Derivation and Validity of the Quantum Molecular Dynamics Equations

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[1] Derivation of QMD Equations

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

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

§. Transformation Function

(System : N nuclei with charge ze and n electrons)

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

(Transformation Function)

Suppose at the initial time t_0, the nuclei are at R and the electron state are specified by the density matrix $\rho_k(R)$.

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

where

$$\mathcal{U}_\pm(t,t') = T_\pm \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} dt_1\, H_\pm(t_1)\right], \tag{4}$$

$T_{+(-)}$ are the usual (anti) time-ordering operators. $H_\pm(t)$ are the Hamiltonian in the presence of different external potentials $V_\pm, v_\pm$.

(Usage)

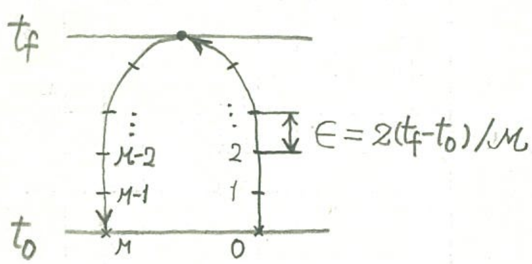
Add the Hamiltonian an additional term $XF_{\pm}(t)$, then

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

where $|k(t),R\rangle = \mathcal{U}_+(t,t_0)|k,R\rangle$.

§. Decoupling of Nucleus-Electron Motions

Here, we confine ourselves to the case $N=1$. Define the closed time path as $t_0 \xrightarrow[t_+]{} t_f \xrightarrow[t_-]{} t_0$.



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

where

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

$$T = \frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\langle k,R|\overbrace{T_p \exp\left[-\frac{i}{\hbar}\int_p h(r,R(t),t)\right]}^{\mathcal{U}_h}|k,R\rangle \qquad (8)$$

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

Here, T_p is the time-ordering operator on the closed time path, and p denotes the integration over the path.

$$\mathcal{C} = \langle k,R \,|\, T_P \exp\left[-\frac{i}{\hbar}\int_P dt\, H(t)\right] |k,R\rangle$$

$$= \int dR_1 \cdots \int dR_{\mathcal{N}-1} \langle k,R|e^{-iH(t_{\mathcal{N}-1})\epsilon/\hbar}|R_{\mathcal{N}-1}\rangle \cdots \langle R_2|e^{-iH(t_1)\epsilon/\hbar}|R_1\rangle\langle R_1|e^{-iH(t_0)\epsilon/\hbar}|R_0\rangle$$

Here,

$$\langle R_j|e^{-iH(t_{j-1})\epsilon/\hbar}|R_{j-1}\rangle = \underbrace{\langle R_j|e^{-iP^2\epsilon/2M\hbar}|R_{j-1}\rangle}_{\int\frac{d^3P}{(2\pi\hbar)^3}\exp\left(-\frac{iP^2\epsilon}{2M\hbar}\right)\exp\left(i\frac{P\cdot(R_j-R_{j-1})}{\hbar}\right) = \left(\frac{M}{2\pi i\epsilon\hbar}\right)^{3/2}\exp\left(\frac{iM|R_j-R_{j-1}|^2}{2\hbar\epsilon}\right)} e^{-ih(r,R_{j-1},t_{j-1})\epsilon/\hbar}$$

so that

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

$$\times \langle k,R|e^{-ih(r,R_{\mathcal{N}-1},t_{\mathcal{N}-1})\epsilon/\hbar}\cdots e^{-ih(r,R_0,t_0)\epsilon/\hbar}|k,R\rangle \quad //$$

(Stationary-phase Approximation)

We expand $\mathcal{S}$ in powers of $\hbar$; the first term is given by

$$\boxed{\mathcal{S} = \exp\left(\frac{i}{\hbar}\left\{S_0[R_c(t)] + \frac{\hbar}{i}\ln T[R_c(t)]\right\}\right) \quad (10)}$$

where

$$\boxed{\delta\left\{S_0[R_c(t)] + \frac{\hbar}{i}\ln T[R_c(t)]\right\} = 0 \quad (11)}$$

