CHM4M4 Simulation : Lecture Note

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Contents

(∗ = **advanced topics**)

1 Molecular Hamiltonian

Molecules = electrons + nuclei

$$H = T_N + T_e + V_{eN} + V_{ee} + V_{NN}$$

e.g., $\quad T_N = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2, \qquad V_{eN} = -\sum_I \sum_i \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}$

Ideally, we wish to solve the whole problem,

$$H\Psi(\mathbf{R}, \mathbf{r}) = E\Psi(\mathbf{R}, \mathbf{r})$$

But this is too difficult for most of chemically interesting (complex) systems.

⇒ useful to separate the electronic and nuclear problems.

Electronc Hamiltonian

$$H_e = H - T_N = T_e + V_{eN} + V_{ee} + V_{NN}$$

2 Adiabatic Approximation (Born-Oppenheimer)

Stage 1 : Fix $\{\mathbf{R}\}$ and solve the electronic problem

$$H_e\varphi_n(\mathbf{r}; \mathbf{R}) = W_n(\mathbf{R})\varphi_n(\mathbf{r}; \mathbf{R})$$

$\varphi_n(\mathbf{r}; \mathbf{R}) \cdots$ electronic wavefunction (parametrically dependent on $\{\mathbf{R}\}$)

$W_n(\mathbf{R}) \cdots$ electronic energy levels at $\{\mathbf{R}\}$

Stage 2 : Repeat at various $\{\mathbf{R}\}$

⇒ Potential energy surface $W_n(\mathbf{R})$

Diagram : Potential energy curves W_1 and W_2 (diatomic)

- Stages 1-2 = "Quantum chemistry" (narrow meaning)

Stage 3 : Examine nuclear dynamics on PES $W_n(\mathbf{R})$

- quantum energy levels :

$$H_n^{(N)} \equiv T_N + W_n(\mathbf{R}) \qquad \text{(nuclear Hamiltonian on } n\text{-th PES)}$$

$$H_n^{(N)}\chi_v(\mathbf{R}) = E_{n,v}\chi_v(\mathbf{R})$$

- quantum dynamics : wavepacket simulations, $i\hbar\frac{\partial}{\partial t}\chi_n(\mathbf{R}) = H_n^{(N)}\chi_v(\mathbf{R})$

- classical dynamics : moelcular dynamics (MD) simulations, $M_I\ddot{\mathbf{R}} = -\frac{\partial W_n(\mathbf{R})}{\partial \mathbf{R}}$

- statistical mechanics : Monte Carlo simulations (quantum or classical)

Stage 4 : Analysis of simulation results (statistical or dynamical)

3 Non-adiabatic couplings*

Expand the total wavefunction in terms of the electronic wavefunction $\{\varphi_n(\mathbf{r};\mathbf{R})\}$

$$\Psi(r,R) = \sum_n \chi_n(R)\varphi_n(r;R) \tag{1}$$

Schrödinger equation with the total Hamiltonian: $H = T_N + H_e$

$$[T_N + H_e]\Psi(r,R) = E\Psi(r,R) \tag{2}$$

Put (1) into (2), multiply φ_k^* and integrate over the electronic coordinate (i.e., $\langle\varphi_k|\times$)

Use $H_e\varphi_n = W_n\varphi_n$ and $\langle\varphi_k|\varphi_n\rangle = \delta_{kn}$,

$$\sum_n \langle\varphi_k(r;R)|T_N|\varphi_n(r;R)\rangle\chi_n(R) + W_k(R)\chi_k(R) = E\chi_k(R) \tag{3}$$

Noting that $T_N = -\sum_I(\hbar^2/2M_I)\nabla_I^2$ operates to both $\varphi(r;R)$ and $\chi(R)$,

$$\begin{aligned}\sum_n\left[\langle\varphi_k|T_N|\varphi_n\rangle - \sum_I\frac{\hbar^2}{M_I}\langle\varphi_k|\nabla_I|\varphi_n\rangle\cdot\nabla_I\right]\chi_n(R)&\\ +T_N\chi_k(R) + W_k(R)\chi_k(R) &= E\chi_k(R)\end{aligned} \tag{4}$$

[Here, T_N and ∇_I within $\langle\varphi|\cdots|\varphi\rangle$ do not operate to the further right]

<u>**Adiabatic approximation:**</u> Neglect the 1st line of (4)

$$[T_N + W_k(R)]\chi_k(R) = E\chi_k(R) \qquad (= i\hbar\frac{\partial\chi_k}{\partial t}) \tag{5}$$

$\Leftarrow$ Schrödinger eq for the nuclear wfn $\chi(R)$ on a (single adiabatic) PES $W_k(R)$

neglected terms = **Non-adiabatic couplings**

$\Rightarrow$ induce mixing/transition among different electronic states $k \leftrightarrow n$

- 1st order NA coupling : $\frac{\hbar^2}{M_I}\langle\varphi_k|\nabla_I|\varphi_n\rangle$
- 2nd order NA coupling : $\frac{\hbar^2}{2M_I}\langle\varphi_k|\nabla_I^2|\varphi_n\rangle$

3.1 Mixed Quantum-classical Simulation

Assume: Nuclear motions follow classical trajectories $\mathbf{R}(t)$

$$\Phi(\mathbf{r},\mathbf{R},t) \simeq \sum_n c_n(t)\varphi_n(\mathbf{r};\mathbf{R}(t)) \tag{6}$$

$|c_n(t)|^2$ = probability of finding the system in the n-th electronic state.

How to determine $\mathbf{R}(t)$? — not a trivial task

- Most conveniently, classical trajectories on the adiabatic PES $W_n(R)$
- Then, switch among PES's *via non-adiabatic transitions* (“**surface-hopping**”)

$\boxed{\text{Diagram : Curve crossing}}$

Put (6) into the time-dependent Schrödinger eq : $i\hbar\frac{\partial\Phi}{\partial t} = [T_N + H_e]\Phi$

$$i\hbar\sum_n\left(\frac{\partial c_n}{\partial t}\varphi_n + c_n\frac{\partial\varphi_n}{\partial t}\right) = \sum_n c_n[T_N + W_n(R)]\varphi_n$$

Multiply φ_k^* and integrate over the electronic coordinates (i.e., $\langle\varphi_k^*|\times$)

Note the orthonormality $\langle\varphi_k|\varphi_n\rangle = \delta_{kn}$

$$i\hbar\frac{\partial c_k}{\partial t} + i\hbar\sum_n c_n\left\langle\varphi_k|\frac{\partial\varphi_n}{\partial t}\right\rangle = W_k(R)c_k + \sum_n c_n\langle\varphi_k|T_N|\varphi_n\rangle$$

