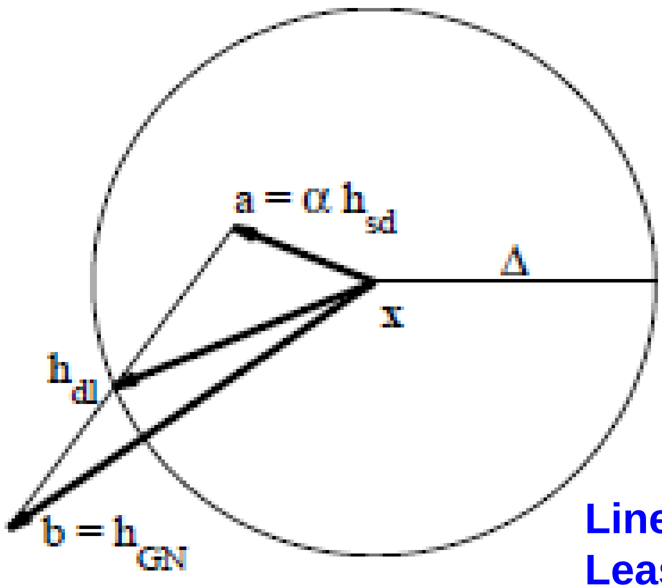
if $\|\mathbf{h}_{gn}\| \leq \Delta$
$\quad \mathbf{h}_{dl} := \mathbf{h}_{gn}$
elseif $\|\alpha \mathbf{h}_{sd}\| \geq \Delta$
$\quad \mathbf{h}_{dl} := (\Delta / \|\mathbf{h}_{sd}\|) \mathbf{h}_{sd}$
else
$\quad \mathbf{h}_{dl} := \alpha \mathbf{h}_{sd} + \beta(\mathbf{h}_{gn} - \alpha \mathbf{h}_{sd})$
$\quad\quad$ with β chosen so that $\|\mathbf{h}_{dl}\| = \Delta$.

With a and b as defined above, and $c = \mathbf{a}^\top(\mathbf{b}-\mathbf{a})$ we can write

$$\psi(\beta) \equiv \|\mathbf{a} + \beta(\mathbf{b}-\mathbf{a})\|^2 - \Delta^2 = \|\mathbf{b}-\mathbf{a}\|^2\beta^2 + 2c\beta + \|\mathbf{a}\|^2 - \Delta^2 .$$

We seek a root for this second degree polynomial, and note that $\psi \to +\infty$ for $\beta \to -\infty$; $\psi(0) = \|\mathbf{a}\|^2 - \Delta^2 < 0$; $\psi(1) = \|\mathbf{h}_{gn}\|^2 - \Delta^2 > 0$. Thus, ψ has one negative root and one root in $]0, 1[$. We seek the latter, and the most accurate computation of it is given by

if $c \leq 0$
$$\beta = \left(-c + \sqrt{c^2 + \|\mathbf{b}-\mathbf{a}\|^2(\Delta^2 - \|\mathbf{a}\|^2)}\right) / \|\mathbf{b}-\mathbf{a}\|^2$$
else
$$\beta = (\Delta^2 - \|\mathbf{a}\|^2) / \left(c + \sqrt{c^2 + \|\mathbf{b}-\mathbf{a}\|^2(\Delta^2 - \|\mathbf{a}\|^2)}\right)$$



gain ratio

$$\varrho = \frac{F(\mathbf{x}) - F(\mathbf{x}+\mathbf{h})}{L(\mathbf{0}) - L(\mathbf{h})} ,$$

if $\varrho < 0.25$
$\quad \Delta := \Delta/2$
elseif $\varrho > 0.75$
$\quad \Delta := \max\{\Delta, 3 * \|h\|\}$

$$L(\mathbf{0}) - L(\mathbf{h}_{dl}) = \begin{cases} F(\mathbf{x}) & \text{if } \mathbf{h}_{dl} = \mathbf{h}_{gn} \\ \dfrac{\Delta(2\|\alpha\mathbf{g}\| - \Delta)}{2\alpha} & \text{if } \mathbf{h}_{dl} = \dfrac{-\Delta}{\|\mathbf{g}\|}\mathbf{g} \\ \frac{1}{2}\alpha(1-\beta)^2\|\mathbf{g}\|^2 + \beta(2-\beta)F(\mathbf{x}) & \text{otherwise} \end{cases}$$

Linear or Non-Linear Least Squares Problem

$$F(x) = \frac{1}{2}\sum_{i=1}^{m}(g_i(x))^2$$

$$g(x+h) \cong l(h) \equiv g(x) + J(x)h \Rightarrow L(h) \equiv \frac{1}{2} l(h)^T l(h)$$