This transformation function is equivalent to calculate expectation values by solving the following QMD equations:

$$\begin{cases} M\ddot{R}(t) = -\dfrac{1}{\sum_k \rho_k(R)}\sum_k \rho_k(R)\langle k(t),R|\dfrac{\partial h(r,R(t),t)}{\partial R(t)}|k(t),R\rangle \dashrightarrow \text{MD} & (12) \\ i\hbar\dfrac{\partial}{\partial t}|k(t),R\rangle = h(r,R(t),t)\,|k(t),R\rangle \text{ with } |k(t=t_0),R\rangle = |k,R\rangle & (13) \end{cases}$$

$\dashrightarrow$ 1-particle Schrödinger equation

time-dependent Density-functional theory (TDDFT)

$\because\ \delta S_0/\delta R(t) = -M\ddot{R}(t)$ and

$$\frac{\delta}{\delta R(t)}\frac{\hbar}{i}\ln T = \frac{\hbar}{iT}\frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\langle k,R|T_p[\mathcal{U}_h(-\tfrac{i}{\hbar})\frac{\delta h(r,R(t),t)}{\delta R(t)}]|k,R\rangle$$

$$= -\frac{1}{T\sum_k P_k(R)}\sum_k P_k(R)\langle k,R|\mathcal{U}_-^h(t_0,t)\frac{\delta h(r,R(t),t)}{\delta R(t)}\mathcal{U}_+^h(t,t_0)|k,R\rangle$$

For $H_+ = H_-$, $T = 1$ and $\mathcal{U}_-^h(t_0,t) = [\mathcal{U}_+^h(t,t_0)]^\dagger$. //

※(Stationary-phase approximation as a Small $\hbar$ Expansion)

$$S = \exp\Big\{\frac{\hbar}{i}\Big[S_0[R_c(t)] + \frac{\hbar}{i}\ln[R_c(t)]\Big] - \frac{1}{2}\ln\det\Big(M\frac{d^2}{dt^2} + \Big\langle\frac{\delta^2 h}{\delta R_c(t)^2}\Big\rangle\Big)$$

$$-\frac{i}{\hbar}\Big[\Big\langle\Big(\frac{\delta h}{\delta R_c(t)}\Big)^2\Big\rangle - \Big\langle\frac{\delta h}{\delta R_c(t)}\Big\rangle^2\Big] + O(h)\Big\} \qquad (14)$$

[2] Validity of Classical Path Methods

Ref) J.C. Tully, in "Dynamics of Mollecular Collisions, Part B", ed. W.H. Miller (Plenum, 1976).

We consider the same system as that in [1] except $V = \mathcal{V} = 0$.

(Adiabatic Representation)

$$\psi(r,R,t) = \sum_k \psi_k(r,R)\,\chi_k(R,t) \qquad (15)$$

where the adiabatic basis are given by

$$h(r,R)\,\psi_k(r,R) = E_k(R)\,\psi_k(r,R) \qquad (16)$$

Then, the Schrödinger equation

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

becomes

$$\boxed{\begin{aligned}\left[i\hbar\frac{\partial}{\partial t} + \sum_{I=1}^{N}\frac{\hbar^2}{2M}\nabla_I^2 - E_k(R) - T_{kk}(R)\right]\chi_k(R,t) \\ = \sum_{k'\neq k} T_{kk'}(R)\,\chi_{k'}(R,t) \qquad (17)\end{aligned}}$$

where

$$T_{kk'}(R) = \sum_{I=1}^{N}\langle k,R|\frac{\hbar}{i}\nabla_I|k',R\rangle\cdot\frac{\hbar}{iM}\nabla_I - \sum_{I=1}^{N}\langle k,R|\frac{\hbar^2}{2M}\nabla_I^2|k',R\rangle \qquad (18)$$

If we set $T_{kk'}=0$ in Eq. (17), we get a nucleus motion in the presence of the potential $E_k(R)$; the same picture as that in QMD. In reality, because of the quantum nature of nuclei, quantum jumps governed by $T_{kk'}$ should occur.