- Neglect the 2nd order NA couplings $\langle\varphi_k|T_N|\varphi_n\rangle$
- Use $\left\langle\varphi_k|\frac{\partial}{\partial t}\varphi_n(\mathbf{r};\mathbf{R}(t))\right\rangle = \langle\varphi_k|\nabla_R|\varphi_n\rangle\cdot\dot{\mathbf{R}}(t) \quad \equiv \mathbf{d}_{kn}(\mathbf{R})\cdot\dot{\mathbf{R}}(t)$

$$\Rightarrow \quad i\hbar\dot{c}_k(t) = W_k(\mathbf{R})c_k(t) - i\hbar\sum_n \mathbf{d}_{kn}(\mathbf{R})\cdot\dot{\mathbf{R}}(t)c_n(t)$$

(coupled equations for the probability amplitudes $\{c_n(t)\}$)

4 Electronic part (Quantum chemistry)

4.1 Hartree-Fock Method

Electronic Hamiltonian

$$\begin{aligned} H_e &= T_e + V_{eN} + V_{ee} + V_{NN} \\ &= \sum_i\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \sum_I\frac{Z_I}{R_{Ii}}\right) + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{I<J}\frac{Z_IZ_J}{R_{IJ}} \\ &= \sum_i H^{core}(i) + V_{ee} + V_{NN} \end{aligned} \tag{7}$$

V_{NN} is just a constant in the electronic problem (adiabatic approximation), so we hereafter consider $h_e \equiv H_e - V_{NN}$

Two-electron molecules (e.g., H$_2$)

$$h_e = H^{core}(1) + H^{core}(2) + \frac{1}{r_{12}}$$

Slater determinant : $\psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_1(1) & \varphi_1(2)\\ \varphi_2(1) & \varphi_2(2)\end{vmatrix} = \frac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)) = \frac{1}{\sqrt{2}}|\varphi_1\varphi_2|$

Spin-orbitals : $\begin{aligned}\varphi_1(1) &= \phi_1(1)\alpha(1) = \phi_1(1)\\ \varphi_2(1) &= \phi_1(1)\beta(1) = \bar{\phi}_1(1)\end{aligned}$ (space orbital) × (spin function α, β)

Diagram : orbital diagrams $\phi_1\bar{\phi}_1$, $\phi_1\bar{\phi}_2$, $\phi_1\phi_2$

Slater-determinants satisfy the **Pauli-Principle** of many-electron systems:

- Anti-symmetry : $\psi(2,1) = -\psi(1,2)$
- Exclusion principle : $\psi(1,2) = 0$ if $\varphi_1 = \varphi_2$ (space and spin)

Energy : $E = \langle \psi(1,2)|h_e|\psi(1,2)\rangle = \int\int \psi(1,2)^* h_e \psi(1,2) d\tau_1 d\tau_2$

$$= \frac{1}{2}(\langle \phi_1(1)\bar{\phi}_1(2)|h_e|\phi_1(1)\bar{\phi}_1(2)\rangle - \langle \phi_1\bar{\phi}_1|h_e|\bar{\phi}_1\phi_1\rangle - \langle \bar{\phi}_1\phi_1|h_e|\phi_1\bar{\phi}_1\rangle + \langle \bar{\phi}_1\phi_1|h_e|\bar{\phi}_1\phi_1\rangle)$$

- The 1st term $= \langle \phi_1(1)\bar{\phi}_1(2)|H^{core}(1) + H^{core}(2) + \frac{1}{r_{12}}|\phi_1(1)\bar{\phi}_1(2)\rangle$

  $= \langle \phi_1(1)|H^{core}(1)|\phi_1(1)\rangle\langle \bar{\phi}_1(2)|\bar{\phi}_1(2)\rangle + \langle \phi_1(1)|\phi_1(1)\rangle\langle \bar{\phi}_1(2)|H^{core}(2)|\bar{\phi}_1(2)\rangle + \langle \phi_1\bar{\phi}_1|\frac{1}{r_{12}}|\phi_1\bar{\phi}_1\rangle$

  $\equiv 2H_{11}^{core} + J_{11}$

- The 4th term gives the same result : $2H_{11}^{core} + J_{11}$
- The 2nd term $= \langle \phi_1|H^{core}|\bar{\phi}_1\rangle\langle \bar{\phi}_1|\phi_1\rangle + \langle \phi_1|\bar{\phi}_1\rangle\langle \bar{\phi}_1|H^{core}|\phi_1\rangle + \langle \phi_1\bar{\phi}_1|\frac{1}{r_{12}}|\bar{\phi}_1\phi_1\rangle$

  $= 0$ because $\langle \alpha|\beta\rangle = 0$

- The 3rd term is also zero.

Thus, $E = 2H_{11}^{core} + J_{11}$

Let us next consider an open-shell singlet configuration $|\phi_1\bar{\phi}_2|$ (α electron in ϕ_1 and β in ϕ_2)

In the similar way, we get

$$E = H_{11}^{core} + H_{22}^{core} + J_{12}$$

where $J_{12} \equiv \langle \phi_1\phi_2|\frac{1}{r_{12}}|\phi_1\phi_2\rangle \equiv \langle 12||12\rangle = J_{21} = \langle \phi_2\phi_1|\frac{1}{r_{12}}|\phi_2\phi_1\rangle \equiv \langle 21||21\rangle$

Triplet configuration $|\phi_1\phi_2|$ (α electrons in both ϕ_1 and ϕ_2) gives

$$E = H_{11}^{core} + H_{22}^{core} + J_{12} - K_{12}$$

where $K_{12} \equiv \langle 12||21\rangle = K_{21}$

J_{ij} and K_{ij} are called **Coulomb** and **Exchange** integrals, respectively.

These examples suggest the following rule to write down **energies** of **electron configurations**

- Each electron in orbital ϕ_i contributes H_{ii}^{core}

- Each electron pair in orbitals ϕ_i and ϕ_j contributes J_{ij} (regardless of the spin)

- Each electron pair of the same spin in orbitals ϕ_i and ϕ_j contributes $-K_{ij}$

Exercise : Write down the energy expression for the following electron configurations.

