Derivation of the Quantum Molecular Dynamics Equations

1989. 10. 19

Ref) 1) P. Pechukas, Phys. Rev. 181, 174 (1969).

2) J. Schwinger, J. Math. Phys. 2, 407 (1961).

§. Transformation Function

(System)

$$\begin{cases} H(t) = \sum_{I=1}^{N} \frac{P_I^2}{2M} + h(r,R,t) & (1) \\ h(r,R,t) = \sum_{i=1}^{n}\left[\frac{P_i^2}{2m} + v(r_i,t)\right] + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i-r_j|} - \sum_{i,J}\frac{ze^2}{|r_i-R_J|} \\ \qquad + \frac{1}{2}\sum_{I\neq J}\frac{(ze)^2}{|R_I-R_J|} + \sum_{I=1}^{N} V(R_I,t) & (2) \end{cases}$$

where M, R_I, P_I are the mass, coordinates, and momenta of nuclei of charge ze; m, r_i, p_i are the same for electrons.

(Transformation Function)

$$\boxed{S = \frac{1}{\sum_k P_k(R)} \sum_k P_k(R) \langle kR|\mathcal{U}_-(t_0,t_f)\,\mathcal{U}_+(t_f,t_0)|kR\rangle} \qquad (3)$$

where

$$\mathcal{U}_\pm(t,t') = T_\pm \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} d\tau\, H_\pm(\tau)\right] \qquad (4)$$

and at the initial time t_0, the neuclei are located at R and the electrons are in a mixed state represented by the statistical matrix $P_k(R)$.

(ex)

(Physical Meaning)

Suppose the Hamiltonian includes a term $\hat{X}F(t)$, then

$$\frac{\delta S}{\delta F(t)} = \frac{1}{\sum_k \rho_k(R)} \sum_k \rho_k(R) \underbrace{\langle kR | \frac{\delta}{\delta F(t)} T_P \exp\left[-\frac{i}{\hbar}\int_P dt\, H(t)\right] | kR\rangle}$$

$$-\frac{i}{\hbar}\langle kR | T_P[X_t\, \mathcal{U}] | kR\rangle$$

$$\xrightarrow[F_+=F_-]{} -\frac{i}{\hbar}\langle kR | \mathcal{U}_-(t_0,t) X \mathcal{U}_+(t,t_0) | kR\rangle$$

$$\mathcal{U}_-(t_0,t) = [\mathcal{U}_+(t,t_0)]^\dagger$$

$$= -\frac{i}{\hbar}\langle k(t) | X | k(t)\rangle$$

$$\boxed{\left.\frac{\delta S}{\delta F_+(t)}\right|_{F_+=F_-} = -\frac{i}{\hbar}\frac{1}{\sum_k \rho_k(R)} \sum_k \rho_k(R) \langle k(t) | X | k(t)\rangle \qquad (5)}$$

$\because$

$$\frac{\delta}{\delta F(t)}\mathcal{U} = \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\right)^n \underbrace{\frac{\delta}{\delta F(t)} \int_P dt_1 \cdots \int_P dt_n\, T_P[H(t_1)\cdots H(t_n)]}_{n \int_P dt_2 \cdots \int_P dt_n\, T_P[X_t H(t_2)\cdots H(t_n)]}$$

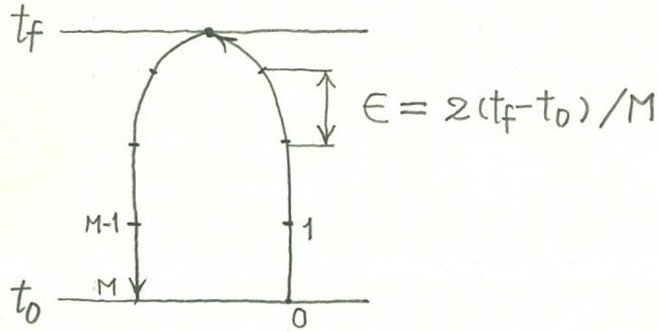
$$= \sum_{n=1}^{\infty} \frac{1}{(n-1)!}\left(-\frac{i}{\hbar}\right)^n T_P\left\{X_t \int_P dt_2 \cdots \int_P dt_n\, T_P[H(t_2)\cdots H(t_n)]\right\}$$

$$= -\frac{i}{\hbar} T_P[X_t\, \mathcal{U}] \qquad //$$

※ If we add an approprate external field to the system, and differentiate S with respect to the field and set $F_+=F_-$, we can calculate the physical average value of the quantity.