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

$$\chi_k(R,t) = \zeta_k(R,t)\exp[-iE_k(R)t/\hbar] \qquad (19)$$

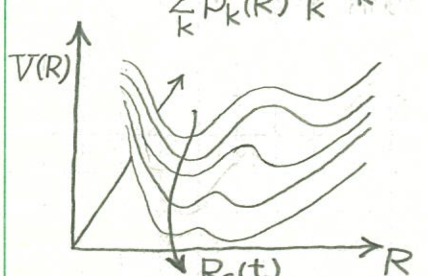
and assume $\zeta_k(R,t=0) = \delta_{k,l}$. Then, for $k\neq l$,

$$|\zeta_k(R,t)|^2 = 4\left|\frac{T_{kl}(R)}{E_k(R)-E_l(R)}\right|^2\sin^2\left[\frac{(E_l(R)-E_k(R))t}{\hbar}\right] \qquad (20)$$

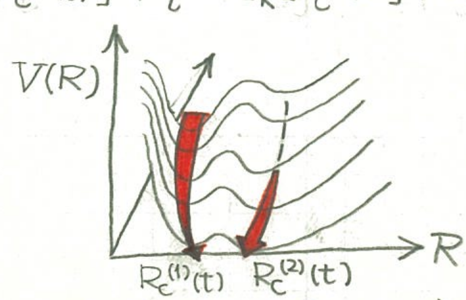
For $T_{kl}(R)\sim k_BT \ll E_k(R)-E_l(R)$, no transition occur.

[3] Extension of QMD Equations?

$$S = \frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\exp\left[\frac{\hbar}{i}\left\{S_0[R_c^{(k)}(t)] + \frac{\hbar}{i}\ln T_k[R_c^{(k)}(t)] + \text{coupling}\right\}\right] \qquad (21)$$



(single-path method)



(multipath method)

$$S = \int_P^{R(t_0)=R} \mathcal{D}[R(t)] \, \frac{1}{\sum_k \rho_k(R)} \sum_k \rho_k(R) \exp\left(\frac{i}{\hbar} S_0[R(t)] + \ln T_k[R(t)]\right)$$

$$\simeq \frac{1}{\sum_k \rho_k(R)} \sum_k \rho_k(R) \exp\left[\frac{\hbar}{i}\left\{S_0[R_c^{(k)}(t)] + \frac{\hbar}{i} \ln T_k[R_c^{(k)}(t)]\right\}\right]$$

where

$$T_k = \langle k,R | T_P \exp\left[-\frac{i}{\hbar}\int_P h(r, R(t), t)\right] | k,R \rangle$$

$$\frac{d}{dt}\left[\frac{1}{2}M\left(\frac{dR}{dt}\right)^2+\frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\langle k(t),R|\,h(r,R(t),t)\,|k(t),R\rangle\right]=\frac{1}{\sum_k P_k(R)}\sum_k P_k(R)\langle k(t),R|\frac{\partial h}{\partial t}|k(t),R\rangle \qquad 5'$$

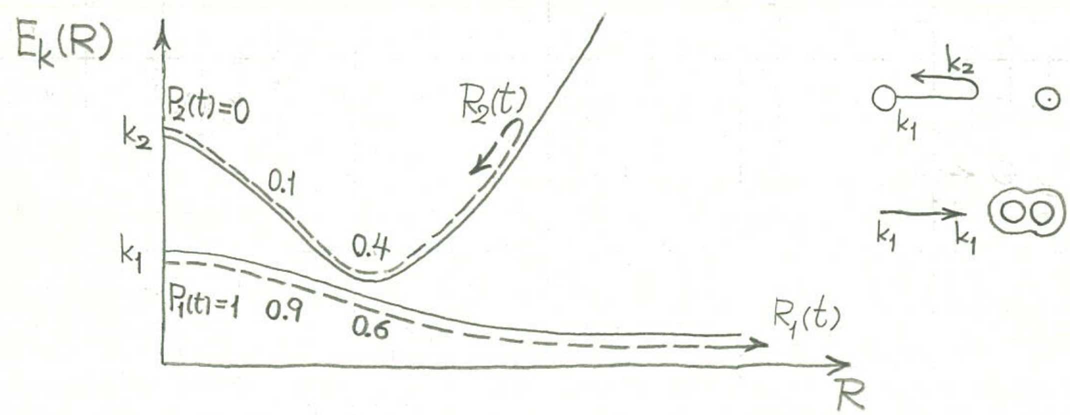
$$\boxed{\begin{aligned}&\left[i\hbar\frac{\partial}{\partial t}+\sum_{I=1}^{N}\frac{\hbar^2}{2M}\nabla_I^2-E_k(R)-T_{kk}(R)\right]\chi_k(R,t)\\&\qquad=\sum_{k'\neq k}T_{kk'}(R)\,\chi_{k'}(R,t)\end{aligned}} \qquad (17)$$