1. α and β electron pair in ϕ_1 and an α electron in ϕ_2 (open-shell doublet)

2. paired (α and β) electrons in both ϕ_1 and ϕ_2 (closed-shell)

   Answer :

   1. $E = 2H_{11}^{core} + H_{22}^{core} + J_{11} + 2J_{12} - K_{12}$

   2. $E = 2H_{11}^{core} + 2H_{22}^{core} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$

In general, for closed-shell N-electron systems,

$$E = \sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2} J_{ii} + \sum_{i=1}^{N/2} \sum_{j=i+1}^{N/2} (4J_{ij} - 2K_{ij})$$

This can be simplified by noting $J_{ii} = K_{ii}$

$$E = \sum_{i=1}^{N/2} H_{ii}^{core} + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij})$$

Hartree-Fock Method

= find variationally best MOs $\{\phi_i\}$ under the orthonormality condition $\langle\phi_i|\phi_j\rangle = \delta_{ij}$

⇒ minimize $L \equiv E + \sum_i \sum_j \epsilon_{ij}(\delta_{ij} - \langle\phi_i|\phi_j\rangle)$ w.r.t. the variation of MOs $\phi_i \to \phi_i + \delta\phi_i$

(where ϵ_{ij} is the Lagrange multiplier)

⇒ Hartree-Fock equation : $\hat{F}_i\phi_i = \sum_j \epsilon_{ij}\phi_j$

where the Fock-operator is defined as $\hat{F}_i \equiv \hat{H}^{core} + \sum_{j=1}^{N/2}(2\hat{J}_j - \hat{K}_j)$ [for closed-shell systems]

The Coulomb and Exchange operators $\hat{J}_j$ and $\hat{K}_j$ are defined by

$$\hat{J}_j(1)\phi_i(1) = \langle\phi_j(2)|\tfrac{1}{r_{12}}|\phi_j(2)\rangle\phi_i(1)$$

$$\hat{K}_j(1)\phi_i(1) = \langle\phi_j(2)|\tfrac{1}{r_{12}}|\phi_i(2)\rangle\phi_j(1)$$

Comment : The bottleneck for the first-learner would be the abstractness of the functional variation of MOs $\phi_i \to \phi_i + \delta\phi_i$. In practical calculations, however, we employ LCAO-MO expansion of the MOs $\phi_i = \sum_{\nu} c_{\nu i}\chi_\nu$ where χ is the atomic orbitals (AO), and optimize the coefficients $c_{\nu i}$. This reduces the problem to a (non-linear) matrix eigenvalue problem which is much more handy for computer implementations. (**Hartree-Fock-Roothaan-Hall method**)

Summary of Hartree-Fock method

- Assumes a single Slater-determinant for the electronic wavefunction, which satisfies the Pauli Principle of many-electron systems
- and variationally optimizes the MOs by minimizing the exact energy expression for the Slater-determinant wavefunction under the orthonormality condition of the MOs.
- The electronic energy is expressed by one-electron integrals H_{ii}^{core} and Coulomb and Exchange two-electron integrals J_{ij} and K_{ij}.

4.2 Electron Correlation Problem

4.2.1 Static and Dynamic Correlations

4.2.2 Various Methods

- CI, MPn, MCSCF, MRCI, CC, MRMP, etc.

4.3 Density Functional Theory

4.3.1 Kohn-Sham theory

4.3.2 Hybrid Hartree-Fock / DFT

4.4 Other Methods

- Valence-Bond Method
  - non-orthogonal orbitals
  - chemically intuitive resonance structures
- Semi-empirical MO Methods
  - Approximations: neglect of differential overlaps, empirical parameters
  - CNDO, INDO, MINDO, PM3, AM1, etc. etc.

5 Potential Energy Surfaces

Functional fitting

- Choice of the functional form (physically adequate asymptotic behavior, symmetry etc.)
- Empirical parametrization using e.g. spectroscopic data
- Ab initio parametrization using quantum chemical calculations
- Dimensionality problem : when the system has f degrees of freedom ($f = 3N - 6$ for non-linear N-atoms molecules), and if M data points are needed per degree of freedom for the functional fitting, the total number of data points required, M^f, may be prohibitively huge for realistic systems. (e.g., $M \sim 10$ and $N = 6$ requires 10^{12} points.)

On-the-fly evaluation of the potential $W_n(R)$ and gradient $\partial W_n / \partial R$

- Ab initio MD, Car-Parrinello MD
- Still computationally expensive, but becoming feasible along with the increase of the computer power

5.1 Empirical Force-Field

Standard FF for MD simulations of biomolecules

$$W = \sum_{bonds} K_R(R - R_e)^2 + \sum_{angles} K_\theta(\theta - \theta_e)^2 + \sum_{torsions} V_n[1 + \cos(n\phi - \gamma)]$$
$$+ \sum_{atoms(i<j)} \frac{Q_i Q_j}{r_{ij}} + \sum_{atoms(i<j)} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

- First three terms = bonding potential
- Last two terms = non-bonding interaction (Electrostatic + Short-range repulsion)
- Inadequate for bond-breaking and -forming processes
- Lack of electronic polarization effects, charge-transfer interaction

5.2 Hybrid Methods*

5.2.0 Classical Mechanics

$$M_I \ddot{R}_I(t) = -\frac{\partial}{\partial R_I} W_e^{\mathrm{model}}(R(t))$$

5.2.1 TDSCF MD

- On-the-fly evaluation of the local potential $W(R) = \langle \Psi_0(r;R) | H_e(r;R) | \Psi_0(r;R) \rangle_e$
- Time-dependent propagation of the (ground state) electronic wavefunction $\Psi_0(r;R)$.

$$\begin{cases} M_I \ddot{R}_I(t) &= -\frac{\partial}{\partial R_I} \langle \Psi_0 | H_e | \Psi_0 \rangle \\ i\hbar \frac{\partial \Psi_0}{\partial t} &= H_e \Psi_0 \end{cases}$$

Simple model of Ψ_0 is often employed (rather than carrying out quant. chem. calculations), e.g., basis function expansion $\Psi_0(t) = \sum_i c_i(t) F(r;R)$

5.2.2 Born-Oppenheimer MD

$$\begin{cases} M_I \ddot{R}_I(t) &= -\frac{\partial}{\partial R_I} \min_{\Psi_0} \{ \langle \Psi_0 | H_e | \Psi_0 \rangle \} \\ E_0 \Psi_0 &= H_e \Psi_0 \end{cases}$$

Optimize the electronic wavefunction Ψ_0 at each nuclear configuration R (rather than propagating it as in TDSCF MD).

5.2.3 Hartree-Fock BO MD

If we employ the Hartree-Fock wavefunction : $\Psi_0^{\mathrm{HF}} = \det\{\psi_i\}$

where ψ_i = HF orbitals (1-electron, orthonormal),

$$\min_{\Psi_0} \{ \langle \Psi_0 | H_e | \Psi_0 \rangle \} \Rightarrow \min_{\{\psi_i\}} \{ \langle \Psi_0^{\mathrm{HF}} | H_e | \Psi_0^{\mathrm{HF}} \rangle \} \Big|_{\langle \psi_i | \psi_j \rangle = \delta_{ij}}$$

i.e., minimization within the $\{\psi_i\}$-space under the constraint $\langle \psi_i | \psi_j \rangle = \delta_{ij}$.