§. Decoupling of the Nucleus-Electron Motions

We divide the closed time path $t_0 \to t_f \to t_0$ into M sections. Hereafter, we confine ourselves to the case $N=1$.



Then,

$$\langle kR | T_p \exp[-\tfrac{i}{\hbar}\int_p dt\, H(t)] | kR \rangle$$

$$= \langle kR | e^{-iH(t_{M-1})\epsilon/\hbar} \cdots e^{-iH(t_0)\epsilon/\hbar} | kR \rangle$$

$$= \int dR_1 \cdots \int dR_{M-1} \langle kR | e^{-iH(t_{M-1})\epsilon/\hbar} | R_{M-1} \rangle \langle R_{M-1} | e^{-iH(t_{M-2})\epsilon/\hbar} | R_{M-2} \rangle$$

$$\times \cdots \times \langle R_1 | e^{-iH(t_0)\epsilon/\hbar} | kR \rangle$$

Here,

$$\langle R_j | e^{-iH(t_{j-1})\epsilon/\hbar} | R_{j-1} \rangle$$

$$= \underbrace{\langle R_j | e^{-iP^2\epsilon/2M\hbar} | R_{j-1} \rangle}\, e^{-ih(r, R_{j-1}, t_{j-1})\epsilon/\hbar}$$

$$\int d^3p \exp\left(-\frac{iP^2\epsilon}{2M\hbar}\right) \underset{(2\pi\hbar)^{-3/2} e^{ip\cdot R_j/\hbar}}{\langle R_j | P \rangle} \langle P | R_{j-1} \rangle$$

(∵ momentum eigen states $\to$ plane wave)

$$= \int \frac{d^3p}{(2\pi\hbar)^3} \exp\left[-\frac{i\epsilon}{2M\hbar}p^2 + ip\cdot(R_j - R_{j-1})/\hbar\right]$$

$$= \int \frac{d^3p}{(2\pi\hbar)^3} \exp\left\{ -\frac{i\epsilon}{2M\hbar}\left[p_x - \frac{M(R_{jx}-R_{j-1x})}{\epsilon}\right]^2 + \frac{iM(R_{jx}-R_{j-1x})^2}{2\hbar\epsilon} \right\} \times (y) \times (z)$$

$$= \frac{1}{(2\pi\hbar)^3} \exp\left(\frac{iM|R_j-R_{j-1}|^2}{2\hbar\epsilon}\right) \Bigg[\underbrace{\int_{-\infty}^{\infty} dp_x\, e^{-\frac{i\epsilon p_x^2}{2M\hbar}}}_{\left(\frac{2\pi M\hbar}{i\epsilon}\right)^{1/2}} \Bigg]^3$$

$$= \left(\frac{M}{2\pi i\epsilon\hbar}\right)^{3/2} \exp\left(\frac{iM|R_j-R_{j-1}|^2}{2\hbar\epsilon}\right)$$

$$\therefore \langle R_j | e^{-iH(t_{j-1})\epsilon/\hbar} | R_{j-1}\rangle = \left(\frac{M}{2\pi i\epsilon\hbar}\right)^{3/2} \exp\left(\frac{iM|R_j-R_{j-1}|^2}{2\hbar\epsilon}\right)$$

$$\therefore \langle kR | T_p \exp\left[-\frac{i}{\hbar}\int_p dt\, H(t)\right] | kR\rangle$$

$$= \int dR_1 \cdots \int dR_{M-1} \left(\frac{M}{2\pi i\hbar\epsilon}\right)^{3M/2} \exp\left(\frac{i\epsilon}{\hbar}\sum_{i=1}^{M}\frac{M}{2}\left|\frac{R_j-R_{j-1}}{\epsilon}\right|^2\right)$$

$$\times \langle kR | \underbrace{e^{-ih(r,R_{M-1},t_{M-1})\epsilon/\hbar} \cdots e^{-ih(r,R_0,t_0)\epsilon/\hbar}}_{T_p \exp\left[-\frac{i}{\hbar}\int_p dt\, h(r,R(t),t)\right]} | kR\rangle$$