Full Jacobian with all constrained equations about internal coordinates

J. Comput. Phys. 220 (2007) 740–750.
J. Comput. Phys. 23 (1977) 327–341.
J. Comput. Chem. 22 (5) (2001) 501–508.
computer physics reports 4 (1986) 346-392

- **Bond length constraints**

$$\boxed{g_k^b(q) = q_{k_1k_2}^2 - d_{k_1k_2}^2 = 0, \qquad k = 1, \ldots, N_c^b}$$

- **Bond angle constraints**

$$g_k^a = \cos\theta_{k_1k_2k_3} \, |\mu^a| \, |\nu^a| - \mu^a \cdot \nu^a = 0$$

$$\mu^a = q_{k_1} - q_{k_2}, \qquad \nu^a = q_{k_3} - q_{k_2}$$

$$\mu^a \cdot \nu^a = \mu^a{}_x \nu^a{}_x + \mu^a{}_y \nu^a{}_y + \mu^a{}_z \nu^a{}_z \,, \qquad k = 1, \ldots, N_c^a$$

Full Jacobian with all constrained equations about internal coordinates

- **Dihedral angle constraints**

$$g_k^d = \cos\phi_{k_1k_2k_3k_4} |\mu^d||\nu^d| - \mu^d \cdot \nu^d = 0$$

$$\mu^{d\,2} = (\mu^{d\,2}_x + \mu^{d\,2}_y + \mu^{d\,2}_z), \qquad \nu^{d\,2} = (\nu^{d\,2}_x + \nu^{d\,2}_y + \nu^{d\,2}_z)$$

$$\mu^d \cdot \nu^d = \mu^d{}_x \nu^d{}_x + \mu^d{}_y \nu^d{}_y + \mu^d{}_z \nu^d{}_z\,, \qquad k = 1, \ldots, N_c^d$$

$$\mu^d{}_x = (y_{k_2} - y_{k_1})(z_{k_3} - z_{k_2}) - (z_{k_2} - z_{k_1})(y_{k_3} - y_{k_2})$$

$$\mu^d{}_y = (z_{k_2} - z_{k_1})(x_{k_3} - x_{k_2}) - (x_{k_2} - x_{k_1})(z_{k_3} - z_{k_2})$$

$$\mu^d{}_z = (x_{k_2} - x_{k_1})(y_{k_3} - y_{k_2}) - (y_{k_2} - y_{k_1})(x_{k_3} - x_{k_2})$$

$$-\nu^d{}_x = (y_{k_4} - y_{k_3})(z_{k_3} - z_{k_2}) - (z_{k_4} - z_{k_3})(y_{k_3} - y_{k_2})$$

$$-\nu^d{}_y = (z_{k_4} - z_{k_3})(x_{k_3} - x_{k_2}) - (x_{k_4} - x_{k_3})(z_{k_3} - z_{k_2})$$

$$-\nu^d{}_z = (x_{k_4} - x_{k_3})(y_{k_3} - y_{k_2}) - (y_{k_4} - y_{k_3})(x_{k_3} - x_{k_2})$$

Full Jacobian with all constrained equations about internal coordinates

The position vector

$$q_{k_\beta}(t+\Delta t) = q_{k_\beta}^{uc}(t+\Delta t) - m_{k_\beta}^{-1}(\Delta t)^2$$

$$\{ \sum_{k'=1}^{N_C^b} \lambda_{k'}^b(t)[\delta_{k_1'k_\beta} \frac{\partial g_{k'}^b(t)}{\partial q_{k_1'}(t)} + \delta_{k_2'k_\beta} \frac{\partial g_{k'}^b(t)}{\partial q_{k_2'}(t)}]$$

$$+ \sum_{k'=1}^{N_C^a} \lambda_{k'}^a(t)[\delta_{k_1'k_\beta} \frac{\partial g_{k'}^a(t)}{\partial q_{k_1'}(t)} + \delta_{k_2'k_\beta} \frac{\partial g_{k'}^a(t)}{\partial q_{k_2'}(t)} + \delta_{k_3'k_\beta} \frac{\partial g_{k'}^a(t)}{\partial q_{k_3'}(t)}]$$

$$+ \sum_{k'=1}^{N_C^d} \lambda_{k'}^d(t)[\delta_{k_1'k_\beta} \frac{\partial g_{k'}^d(t)}{\partial q_{k_1'}(t)} + \delta_{k_2'k_\beta} \frac{\partial g_{k'}^d(t)}{\partial q_{k_2'}(t)} + \delta_{k_3'k_\beta} \frac{\partial g_{k'}^d(t)}{\partial q_{k_3'}(t)} + \delta_{k_4'k_\beta} \frac{\partial g_{k'}^d(t)}{\partial q_{k_4'}(t)}]$$

$$\}, q = x, y, z$$

$$\boxed{q_i^{uc}(t+\Delta t) = q_i^{uc}(t) + \frac{F_i^{uc}(t)}{2m_i}(\Delta t)^2 + \frac{p_i^{uc}(t)}{m_i}\Delta t}$$