HF Lagrangian : $\mathcal{L}_e^{\mathrm{HF}} = \langle \Psi_0^{\mathrm{HF}} | H_e | \Psi_0^{\mathrm{HF}} \rangle - \sum_{i,j} \epsilon_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})$

ϵ_{ij} = Lagrange multipliers

Variational (stationary) condition :

$$\frac{\delta \mathcal{L}_e^{\mathrm{HF}}}{\delta \psi_i^*} = \frac{\delta \mathcal{L}_e^{\mathrm{HF}}}{\delta \psi_i} = 0 \quad \Rightarrow \quad \hat{F}_i \psi_i = \sum_j \epsilon_{ij}\ \psi_j \quad \text{(HF equation)}$$

- Fock-operator : $\hat{F}_i \equiv \hat{H}^{\text{core}} + \sum_{j=1}^{N/2}(2\hat{J}_j - \hat{K}_j)$ [for closed-shell systems]
- canonical (diagonal) form : $\hat{F}_i\psi_i = \epsilon_i\psi_i$ (ϵ_i = orbital energy)
- may also use Kohn-Sham (DFT) $\hat{F}^{\text{KS}}$ and KS orbitals

HF BO MD :

$$\begin{cases} M_I\ddot{R}_I(t) = -\dfrac{\partial}{\partial R_I}\langle\Psi_0^{\text{HF}}|H_e|\Psi_0^{\text{HF}}\rangle & (\Psi_0^{\text{HF}} = \det\{\psi_i\}) \\ 0 = -\hat{F}_i\psi_i + \sum_j \epsilon_{ij}\psi_j \end{cases}$$

This set of equations can be derived from an <u>Extended Lagrangian</u> :

$$\mathcal{L}_{\text{BO}} = \sum_I \frac{1}{2}M_I\dot{R}_I^2 - \langle\Psi_0^{\text{HF}}|H_e|\Psi_0^{\text{HF}}\rangle + \sum_{i,j}\epsilon_{ij}(\langle\psi_i|\psi_j\rangle - \delta_{ij})$$

by assuming that the <u>Euler-Lagrange equation</u> of the classical mechanics applies for both the nuclear and electronic (orbital) degrees of freedom

$$\Rightarrow \text{Euler-Lagrange eq :} \quad \frac{d}{dt}\frac{\partial\mathcal{L}_{\text{BO}}}{\partial\dot{q}} - \frac{\partial\mathcal{L}_{\text{BO}}}{\partial q} = 0 \quad \text{for} \quad q = R_I, \psi_i, \psi_i^*$$

(Note : <u>functional</u> derivatives for ψ_i and ψ_i^*)

5.2.4 Car-Parrinello MD

Introduce : <u>fictious mass</u> and <u>kinetic energy</u> for electronic (orbital) degrees of freedom

$\Rightarrow$ Extended Lagrangian :

$$\mathcal{L}_{\text{CP}} = \sum_I \frac{1}{2}M_I\dot{R}_I^2 + \sum_i \frac{1}{2}\mu_i|\dot{\psi}_i|^2 - \langle\Psi_0^{\text{HF}}|H_e|\Psi_0^{\text{HF}}\rangle + \text{constraints}$$

e.g., constraints = MO orthonormality = $\sum_{i,j}\epsilon_{ij}(\langle\psi_i|\psi_j\rangle - \delta_{ij})$

$$\text{Euler-Lagrange eq} \Rightarrow \begin{cases} M_I\ddot{R}_I(t) = -\dfrac{\partial}{\partial R_I}\langle\Psi_0^{\text{HF}}|H_e|\Psi_0^{\text{HF}}\rangle + \dfrac{\partial}{\partial R_I}\{\text{constraints}\} \\ \mu_i\ddot{\psi}_i(t) = -\dfrac{\delta}{\delta\psi_i^*}\langle\Psi_0^{\text{HF}}|H_e|\Psi_0^{\text{HF}}\rangle + \dfrac{\delta}{\delta\psi_i^*}\{\text{constraints}\} \end{cases}$$

Car-Parrinello HF MD

$$\begin{cases} M_I\ddot{R}_I(t) = -\dfrac{\partial}{\partial R_I}\langle\Psi_0^{\text{HF}}|H_e|\Psi_0^{\text{HF}}\rangle & (\Psi_0^{\text{HF}} = \det\{\psi_i\}) \\ \mu_i\ddot{\psi}_i(t) = -\hat{F}_i\psi_i + \sum_j \epsilon_{ij}\psi_j \end{cases}$$

(may also use Kohn-Sham Fock operator $\hat{F}^{KS}$)

- Electronic (orbital) degrees of freedom (El-DoF) are treated as dynamical variables
- No (strict) minimization in the MO $\{\psi_i\}$-space
- Deviate from BO-MD due to thermal fluctuations of the El-DoF
- The dynamics of the El-DoF must be kept cool (eg using constraints)

Diagram : CP-MD trajectory in the coordinate and orbital space

6 Molecular Dynamics Simulation

6.1 Summary of Classical Mechanics

- **Newtonian EOM**

$$m\ddot{x} = F = -\frac{\partial V(x)}{\partial x}$$

- **Principle of Least Action**

$$\text{Action : } I \equiv \int_{t_1}^{t_2} \mathcal{L}(x, \dot{x}) dt$$

The classical trajectory $x(t_1) \rightarrow x(t_2)$ minimizes the action I against small variation $\delta x(t)$ (with fixed ends $\delta x(t_1) = \delta x(t_2) = 0$).

$$\begin{aligned}
\delta I &= \int_{t_1}^{t_2} dt\, \delta\mathcal{L} = \int_{t_1}^{t_2} dt \left(\frac{\partial \mathcal{L}}{\partial x}\delta x + \frac{\partial \mathcal{L}}{\partial \dot{x}}\delta \dot{x} \right) \\
&= \int_{t_1}^{t_2} dt \left\{ \frac{\partial \mathcal{L}}{\partial x} - \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}} \right) \right\} \delta x + \left. \frac{\partial \mathcal{L}}{\partial \dot{x}}\delta x \right|_{t_1}^{t_2}
\end{aligned}$$

Stationary condition $\delta I = 0$ for arbitrary $\delta x(t)$

$$\Rightarrow \textbf{Euler-Lagrange eq :} \; \frac{\partial \mathcal{L}}{\partial x} - \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}}\right) = 0$$

This is easily seen to give the Newtonian EOM for $\mathcal{L} = T - V = \frac{m}{2}\dot{x}^2 - V(x)$

- **Hamiltonian EOM :** Momentum and Hamiltonian are defined by

$$p \equiv \frac{\partial \mathcal{L}}{\partial \dot{x}} \quad \text{and} \quad H \equiv p\dot{x} - \mathcal{L}$$

For Cartesian coordinates, we get $p = m\dot{x}$ and $H = p^2/2m + V(x)$, and it is easy to see that the following Hamiltonian EOM is equivalent to Newtonian EOM:

$$\dot{x} = \frac{\partial H}{\partial p} \quad \text{and} \quad \dot{p} = -\frac{\partial H}{\partial x}$$

Lagrange and Hamilton theories are more flexible and convenient when dealing with general coordinate systems other than the Cartesian.