consistency of path
energy conservation

where

$$T_{kk'}(R)=\sum_{I=1}^{N}\langle k,R|\frac{\hbar}{i}\nabla_I|k',R\rangle\cdot\frac{\hbar}{iM}\nabla_I-\sum_{I=1}^{N}\langle k,R|\frac{\hbar^2}{2M}\nabla_I^2|k',R\rangle \qquad (18)$$

If we set $T_{kk'}=0$ in Eq. (17), we get a nucleus motion in the presense of the adiabatic potential surface $E_k(R)$. In the QMD equations, Eqs. (12) and (13), the electronic part makes nonadiabatic transitions between adiabatic surfaces, while the classical neucleus path is given by some average on several surfaces. This is unsatisfactory because paths on different surfaces are known to exhibit quite different behaviours.



(Validity of Adiabatic Approximation)

$$\chi_k(R,t)=\zeta_k(R,t)\exp[-iE_k(R)(t-t_0)/\hbar] \qquad (19)$$

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

$$|\zeta_k(R,t)|^2\sim 4\left|\frac{T_{k0}(R)}{E_k(R)-E_0(R)}\right|^2\sin^2\left[\frac{[E_0(R)-E_k(R)](t-t_0)}{\hbar}\right] \qquad (20)$$

For $|T_{k0}(R)|\ll|E_k(R)-E_0(R)|$, no nonadiabatic transition occurs. Or, in the QMD calculations, if the violation of the condition

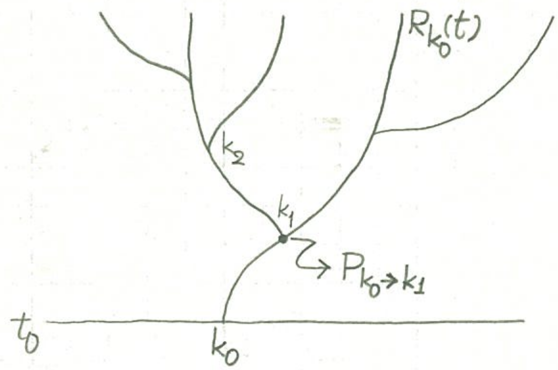
$$P_{k0}(t) = \langle k, R(t) | 0(t), R \rangle \ll 1 \quad \text{for} \quad k \neq 0 \tag{21}$$

is detected, the solution is no more accurate [A. Selloni, P. Carnevali, R. Car, and M. Parrinello, Phys. Rev. Lett. 59, 823 (1987)].

[3] Extension of the QMD Equations?

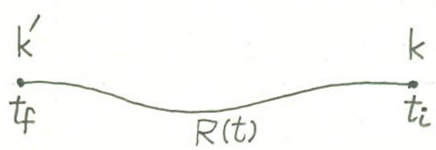
Cf.1 Surface-Hopping Trajectory Approximation

[J. C. Tully and R. K. Preston, J. Chem. Phys. 55, 562 (1971)]



Cf.2 Scattering Theory by Pechukas

[Pechukas (1969)]



$$M\ddot{R}(t) = -\langle k', R' | \mathcal{U}_h(t_f, t) \frac{\partial}{\partial R} h(r, R(t), t) \mathcal{U}_h(t, t_i) | k, R \rangle / \langle k', R' | \mathcal{U}_h(t_f, t_i) | k, R \rangle \tag{22}$$

where

$$\mathcal{U}_h(t, t_i) = T \exp\left(-\frac{i}{\hbar} \int dt \, h(r, R(t), t) \right) \tag{23}$$