

# Lecture Notes

## Simulation Methods 2

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# 1 Element of quantum mechanics

Time dependent Schrödinger equation:  $H\psi(\vec{r}, t) = i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t}$ .  
Decoupling of space and time:  $\psi(\vec{r}, t) = \phi(\vec{r})f(t)$ .  
Time independent Schrödinger equation:  $H\phi(\vec{r}) = E\phi(\vec{r})$ .

The state of a quantum mechanical system is completely specified by  $\psi(\vec{r}, t)$ .

The probability of finding a particle within the volume element  $V$  at  $\vec{r}$  and time  $t$  is:  $\psi^*(\vec{r}, t)\psi(\vec{r}, t) dV$

Normalization condition:  $\int_{-\infty}^{+\infty} \psi^*(\vec{r}, t)\psi(\vec{r}, t)dV = 1$ ,

with  $\psi(\vec{r}, t)$  single-valued, continuous and finite.

- For every observable in classical mechanics there is a corresponding hermitian operator in quantum mechanics.
- In any measurement of the observable associated with operator  $\hat{A}$ , the only values that will be observed are the eigenvalues  $a$ :  $\hat{A}\psi(\vec{r}, t) = a\psi(\vec{r}, t)$ .

In most situations the time-independent Schrödinger equation needs to be solved:

$$H\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}) \quad \text{with} \quad \int \phi_i^*(\vec{r})\phi_j(\vec{r})d\vec{r} = \delta_{ij} \tag{1.1}$$

$\{\phi_i(\vec{r})\}$  is a complete basis set, spanning the Hilbert space of the Hamiltonian  $H$ .  
A general state of the system is:

$$\xi(\vec{r}) = \sum_i c_i\phi_i(\vec{r}) \tag{1.2}$$

where, due to orthonormality,

$$c_i = \int \phi_i^*(\vec{r})\xi(\vec{r})d\vec{r} \tag{1.3}$$

Using the Bra-ket notation, one can write:

expectation value of operator $\hat{A}$	$\langle \phi   A   \phi \rangle = \int \phi^*(\vec{r}) A(\vec{r}) \phi(\vec{r}) d\vec{r}$
orthonormality	$\langle \phi_i   \phi_j \rangle = \delta_{ij}$
general state	$ \xi\rangle = \sum_i \langle \phi_i   \xi \rangle  \phi_i\rangle$
identity operator	$\sum_i  \phi_i\rangle \langle \phi_i  = 1$
many-body wave function (e.g. electrons in a solid) in the position representation	$\langle \vec{r}_1, \dots, \vec{r}_N   \Phi \rangle = \Phi(\vec{r}_1, \dots, \vec{r}_N)$
commutator of two operators	$[A_1, A_2] = A_1 A_2 - A_2 A_1$

## 1.1 Indistinguishable particles

The many-body wave function must have certain symmetries.

- Fermions  
antisymmetric - change of sign upon interchange of all coordinates of any two particles
- Bosons  
symmetric - no change of sign upon interchange of all coordinates

## 1.2 Linear combination of atomic orbitals (LCAO)

A quantum superposition of atomic orbitals for calculating molecular orbitals.

When two atoms come close, e.g. to form a chemical bond, the atomic orbitals are modified, i.e. the electron cloud shape is changed according to the type of atoms participating in the chemical bond.

LCAO was introduced in 1929 by Lennard-Jones, but was already used for  $H_2^+$  by Pauling.

Assumption:

The number of molecular orbitals is equal to the number of atomic orbitals in the expansion.

$i$ -th molecular orbital  $\phi_i = c_{1i}\xi_1 + c_{2i}\xi_2 + \dots + c_{ni}\xi_n = \sum_{r=1}^n c_{ri}\xi_r$ .

The  $r = 1, \dots, n$  define atomic orbitals,  $c_{ri}$  are the weights of the contribution of the  $r^{th}$  atomic orbital to the molecular orbital.