6.2 Integration

6.2.1 Verlet algorithm

$$\begin{aligned} \mathbf{r}(t+\delta t) &= \mathbf{r}(t) + \dot{\mathbf{r}}(t)\delta t + \tfrac{1}{2}\ddot{\mathbf{r}}(t)\delta t^2 + \cdots \\ &= \mathbf{r}(t) + \mathbf{v}(t)\delta t + \tfrac{1}{2}\mathbf{a}(t)\delta t^2 + \cdots \\ \mathbf{r}(t-\delta t) &= \\ \Rightarrow \quad \mathbf{r}(t+\delta t) &= 2\mathbf{r}(t) - \mathbf{r}(t-\delta t) + \mathbf{a}(t)\delta t^2 \end{aligned}$$

- error is of order $\mathcal{O}(\delta t^4)$
- time-reversible
- requires storage of the previous position $\mathbf{r}(t+\delta t)$
- small term $\mathbf{a}(t)\delta t^2$ is added to a difference of large terms $2\mathbf{r}(t) - \mathbf{r}(t-\delta t)$

  $\Rightarrow$ numerical round-off imprecisions
- velocities are unnecessary to evolve the trajectory, but needed when calculating the kinetic energy

$$\mathbf{v}(t) = \frac{\mathbf{r}(t+\delta t) - \mathbf{r}(t-\delta t)}{2\delta t}$$

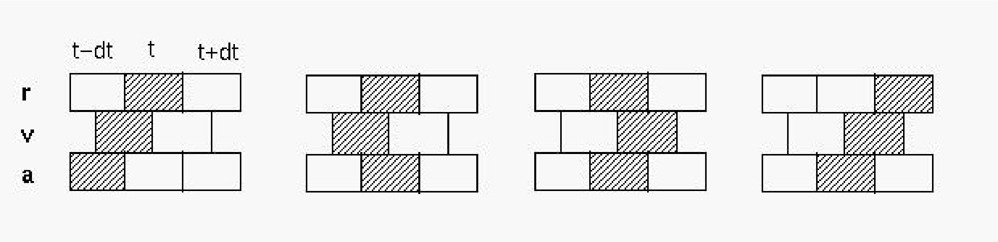
  - error is of order $\mathcal{O}(\delta t^3)$
  - small difference is divided by the small timestep $\Rightarrow$ numerical imprecisions

6.2.2 Leap-frog algorithm

Propagate position and velocity

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{v}(t+\tfrac{\delta t}{2})\delta t$$

$$\mathbf{v}(t+\tfrac{\delta t}{2}) = \mathbf{v}(t-\tfrac{\delta t}{2}) + \mathbf{a}(t)\delta t$$



- mathematically equivalent to Verlet method (easily verified by eliminating the velocities)
- velocities (& kinetic energy) at time t

$$\mathbf{v}(t) = \frac{\mathbf{v}(t+\frac{\delta t}{2}) + \mathbf{v}(t-\frac{\delta t}{2})}{2}$$

- advantages over the original Verlet
  - less problematic on the numerical round-off due to taking differences
  - explicit appearance of velocities
  - criticisms : treatment of velocities — still not very satisfactory

6.2.3 Velocity-Verlet algorithm

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \tfrac{1}{2}\mathbf{a}(t)\delta t^2$$

$$\mathbf{v}(t+\tfrac{\delta t}{2}) = \mathbf{v}(t) + \mathbf{a}(t)\tfrac{\delta t}{2}$$

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t+\tfrac{\delta t}{2}) + \mathbf{a}(t+\delta t)\tfrac{\delta t}{2}$$

- mathematically equivalent to the previous two

6.3 Treatment of Molecules

- Time scales :

  bond stretch < bend < torsion < collective motions < rotation < translation

- Fixing bond lengths (to save CPU)
  1. treat as a rigid body (small molecules such as H_2O)
  2. transform the EOM to internal coordinates (e.g., GF-matrix method)
  3. introduce bond constraint condition to the Lagrangian

     ⇒ constrained EOM (SHAKE and RATTLE methods)

- Multiple time step method(s)
  - small time step for fast motions
  - frequent update of short-range interactions

6.3.1 Multiple time step method (r-RESPA)*

r-RESPA = reversible REference System Propagator Algorithm

Classical Liouville operator :

$$iL \equiv \{..., H\} = \sum_{i=1}^{f} \left[\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right]$$

$$\text{Poisson bracket : } \{A, B\} = \sum_{i=1}^{f} \left[\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right]$$

Propagation of the phase-space point $\Gamma = \{q_i(t), p_i(t)\}$

$$\Gamma(t + \Delta t) = e^{iL\Delta t}\, \Gamma(t)$$

In Cartesian coordinate with $H = \sum_i \frac{p_i^2}{2m_i} + V(\mathbf{x})$, $\quad p_i = m_i v_i$, $\quad \left(F_i = -\frac{\partial V}{\partial x_i} = \text{force} \right)$

$$iL = \sum_i \left[v_i \frac{\partial}{\partial x_i} + \frac{F_i}{m_i} \frac{\partial}{\partial v_i} \right]$$

Using $e^{c \frac{\partial}{\partial y}} f(y) = f(y + c)$, we find :

- $e^{v\Delta t \frac{\partial}{\partial x}}$ propagates x to $x + v\Delta t$
- $e^{\Delta t \frac{F}{m} \frac{\partial}{\partial v}}$ propagates v to $v + \frac{F}{m}\Delta t$

Trotter decomposition

$$e^{i(L_1+L_2)\Delta t} = e^{iL_1\Delta t/2} e^{iL_2\Delta t} e^{iL_1\Delta t/2} + \mathcal{O}(\Delta t^3)$$

If we choose : $iL_1 = \frac{F}{m}\frac{\partial}{\partial v}, \quad iL_2 = v\frac{\partial}{\partial x}$

$$\Gamma(t+\Delta t) = e^{\frac{\Delta t}{2}\frac{F}{m}\frac{\partial}{\partial v}} e^{\Delta t v \frac{\partial}{\partial x}} e^{\frac{\Delta t}{2}\frac{F}{m}\frac{\partial}{\partial v}} \cdot \Gamma(t) + \mathcal{O}(\Delta t^3)$$

From right to left :

- $e^{\frac{\Delta t}{2}\frac{F}{m}\frac{\partial}{\partial v}}$ propagates v to $v + \frac{F}{m}\frac{\Delta t}{2}$
- $e^{\Delta t v \frac{\partial}{\partial x}}$ propagates x to $x + v\Delta t$
- $e^{\frac{\Delta t}{2}\frac{F}{m}\frac{\partial}{\partial v}}$ propagates v to $v + \frac{F}{m}\frac{\Delta t}{2}$ (with updated force $F(x)$)