$$\therefore S = \frac{1}{\sum_k P_k(R)} \sum_k P_k(R) \int dR_1 \cdots \int dR_{M-1} \left(\frac{M}{2\pi i\hbar\epsilon}\right)^{3M/2} \exp\left(\frac{i}{\hbar}\int_p dt\, \frac{M}{2}\dot{R}^2(t)\right)$$

$$\times \langle kR | T_p \exp\left[-\frac{i}{\hbar}\int_p dt\, h(r,R(t),t)\right] | kR\rangle$$

$$\mathcal{S} = \int_p^{R(t_0)=R} \mathcal{D}[R(t)] \exp\left(\frac{i}{\hbar} S_0[R(t)]\right) \mathcal{T}[R(t)] \tag{6}$$

where

$$S_0 = \int_p dt \, \frac{M}{2}\left(\frac{dR}{dt}\right)^2 \tag{7}$$

$$T = \frac{1}{\sum_k \rho_k(R)} \sum_k \rho_k(R) \, \langle kR | T_p \overbrace{\exp\left[-\frac{i}{\hbar}\int_p dt \, h(r, R(t), t)\right]}^{u} | kR \rangle \tag{8}$$

$$\int_p^{R(t_0)=R} \mathcal{D}[R(t)] = \lim_{M\to\infty} \left(\frac{M}{2\pi i \hbar \epsilon}\right)^{3M/2} \prod_{j=1}^{M-1} \int dR_j \tag{9}$$

§. Stationary-phase Approximation

$$\exp\left(\frac{i}{\hbar}S_0\right)\underbrace{T}_{\exp(\ln T)}$$

$$= \exp\left[\frac{i}{\hbar}\left(S_0 + \frac{\hbar}{i}\ln T\right)\right]$$

We expand the above quantity in a power series in $\hbar$; the most significant contribution comes from the stationary point,

$$\boxed{\delta\left\{S_0[R(t)] + \frac{\hbar}{i}\ln T[R(t)]\right\} = 0 \qquad (10)}$$

※ (Saddle-point Method)

$$I = \int_{-\infty}^{\infty} dx \exp\left[\underbrace{\frac{i}{\hbar}S(x)}_{\frac{i}{\hbar}\left[S(x_0) + \frac{1}{2}S''(x_0)(x-x_0)^2 + \sum_{n=3}^{\infty}\frac{(x-x_0)^n}{n!}S^{(n)}(x_0)\right]}\right]$$

where $S'(x_0) = 0$

$$= \exp\left[\frac{i}{\hbar}S(x_0)\right]\int_{-\infty}^{\infty} dx \exp\left[\frac{i}{2\hbar}S''(x_0)(x-x_0)^2 + \frac{i}{\hbar}\sum_{n=3}^{\infty}\frac{(x-x_0)^n}{n!}S^{(n)}(x_0)\right]$$

$$\Big\downarrow \ \sqrt{\frac{i}{2\hbar}S''(x_0)}\,(x-x_0) = -r$$

$$= \exp\left[\frac{i}{\hbar}S(x_0)\right]\sqrt{\frac{2\hbar}{iS''(x_0)}}\int_{-\infty}^{\infty} dr \exp\left(-r^2 + \frac{i}{\hbar}\sum_{n=3}^{\infty}\frac{S^{(n)}}{n!}\left(\frac{2\hbar}{iS''(x_0)}\right)^{n/2} r^n\right)$$

$$= \exp\left[\frac{i}{\hbar}S(x_0) + \ln\sqrt{\frac{2\hbar}{iS''(x_0)}}\right] + O(h)$$

Thus, the stationary-phase approximation is <u>a small $\hbar$ expansion</u>.

Here,

① $$\frac{\delta}{\delta R(t)}\frac{\hbar}{i}\ln T = \underbrace{\frac{\hbar}{iT}}_{\to =1 \text{ for } u_- = u_+}\frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\langle kR|T_p[u(-\tfrac{i}{\hbar})\frac{\delta h(r,R(t),t)}{\delta R(t)}]|kR\rangle$$

$$= -\frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\underbrace{\langle kR|u_-(t_0,t)}_{\langle k(t),R|}\frac{\delta h(r,R(t),t)}{\delta R(t)}\underbrace{u_+(t,t_0)|kR\rangle}_{|k(t),R\rangle}$$

$$= -\frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\langle k(t),R|\frac{\delta h(r,R(t),t)}{\delta R(t)}|k(t),R\rangle$$