Within the Hartree-Fock method the  $c_{ri}$  coefficients are calculated.

The tight-binding method is also based on LCAO

The basis functions  $\xi_r$  are the one-electron functions centered on the nucleus of a specific atom of the molecule.

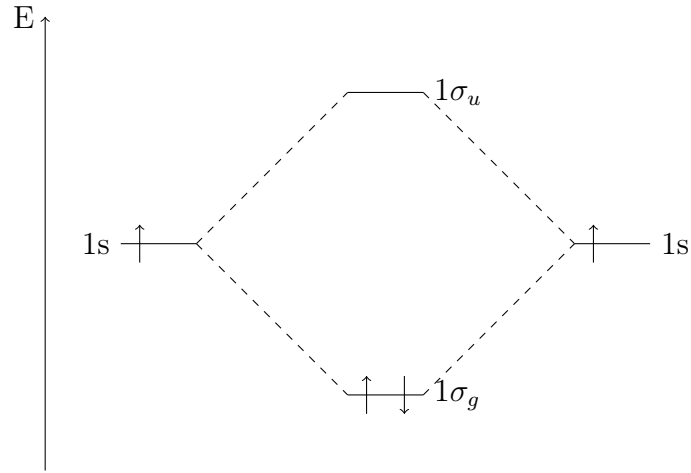
Qualitative LCAO representation:

through molecular orbitals, e.g.  $H_2$ :

Quantitative LCAO treatment:

Hückel method, extended Hückel method, Pariser-Parr-Pople method.

**Hückel method** LCAO treatment to determine energies of molecular orbitals of  $n$  electrons in hydrocarbon systems.  $\sigma$ -electrons are ignored because they do not play a significant role in the



properties of molecules.

**Example: Ethylene  $C_2H_2$  Hückel treatment:**

$$\Phi = c_1\phi_1 + c_2\phi_2, \quad \phi_1, \phi_2 \quad 2p \text{ atomic orbitals of carbon} \quad (1.4)$$

$$H\Phi = E\Phi \quad (1.5)$$

$$\begin{aligned} \int [\text{Eq. (1.4)} + \text{Eq. (1.5)}] * \phi_1 &\rightarrow c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \\ \int [\text{Eq. (1.4)} + \text{Eq. (1.5)}] * \phi_2 &\rightarrow c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0 \end{aligned}$$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} * \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0, \quad (1.6)$$

where  $H_{ij} = \int \phi_i H \phi_j d\vec{r}$  and  $S_{ij} = \int \phi_i \phi_j d\vec{r}$ .

Hückel assumes:

- $S_{ij} = \delta_{ij}$
- $H_{ij} \neq 0$  when atoms i and j share a bond
- overlap between the two atomic orbitals is zero

$$\begin{aligned} H_{11} = H_{22} &= a & S_{11} = S_{22} &= 1 \\ H_{12} = H_{21} &= b & S_{12} = S_{21} &= 0 \end{aligned}$$

Inserting the assumptions into Eq. (1.6) it follows that

$$\begin{pmatrix} a - E & b \\ b & a - E \end{pmatrix} * \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (1.7)$$

The solution is

$$c_2 = \mp c_1 \rightarrow \Phi = c_1(\phi_1 \mp \phi_2) \stackrel{\text{norm.}}{=} \frac{\phi_1 \mp \phi_2}{\sqrt{2}} \quad (1.8)$$

$b < 0 \rightarrow \Phi = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$  is the lower energy level (HOMO) and  $\Phi = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$  is the higher energy level (LUMO).

**Exchange property of electrons** If two electrons of the same spin interchange positions,  $\Phi$  must change sign as a manifestation of the Pauli exclusion principle.

**Correlation property of electrons** Each electron is affected by the motion of every other electron in the system.

Electron exchange and correlation is crucial in superconductivity, the transport properties in high magnetic fields (e.g. quantum Hall effect), etc.