This is exactly the Velocity-Verlet algorithm

Decomposition of forces : (fast/slow, tight/soft, short/long-range etc.)

$$F = F_{\text{fast}} + F_{\text{slow}}$$

Accordingly, $iL_1 = \frac{F_{\text{slow}}}{m}\frac{\partial}{\partial v} \quad iL_2 = v\frac{\partial}{\partial x} + \frac{F_{\text{fast}}}{m}\frac{\partial}{\partial v},$
Then, the propagator will be

$$e^{\frac{\Delta t}{2}\frac{F_{\text{slow}}}{m}\frac{\partial}{\partial v}} e^{\Delta t(v\frac{\partial}{\partial x} + \frac{F_{\text{fast}}}{m}\frac{\partial}{\partial v})} e^{\frac{\Delta t}{2}\frac{F_{\text{slow}}}{m}\frac{\partial}{\partial v}}$$

We further decompose the propagator in the middle into $\underline{n \text{ micro-steps}}$ with $\delta t \equiv \Delta t/n$

$$e^{\frac{\Delta t}{2}\frac{F_{\text{slow}}}{m}\frac{\partial}{\partial v}} \left[e^{\frac{\delta t}{2}\frac{F_{\text{fast}}}{m}\frac{\partial}{\partial v}} e^{\delta t v \frac{\partial}{\partial x}} e^{\frac{\delta t}{2}\frac{F_{\text{fast}}}{m}\frac{\partial}{\partial v}} \right]^n e^{\frac{\Delta t}{2}\frac{F_{\text{slow}}}{m}\frac{\partial}{\partial v}}$$

Implementation It might be easier to see the code :

```
$\delta t = \Delta t/n$                                   ! micro-timestep (for fast motions)
do istep = 1, nstep                                ! overall simulation steps
    $\mathbf{v} = \mathbf{v} + (\Delta t/2) \cdot (\mathbf{F}_{\text{slow}}/m)$
    do j = 1, $n$                                   ! inner loop for fast motions
        $\mathbf{v} = \mathbf{v} + (\delta t/2) \cdot (\mathbf{F}_{\text{fast}}/m)$
        $\mathbf{x} = \mathbf{x} + \delta t \cdot \mathbf{v}$
        call calculate_force($\mathbf{F}_{\text{fast}}$)
        $\mathbf{v} = \mathbf{v} + (\delta t/2) \cdot (\mathbf{F}_{\text{fast}}/m)$
    end do
    call calculate_force($\mathbf{F}_{\text{slow}}$)
    $\mathbf{v} = \mathbf{v} + (\Delta t/2) \cdot (\mathbf{F}_{\text{slow}}/m)$
end do
```

6.4 Constant Temperature and Pressure Methods

6.4.1 Common Statistical Ensembles

- constant NVE (microcanonical)
- constant NVT (canonical)
- constant NPT (isothermal-isobaric)
- constant μVT (grand canonical) [μ = chemical potential]

Straightforward / standard use of :

- MD $\Rightarrow$ microcanonical (energy conservation of classical mech.)
- MC $\Rightarrow$ canonical (Metropolis algorithm)

Statistical average (constant temperature)

$$\langle A(q,p)\rangle = \frac{1}{Q}\int\int dp\, dq\; A(q,p)\; e^{-H(q,p)/k_BT}$$

where Q is the partition function : $Q \equiv \int\int dp\, dq\; e^{-H(q,p)/k_BT}$

6.4.2 Temperature and Pressure from MD

Equipartition theorem :

$$\langle\frac{p_{\alpha i}^2}{2m_i}\rangle = \frac{k_BT}{2} \qquad (\alpha = x, y, z)$$

i.e. average kinetic energy of $k_BT/2$ for each degree of freedom

The kinetic temperature is thus computed in the classical MD by

$$T = \frac{1}{3Nk_B}\langle\sum_i \frac{\mathbf{p}_i^2}{m_i}\rangle$$

Pressure from MD : $PV = Nk_BT + \langle W\rangle$

$$\text{Virial :} \quad W \equiv \frac{1}{3}\sum_{i=1}^{N}\mathbf{r}_i\cdot\mathbf{f}_i^{\text{int}} \qquad \left(\mathbf{f}_i^{\text{int}} = -\frac{\partial V}{\partial \mathbf{r}_i}\right)$$

6.4.3 Constant NVT MD*

Extended system method (Nosé-Hoover)

Couple with external heat bath ⇒ **friction** parameter η (fictious mass Q)

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}, \quad \dot{\mathbf{p}}_i = \mathbf{f}_i - \frac{p_\eta}{Q}\mathbf{p}_i$$

$$\dot{\eta} = \frac{p_\eta}{Q}, \quad \dot{p}_\eta = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - N_f k_B T$$

(N_f = number of (unconstrained) degrees of freedom $= 3N - N_c$)

- proven to generate canonical ensemble
- Conserved quantity (for coding checks) :

$$E = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}) + \frac{p_\eta^2}{2Q} + N_f k_B T \eta$$

6.4.4 Constant Pressure MD*

Constant pressure P in simulation ⇐ Volume control (as a dynamical variable)

⇒ coordinate scaling : $\mathbf{r}_i = V^{1/3}\mathbf{s}_i$

extended Lagrangian : (Q = fictious mass for V)

$$\mathcal{L} = \frac{1}{2}\sum_i m_i \mathbf{v}_i^2 - V(\mathbf{r}) + \frac{1}{2}Q\dot{V}^2 - PV$$

Euler-Lagrange eq : $\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}} - \frac{\partial \mathcal{L}}{\partial q} = 0$ for $q = \mathbf{s}_i,\ V$

$$\Rightarrow \ddot{\mathbf{s}}_i = \frac{1}{V^{1/3}}\frac{\mathbf{f}_i}{m_i} - \frac{2}{3V}\,\dot{\mathbf{s}}\,\dot{V}, \qquad \ddot{V} = \frac{1}{Q}(\mathcal{P} - P)$$

$$\mathcal{P} \equiv \frac{1}{3V}\left(\sum_i m_i \mathbf{v}_i^2 + W\right) \qquad (W = \text{virial})$$

7 Data Analysis

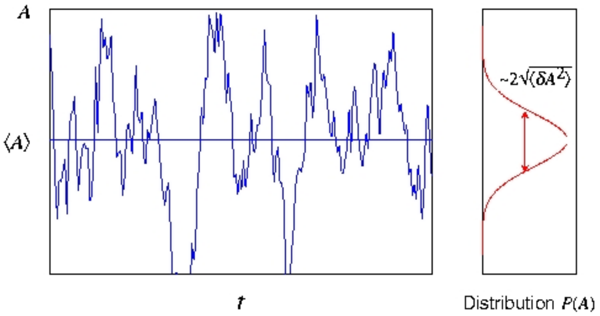
7.1 Static Properties

Ergodic hypothesis : Statistical ensemble average = average over long time

$$\langle A \rangle = \frac{1}{\tau_{\text{run}}}\int_0^{\tau_{\text{run}}} A(t)\, dt = \frac{1}{N_{\text{run}}}\sum_{k=1}^{N_{\text{run}}} A_k$$

where $\tau_{\text{run}} = N_{\text{run}}\Delta t$ (N_{run} steps, $A_k = A(k\Delta t)$)

- RMS deviation $= \sqrt{\langle \delta A^2 \rangle}$ ($\delta A \equiv A - \langle A \rangle$)



Practical

Method 1: save the whole sequence of $A(t)$ $\Rightarrow$ analyse after simulation

Method 2: "on-the-fly" summing up.