Full Jacobian with all constrained equations about internal coordinates

The momentum vector

$$p_{k_\beta}(t+\Delta t)=p_{k_\beta}^{uc}(t+\Delta t)-\Delta t\ \{\ \sum_{k'=1}^{N_C^b}\xi_{k'}^{b}(t+\Delta t)[\delta_{k'_1k_\beta}\frac{\partial g_{k'}^{b}(t+\Delta t)}{\partial q_{k'_1}(t+\Delta t)}+\delta_{k'_2k_\beta}\frac{\partial g_{k'}^{b}(t+\Delta t)}{\partial q_{k'_2}(t+\Delta t)}]$$

$$+\sum_{k'=1}^{N_C^a}\xi_{k'}^{a}(t+\Delta t)[\delta_{k'_1k_\beta}\frac{\partial g_{k'}^{a}(t+\Delta t)}{\partial q_{k'_1}(t+\Delta t)}+\delta_{k'_2k_\beta}\frac{\partial g_{k'}^{a}(t+\Delta t)}{\partial q_{k'_2}(t+\Delta t)}+\delta_{k'_3k_\beta}\frac{\partial g_{k'}^{a}(t+\Delta t)}{\partial q_{k'_3}(t+\Delta t)}]$$

$$+\sum_{k'=1}^{N_C^d}\xi_{k'}^{d}(t+\Delta t)[\delta_{k'_1k_\beta}\frac{\partial g_{k'}^{d}(t+\Delta t)}{\partial q_{k'_1}(t+\Delta t)}+\delta_{k'_2k_\beta}\frac{\partial g_{k'}^{d}(t+\Delta t)}{\partial q_{k'_2}(t+\Delta t)}+\delta_{k'_3k_\beta}\frac{\partial g_{k'}^{d}(t+\Delta t)}{\partial q_{k'_3}(t+\Delta t)}+\delta_{k'_4k_\beta}\frac{\partial g_{k'}^{d}(t+\Delta t)}{\partial q_{k'_4}(t+\Delta t)}]\}$$

$$P_i^{uc}(t+\Delta t)=P_i^{uc}(t)+\frac{1}{2}\left(F_i^{uc}(t)+F_i^{uc}(t+\Delta t)\right)\Delta t$$

Full Jacobian with all constrained equations about internal coordinates

$$J_{kk'}^{g} = \frac{\partial g_k^p(t+\Delta t)}{\partial \lambda_{k'}^p(t)}$$

$$= \sum_{i=1}^{N}\sum_{l=1}^{3}\left[\frac{\partial g_k^p(t+\Delta t)}{\partial q_{l,i}(t+\Delta t)}\frac{\partial q_{l,i}(t+\Delta t)}{\partial \lambda_{k'}^p(t)}\right]$$

$$= -\frac{1}{2}\sum_{i=1}^{N}\sum_{l=1}^{3}\left[\frac{\partial g_k^p(t+\Delta t)}{\partial q_{l,i}(t+\Delta t)}\frac{\partial g_{k'}^p(t)}{\partial q_{l,i}(t)}\frac{(\Delta t)^2}{m_i}\right]$$

$N =$ total atom number; $p = b, a, d; l = x, y, z$

Full Jacobian with all constrained equations about internal coordinates

$$J_{kk'}^{\dot{g}} = \frac{\partial \dot{g}_k^p(t+\Delta t)}{\partial \xi_{k'}^p(t)}$$

$$= \sum_{i=1}^{N}\sum_{l=1}^{3}\left[\frac{\partial \dot{g}_k^p(t+\Delta t)}{\partial p_{l,i}(t+\Delta t)}\frac{\partial p_{l,i}(t+\Delta t)}{\partial \xi_{k'}^p(t+\Delta t)}\right]$$

$$= -\frac{1}{2}\sum_{i=1}^{N}\sum_{l=1}^{3}\left[\frac{\partial g_k^p(t+\Delta t)}{\partial q_{l,i}(t+\Delta t)}\frac{\partial g_{k'}^p(t+\Delta t)}{\partial q_{l,i}(t+\Delta t)}\frac{(\Delta t)}{m_i}\right]$$