Electron exchange and correlation is not crucial for optical excitations, conduction or mechanical properties.

Therefore, in these cases, the single-particle picture (classical ions and single quantum mechanical particles) is a good approximation.

## 2 Hartree-Fock theory

Development of one-electron picture; electron exchange and correlation are taken into account in an average way, i.e. mean field approximation for the electron-electron interactions.

### 2.1 The Hartree approximation

Simplification: Electrons are modeled as non-interacting particles:

$$\Psi^H(\{\vec{r}_i\}) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\dots\phi_N(\vec{r}_N) \quad (2.1)$$

$i$  electron index

$\phi_i(\vec{r}_i)$  normalized single-particle states

Total energy:

$$\begin{aligned} E^H &= \langle \Psi^H | H | \Psi^H \rangle \\ &= \sum_i \left\langle \phi_i \left| \frac{-\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) \right| \phi_i \right\rangle + \frac{e^2}{2} \sum_i \sum_{i \neq j} \left\langle \phi_i \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_j \phi_i \right\rangle \end{aligned}$$

Variational calculation of single-particle states :

Assume  $\Psi^H$  to be a stationary state (any variation in the wave function will give zero variation in energy - similar to a derivative of a function at its maximum, which is zero).

$\langle \delta \phi_i |$ : variation in wave function subject to constraint  $\langle \phi_i | \phi_i \rangle = 1$ .

Introduce a Lagrange multiplier  $\epsilon_i$  to include constraint:

$$\delta \left[ E^H - \sum_i \epsilon_i (\langle \phi_i | \phi_i \rangle - 1) = 0 \right] \Rightarrow \quad (2.2)$$

$$\begin{aligned} \left\langle \delta \phi_i \left| -\frac{\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) \right| \phi_i \right\rangle + e^2 \sum_{i \neq j} \left\langle \delta \phi_i \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_i \phi_j \right\rangle - \epsilon_i \langle \delta \phi_i | \phi_i \rangle &= 0 \\ \left\langle \delta \phi_i \left| \left[ -\frac{\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) + e^2 \sum_i \sum_{i \neq j} \left\langle \phi_i \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_i \phi_j \right\rangle - \epsilon_i \right] \right| \phi_i \right\rangle &= 0 \end{aligned}$$

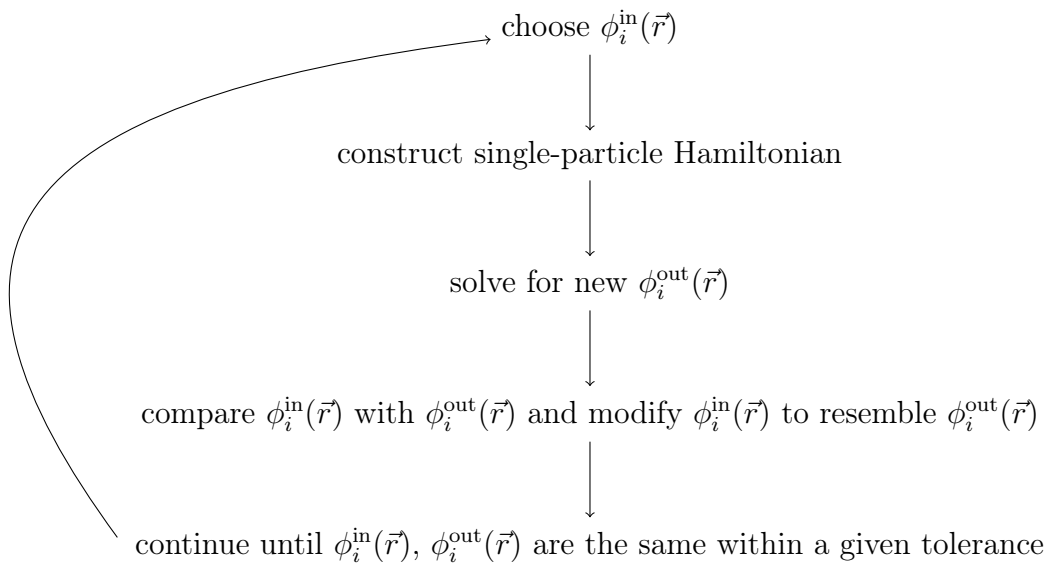
This needs to be true for any variation of  $\langle \delta\phi_i |$ :