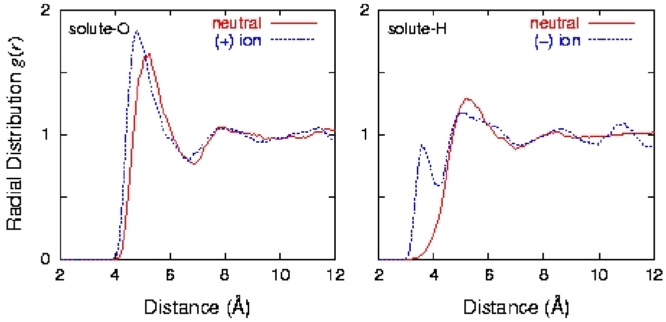
For RMS, we sum up $\delta A = A - \langle A \rangle$. However, we don't know $\langle A \rangle$ until the end of simulation. The following conversion is then useful:

$$\langle \delta A^2 \rangle = \langle (A - \langle A \rangle)^2 \rangle = \cdots = \langle A^2 \rangle - \langle A \rangle^2$$

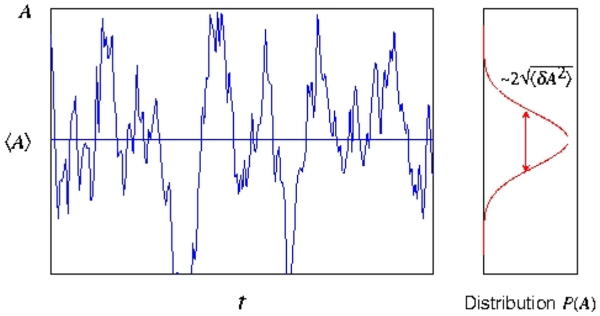
```
sum = 0 ; sum2 = 0
do istep = 1, nstep                ! overall simulation steps
    ...
    call calculate_quantities($A$)
    sum = sum + $A$
    sum2 = sum2 + $A^2$
    ...
end do
average = sum/nstep
variance = sum2/nstep - average$^2$
RMS = $\sqrt{\text{variance}}$
```

7.2 Radial disribution function

Example : Ion pair in water



7.3 Time correlation function



correlation between points with time interval τ

$$C_{AA}(\tau) = \langle \delta A(0) \delta A(\tau) \rangle = \frac{1}{t_{\mathrm{run}} - \tau} \int_0^{t_{\mathrm{run}} - \tau} \delta A(t)\, \delta A(t + \tau)\, dt$$

- $C_{AA}(0) = 1$
- For random motions (e.g. in liquids)

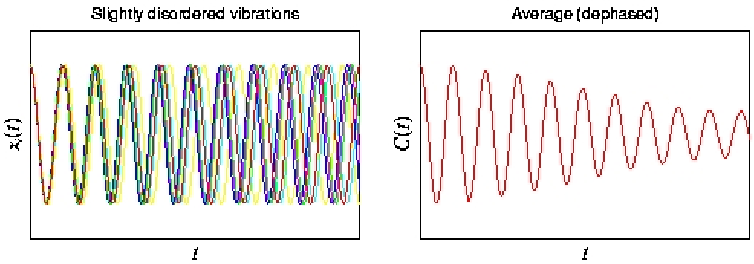
  $C_{AA}(t) \to 0$ as $t \to +\infty$ (loss of correlation)

- For "regular" motions (eg. harmonic oscillators / phonons in "perfect" solids)

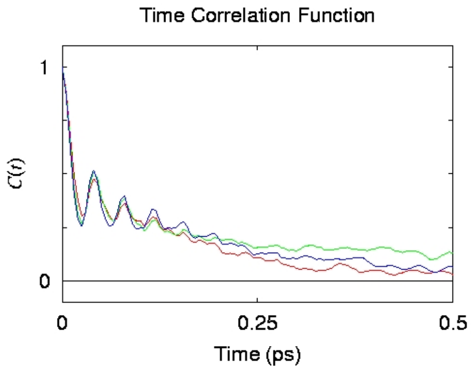
$$\langle x(0) x(t) \rangle = x(0)^2 \cos \omega t$$

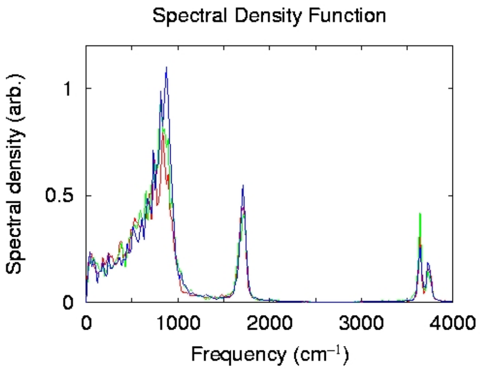
- For (slightly) disordered set of oscillators ⇒ "dephasing"

$$\bar{x}(t) = \sum_i c_i x_i(t) = \sum_i c_i x_i(0) \cos \omega t$$



Example : Dielectric response of water



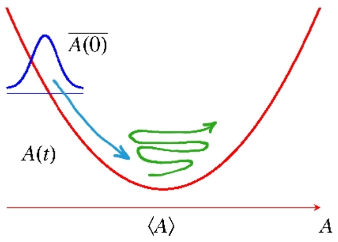


7.3.1 Relaxation Phenomena

Onsager's Regression Hypothesis

$$\frac{\overline{A(t)} - \langle A \rangle}{\overline{A(0)} - \langle A \rangle} = \frac{\langle \delta A(t) \delta A(0) \rangle}{\langle \delta A^2 \rangle}$$

non-equil. response	equil. correlation
decay of (experimentally) prepared non-equil. state	decay of spontaneous fluctuation in equil.