② $$\delta S_0 = \int_p dt\, M\dot{R}(t)\cdot\delta\dot{R}(t)$$

$$= -\int_p dt\, M\ddot{R}(t)\cdot\delta R(t)$$

$$\therefore\ \frac{\delta S_0}{\delta R(t)} = -M\ddot{R}(t)$$

Substituting ① and ② into Eq. (10), we get

$$M\ddot{R}(t) = -\frac{1}{\sum_k \rho_k(R)} \sum_k \langle k(t), R| \frac{\partial h(r, R(t), t)}{\partial R(t)} |k(t), R\rangle \rho_k(R) \tag{11}$$

Since the electronic motion is governed by the propagator

$$\mathcal{U}(t, t') = T_P \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} d\tau\, h(r, R(t), \tau)\right], \tag{12}$$

the dynamics of the electrons is equivalent to solving

$$i\hbar\frac{\partial}{\partial t}|k(t), R\rangle = h(r, R(t), t)\,|k(t), R\rangle \tag{13}$$

with the initial condition,

$$|k(t=t_0), R\rangle = |k, R\rangle \tag{14}$$

§. Quantum Molecular Dynamics

$$\begin{cases} M\ddot{R}(t) = -\frac{1}{\sum_k \rho_k(R)} \sum_k \langle k(t), R| \frac{\partial h(r, R(t), t)}{\partial R(t)} |k(t), R\rangle \dashrightarrow \text{MD} \\ i\hbar\frac{\partial}{\partial t}|k(t), R\rangle = h(r, R(t), t)|k(t), R\rangle \dashrightarrow \text{time-dep. DFT} \end{cases}$$

(1 particle Schrödinger eq.)

(∵ Electrons move in a time dep. external potential. //)

※ The transformation function $S = \exp[\frac{i}{\hbar} S_0(R_c(t))]$ is equivalent to the equation system, (11) and (13).

A. Energy Conservation in the QMD Equations

$\dot{R}(t) \times$ Eq. (11)

① $$M\ddot{R}(t)\cdot\dot{R}(t) = \frac{d}{dt}\left(\frac{1}{2}M\dot{R}(t)^2\right)$$

② $$-\frac{1}{\sum_k \rho_k(R)}\sum_k \langle k(t),R|\,\dot{R}\cdot\frac{\partial h(r,R(t),t)}{\partial R(t)}\,|k(t),R\rangle\,\rho_k(R)$$

Here,

$$-\frac{d}{dt}\frac{1}{\sum_k \rho_k(R)}\sum_k \langle k(t),R|\,h(r,R(t),t)\,|k(t),R\rangle\,\rho_k(R)$$

$$= -\frac{1}{\sum_k \rho_k(R)}\sum_k \rho_k(R)\Bigg(\cancel{\underbrace{\frac{d}{dt}\langle k(t),R|}_{\frac{i}{\hbar}\langle k(t),R|h}\,h\,|k(t),R\rangle} + \cancel{\langle k(t),R|\,h\,\underbrace{|\frac{d}{dt}|k(t),R\rangle}_{-\frac{i}{\hbar}h|k(t),R\rangle}} + \langle k(t),R|\,\dot{R}\cdot\frac{\partial h(r,R(t),t)}{\partial R(t)} + \frac{\partial h(r,R(t),t)}{\partial t}\,|k(t),R\rangle$$

$$\therefore ② = -\frac{d}{dt}\frac{1}{\sum_k \rho_k(R)}\sum_k \langle k(t),R|\,h(r,R(t),t)\,|k(t),R\rangle\,\rho_k(R) + \frac{1}{\sum_k \rho_k(R)}\sum_k \langle k(t),R|\,\frac{\partial h(r,R(t),t)}{\partial t}\,|k(t),R\rangle\,\rho_k(R)$$

$$\boxed{\begin{aligned}\therefore\ &\frac{d}{dt}\left[\frac{1}{2}M\left(\frac{dR(t)}{dt}\right)^2 + \frac{1}{\sum_k \rho_k(R)}\sum_k \langle k(t),R|\,h(r,R(t),t)\,|k(t),R\rangle\right] \\ &= \frac{1}{\sum_k \rho_k(R)}\sum_k \langle k(t),R|\,\frac{\partial h(r,R(t),t)}{\partial t}\,|k(t),R\rangle \qquad (a1)\end{aligned}}$$