$$\left[ -\frac{\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) + e^2 \underbrace{\sum_{j \neq i} \left\langle \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_j \right\rangle}_{V_i^H(\vec{r})} \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad \text{Hartree single-particle Eq.} \quad (2.3)$$

The Hartree potential  $V_i^H(\vec{r})$  is different for each electron and includes only Coulomb repulsion from the other electrons.

This amounts to a mean-field approximation to electron-electron interactions, which is a severe simplification.

Iterative solution:



## 2.2 The Hartree-Fock approximation

The next level of sophistication: include the fermionic nature of electrons.

Choose a wave function which is a properly antisymmetric version of the Hartree wave function, that is, change sign when coordinates of two electrons are interchanged.

The spin degrees of freedom are included by considering both electrons with up and down spins at position  $\vec{r}$ .

Use a Slater determinant for  $N$  electrons to express the wave function of the system:

$$\Psi^{HF}(\{\vec{r}_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_1(\vec{r}_2) & \dots & \phi_1(\vec{r}_N) \\ \phi_2(\vec{r}_1) & \phi_2(\vec{r}_2) & \dots & \phi_2(\vec{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\vec{r}_1) & \phi_N(\vec{r}_2) & \dots & \phi_N(\vec{r}_N) \end{vmatrix} \quad (2.4)$$

Total energy:

$$\begin{aligned}
E^{HF} &= \langle \Psi^{HF} | H | \Psi^{HF} \rangle \\
&= \sum_i \left\langle \phi_i \left| -\frac{\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) \right| \phi_i \right\rangle + \frac{e^2}{2} \sum_{i \neq j} \left\langle \phi_i \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_i \phi_j \right\rangle
\end{aligned}$$

Using again a variational argument, one can write down the single-particle Hartree-Fock equation:

$$\epsilon_i \phi_i(\vec{r}) = \left[ -\frac{\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) + V_i^H(\vec{r}) \right] \phi_i(\vec{r}) - e^2 \delta_{s_i s_j} \sum_{j \neq i} \left\langle \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_i \right\rangle \phi_j(\vec{r}) \quad (2.5)$$

There is one extra term compared to the Hartree equation, and that is the "exchange" term between the electrons.  $s_{i/j}$  is a label for the spin of particle  $i$ , respectively  $j$ .

This term cannot be put simply as  $V_i^x(\vec{r})\phi_i(\vec{r})$ , but by multiplying and dividing by the proper factors the Hartree term can be expressed in a different way:

$$\begin{aligned}
\rho_i(\vec{r}) &= |\phi_i(\vec{r})|^2 && \text{single-particle density} \\
\rho(\vec{r}) &= \sum_i \rho_i(\vec{r}) && \text{total density}
\end{aligned}$$

$$V_i^H(\vec{r}) = e^2 \int \frac{\rho(\vec{r}') - \rho_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (2.6)$$

Furthermore, a single-particle exchange density is constructed:

$$\rho_i^x(\vec{r}, \vec{r}') = \sum_{i \neq j} \frac{\phi_i(\vec{r}') \phi_i^*(\vec{r}) \phi_j(\vec{r}) \phi_j^*(\vec{r}')}{\phi_i(\vec{r}) \phi_i^*(\vec{r})} \quad (2.7)$$

with the exchange potential

$$V_i^x(\vec{r}) = -e^2 \int \frac{\rho_i^x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (2.8)$$