Microscopically proven by Fluctuation-dissipation theorem in the Linear-Response limit

7.3.2 Various Applications

- Transport properties (Diffusion constant) ⇐ velocity TCF
- Microwave & IR spectra ⇐ dipole TCF
- Electronic spectra ⇐ transition dipole TCF
- Electron / excitation transfer rates ⇐ TCF of energy gap (Fermi Golden Rule)
- Chemical reaction rates ⇐ flux-flux TCF

cf. G C Schatz & M A Ratner, "Quantum Mechanics in Chemistry" (Prentice Hall, 1993)

Diffusion constant ≡ mean-squares displacement (Einstein relation)

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = 6Dt$$

Relation to velocity TCF :

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \mathbf{v}(\tau) d\tau \quad \Rightarrow \quad 6Dt = \int_0^t d\tau_1 \int_0^t d\tau_2 \langle \mathbf{v}(\tau_1)\mathbf{v}(\tau_2)\rangle$$

$\frac{\partial}{\partial t}$ both sides

$$6D = 2\int_0^t d\tau \langle \mathbf{v}(\tau)\mathbf{v}(t)\rangle = 2\int_0^t d\tau \langle \mathbf{v}(0)\mathbf{v}(t-\tau)\rangle$$

$\Leftarrow$ TCF depends only on time <u>interval</u> (in stationary equilibrium)

Changing the integration variable from τ to $\tau' \equiv t - \tau$,

$$D = \frac{1}{3}\int_0^t d\tau' \langle \mathbf{v}(0)\mathbf{v}(\tau')\rangle$$

8 Monte Carlo Simulation

Monte Carlo integration $\Leftarrow$ random sampling

$$I = \int_0^1 f(x)dx \simeq \frac{1}{N_{\text{sample}}} \sum_{i=1}^{N_{\text{sample}}} f(x_i)$$

$$\{x_i\} = \text{uniform random numbers in } [0,\, 1]$$

Statistical average (constant temperature) $\Leftarrow$ **Phase-space integration**

$$\langle A(q,p)\rangle = \frac{1}{Q}\int\int dp\; dq\; A(q,p)\; e^{-H(q,p)/k_BT}$$

where Q is the partition function : $Q \equiv \int\int dp\; dq\; e^{-H(q,p)/k_BT}$

For momentum-independent quantities $A(q)$ (with $H = \sum_i \mathbf{p}_i^2/2m_i + V(q)$)

$\Rightarrow$ **Configuration space integration**

$$\langle A\rangle = \frac{1}{Z}\int dq A(q) e^{-V(q)/k_BT}$$

$$\text{where } Z = \int dq e^{-V(q)/k_BT}$$

8.1 Standard MC (Metropolis algorithm)

Metropolis MC

- generates configurations R in canonical ensemble
- Core algorithm :

```
do istep = 1, nstep                                      ! overall Monte Carlo steps
    ...
    $\mathbf{R}_{new} = \mathbf{R}_{old} + \delta\mathbf{R}$                          ! trial move
    call calculate_potential($V(\mathbf{R}_{new})$)
    $\Delta V = V(\mathbf{R}_{new}) - V(\mathbf{R}_{old})$

                                                         ! Metropolis test
    if ( $\Delta V < 0$ ) then                                 ! $\mathbf{R}_{new}$ is more stable
        accept $\mathbf{R}_{new}$
    else if ( $e^{-\Delta V/k_BT}$ > random_number ) then       ! $\mathbf{R}_{new}$ is less stable but thermall acceptable
        accept $\mathbf{R}_{new}$
    else
        reject $\mathbf{R}_{new}$                                 ! stay at $\mathbf{R}_{old}$
    end if
    ...
end do
```

- Statistical average is calculated by:

$$\langle A \rangle = \frac{1}{N_{\text{step}}} \sum_{i=1}^{N_{\text{step}}} A(\mathbf{R}_i)$$

MC vs MD

- direct generation of canonical ensemble (straightforward MD ⇒ microcanonical)
- Phase-space / configration-space average (MD analysis ⇒ time average assuming the ergodic hypothesis)
- no need to evaluate forces
- no time evolution

8.2 Umbrella Sampling Technique

Finite length of MC sampling

⇒ the system may be trapped in local potential minima.

In order to extend the sampling to high potential (unstable) configurations, we augment a bias (weight / window / umbrella) potential $W(q)$ to the original (unbiased) potential $V(q)$. The statistical average obtained from this biased simulation is

$$\langle A(q) \rangle_w = \frac{1}{Q_w} \int dq\ A(q)\ e^{-\beta(V(q)+W(q))} \qquad \left(Q_w = \int dq\ e^{-\beta(U(q)+W(q))} \right)$$

The statistics of the original (unbiased) system are reproduced by

$$\begin{aligned}
\langle A(q)\rangle_0 &= \frac{1}{Q_0}\int dq\ A(q)\ e^{-\beta V(q)} \times \frac{Q_w}{Q_w} \\
&= \frac{Q_w}{Q_0}\frac{1}{Q_w}\ \int dq\ A(q)\ e^{+\beta W(q)} e^{-\beta(V(q)+W(q))} = \frac{Q_w}{Q_0}\ \langle A(q)\ e^{+\beta W(q)}\rangle_w \\
&= \frac{\langle A(q)\ e^{+\beta W(q)}\rangle_w}{\langle e^{+\beta W(q)}\rangle_w} = \langle e^{-\beta W(q)}\rangle_0\ \langle A e^{+\beta W(q)}\rangle_w
\end{aligned}$$

9 Free Energy Surfaces

Remember that the Gibbs free energy is related to the equilibrium constant and thus the probability distributions of the reactant and product species. For example, for $A \rightleftharpoons B$,

$$e^{-\Delta G/k_BT} = K = \frac{[B]}{[A]} = \frac{\text{Prob. B}}{\text{Prob. A}}$$

This would suggest the following generalization to more general "states" of the system

$$\Delta G \equiv G_2 - G_1 = -k_BT\ln\left(\frac{\text{Prob. State 2}}{\text{Prob. State 1}}\right)$$

Now, let X be some coordinate(s) of the system. This may be a position coordinate itself or a function of positions. The free energy curves or surfaces along X can be defined and calculated from the probability distribution of $P(X)$

$$G(X) = -k_BT\ln P(X) \quad \text{or} \quad G(X_2) - G(X_1) = -k_BT\ln\left(\frac{P(X_2)}{P(X_1)}\right)$$

For example, when $P(X)$ is a Gaussian distribution

$$P(X) \propto e^{-aX^2}$$

then the free energy curve $G(X)$ is a harmonic potential

$$G(X) = -k_BT\ln e^{-aX^2} + C = k_BTaX^2 + C$$

where C is just a constant coming from the normalization factor of $P(X)$. It is very straightforward to calculated $P(X)$ from simulations. The umbrella sampling method discussed in the previous section can be employed for high energy (less probable) regions along X.