$N =$ total atom number; $p = b, a, d; l = x, y, z$

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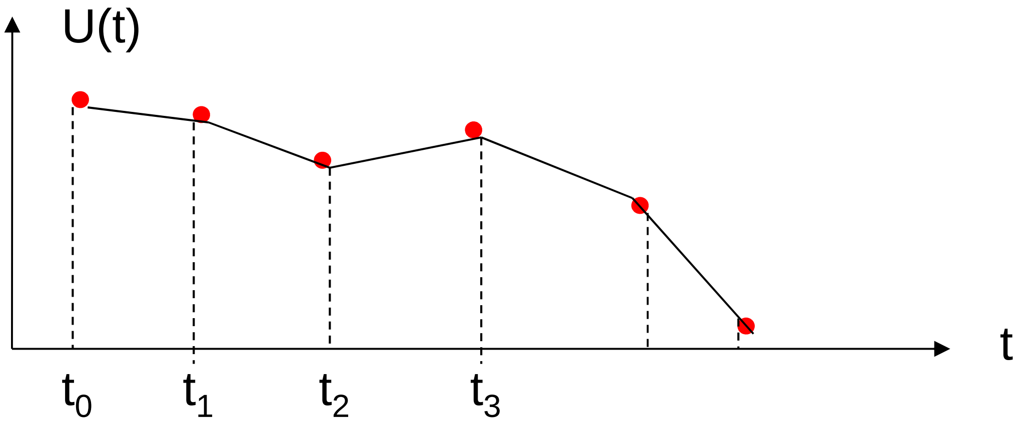
Trajectory



Cartesian coordinates $M = 3N$

$$U(t) = U(q_1, q_2, \cdots, q_M) = U(q_{10}, q_{20}, \cdots, q_{M0}) + \sum_{i=1}^{M} \left(\frac{\partial U}{\partial q_i} \right)_{q=q_0} (q_i - q_{i0})$$

3N dimensional vector (rectangle)

$$\begin{aligned} \mathbf{q} = & x_1 \vec{e}_{x1} + y_1 \vec{e}_{y1} + z_1 \vec{e}_{z1} + \\ & x_2 \vec{e}_{x2} + y_2 \vec{e}_{y2} + z_2 \vec{e}_{z2} + \\ & \cdots \\ & x_N \vec{e}_{xN} + y_N \vec{e}_{yN} + z_N \vec{e}_{zN} \end{aligned}$$

$$\begin{aligned} \nabla U = & \frac{\partial U}{\partial x_1} \vec{e}_{x1} + \frac{\partial U}{\partial y_1} \vec{e}_{y1} + \frac{\partial U}{\partial z_1} \vec{e}_{z1} + \\ & \frac{\partial U}{\partial x_2} \vec{e}_{x2} + \frac{\partial U}{\partial y_2} \vec{e}_{y2} + \frac{\partial U}{\partial z_2} \vec{e}_{z2} + \\ & \cdots \\ & \frac{\partial U}{\partial x_N} \vec{e}_{xN} + \frac{\partial U}{\partial y_N} \vec{e}_{yN} + \frac{\partial U}{\partial z_N} \vec{e}_{zN} \end{aligned}$$

$$\sum_{i=1}^{M} \left(\frac{\partial U}{\partial q_i} \right)_{q=q_0} (q_i - q_{i0}) = (\nabla U)_0 \cdot (\mathbf{q} - \mathbf{q}_0)$$

On-the-fly analytical potential

Around t_0 $$U(t)=U(\mathbf{q})=U(\mathbf{q}_0)+(\nabla U)_0\cdot(\mathbf{q}-\mathbf{q}_0)$$

$\downarrow$

Around t_1 $$U(t)=U(\mathbf{q})=U(\mathbf{q}_1)+(\nabla U)_1\cdot(\mathbf{q}-\mathbf{q}_1)$$

$\downarrow$

Around t_2 $$U(t)=U(\mathbf{q})=U(\mathbf{q}_2)+(\nabla U)_2\cdot(\mathbf{q}-\mathbf{q}_2)$$

$\downarrow$

Around t_3 $$U(t)=U(\mathbf{q})=U(\mathbf{q}_3)+(\nabla U)_3\cdot(\mathbf{q}-\mathbf{q}_3)$$

$\downarrow$

***Because you need constraint motion, you need analytical form of potential , and each time You just use one, then next time, you use continue one …….**

***you need store three continue points of potential and it derivatives in code**