Then Eq. (2.5) becomes:

$$\left[ -\frac{\hbar^2 \nabla_r^2}{2m_e} + V_{ion}(\vec{r}) + V_i^H(\vec{r}) + V_i^x(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad (2.9)$$

Then within the Hartree-Fock approximation the total electron-electron interaction potential is:

$$\begin{aligned}
V_i^{HF}(\vec{r}) &= e^2 \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' - e^2 \int \frac{\rho_i(\vec{r}') + \rho_i^x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \\
&= e^2 \int \frac{\rho(\vec{r}') - \rho_i^{HF}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'
\end{aligned}$$

with  $\rho_i^{HF} = \rho_i(\vec{r}') + \rho_i^x(\vec{r}, \vec{r}')$ .

## Hartree-Fock simplifications

### 1. Born-Oppenheimer approximations assumed



2. No relativistic effects
3. Variational solution is a linear combination of a finite number of basis functions
4. Each energy eigenfunction is described by a single Slater determinant
5. Mean-field approximation: no correlation for electrons with opposite spin, only for parallel spin

### Variational method

The aim is to find approximation to lowest energy eigenstate or ground state

$$H |\psi_\lambda\rangle = \lambda |\psi_\lambda\rangle \quad ; \quad \sum_{\lambda_1, \lambda_2} \langle \psi_{\lambda_1} | \psi_{\lambda_2} \rangle = \delta_{\lambda_1, \lambda_2} \quad (2.10)$$

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \sum_{\lambda_1, \lambda_2} \langle \psi | \psi_{\lambda_1} \rangle \langle \psi_{\lambda_1} | H | \psi_{\lambda_2} \rangle \langle \psi_{\lambda_2} | \psi \rangle \\ &= \sum_{\lambda} \lambda |\langle \psi_\lambda | \psi \rangle|^2 \leq \sum_{\lambda} E_0 |\langle \psi_\lambda | \psi \rangle|^2 = E_0 \end{aligned}$$

This approach can be extended to excited states.

In general: for a Hamiltonian  $H$  and any normalizable wave function  $\psi$ , define the functional:

$$\epsilon[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}.$$

The variational principle states:

- $\epsilon \leq E_0$  :  $E_0$  is the lowest energy eigenstate of  $H$
- $\epsilon = E_0$  : is true if and only if  $\psi$  is exactly equal to the wave function of the ground state
- $\psi$  and  $\psi^*$  can be varied separately

### Electronic structure methods - 2 distinct "worlds"

#### 1. The **wave function** world

$$E_e = E_e[\psi_e(\vec{r}_1), \dots, \vec{r}_N] = \langle \psi_e | H | \psi_e \rangle$$

Variational principle:

$$\Rightarrow E_e^{opt} = \min_{\psi_e} E_e[\psi_e(\vec{r}_1), \dots, \vec{r}_N] \quad (2.11)$$

→  $3N$ -dimensional variational problem (John Pople).

#### 2. The **density** world

$$E_e = E_e[n(\vec{r})]$$

Variational principle:

$$\Rightarrow E_e^{opt} = \min_{n_e} E_e[n_e(\vec{r})] \quad (2.12)$$

→ 3-dimensional variational problem (Walter Kohn).

Both Pople and Kohn were awarded the Nobel prize in chemistry (1998) due to their contributions to understanding the electronic properties of materials.

A general form of the Hamiltonian for a many-body system

$$H = - \sum_i \frac{\hbar^2 \nabla_r^2}{2m_e} - \sum_I \frac{\hbar^2 \nabla_R^2}{2M_I} - \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I \vec{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \quad (2.13)$$

Born-Oppenheimer approximation:

Ions move slowly in space, and electrons respond instantaneously to any ionic motion. Because of this,  $\psi$  explicitly depends only on electron degrees of freedom.

We neglect the potential between the nuclei  $\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}$  and the kinetic energy of the nuclei

$\sum_I \frac{\hbar^2 \nabla_R^2}{2M_I}$ , which are constant as far as the electronic degrees of freedom are concerned.

It follows, that:

$$H = - \sum_i \frac{\hbar^2 \nabla_r^2}{2m_e} - \sum_i V_{ion}(\vec{r}_i) + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (2.14)$$

where the total external potential experienced by an electron due to the presence of ions is  $V_{ion}(\vec{r}_i) = - \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I \vec{r}_i|}$ .

### 3 Density functional theory (DFT)

- Hohenberg-Kohn-Sham theory

Basic concept:

Deal with total density of electrons  $n(\vec{r})$  instead of many body wave function  $\psi(\{\vec{r}_i\})$ .

- conceptually simple
- computationally efficient
- can be combined with Molecular Dynamics of nuclei
- many-body wave function  $\psi(\{\vec{r}_i\})$  does not need to be explicitly defined

→ Develop single-particle equation exactly and then introduce approximations.

Use:

- density

$$n(\vec{r}) = N \int \psi^*(\vec{r}_1, \dots, \vec{r}_N) \psi(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_2 \dots d\vec{r}_N \quad (3.1)$$

- one-particle density matrix

$$\gamma(\vec{r}, \vec{r}') = N \int \psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \psi(\vec{r}', \vec{r}_2, \dots, \vec{r}_N) d\vec{r}_2 \dots d\vec{r}_N \quad (3.2)$$

- two-particle density matrix

$$\Gamma(\vec{r}, \vec{r}' | \vec{r}, \vec{r}') = \frac{N(N-1)}{2} \int \psi^*(\vec{r}, \vec{r}', \vec{r}_3, \dots, \vec{r}_N) \psi(\vec{r}, \vec{r}', \vec{r}_3, \dots, \vec{r}_N) d\vec{r}_3 \dots d\vec{r}_N \quad (3.3)$$

$n(\vec{r}) = \langle \psi | \hat{N} | \psi \rangle$  and  $\hat{N}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i)$  for  $N$  indistinguishable particles.  $\gamma(\vec{r}, \vec{r}) = n(\vec{r})$ .

Extension of the pair correlation function, i.e. probability of finding two particles simultaneously at  $\vec{r}$  and  $\vec{r}'$  is given by the following operator:

$$\mathcal{G}(\vec{r}, \vec{r}') = \frac{1}{2} \sum_{i \neq j}^N \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j)$$

By analogy define a function of four independent variables  $\vec{r}_1, \vec{r}_2, \vec{r}'_1, \vec{r}'_2 \rightarrow \Gamma(\vec{r}_1, \vec{r}_2 | \vec{r}'_1, \vec{r}'_2)$  with the pair correlation function:

$$\begin{aligned} \Gamma(\vec{r}, \vec{r}' | \vec{r}, \vec{r}') &= g(\vec{r}, \vec{r}') \\ &= \int \langle \psi | \vec{r}_1, \dots, \vec{r}_N \rangle \mathcal{G}(\vec{r}, \vec{r}') \langle \vec{r}_1, \dots, \vec{r}_N | \psi \rangle d\vec{r}_1 \dots d\vec{r}_N \end{aligned}$$

It can be shown that the density  $n(\vec{r})$  is uniquely defined given an external potential for the electrons.

Proof by contradiction that  $n(\vec{r})$  is uniquely defined given  $V(\vec{r})$ :

Suppose  $V(\vec{r})$  and  $V'(\vec{r})$  correspond to the same  $n(\vec{r})$  and differ by more than a constant.

$V(\vec{r})$  corresponds to  $E, \psi, H$

$V'(\vec{r})$  corresponds to  $E', \psi', H'$

$$E = \langle \psi | H | \psi \rangle \quad E' = \langle \psi' | H' | \psi' \rangle$$

By the variational principle:

$$\begin{aligned} E &< \langle \psi' | H | \psi' \rangle = \langle \psi' | H + V' - V' | \psi' \rangle \\ &= \langle \psi' | H' + V - V' | \psi' \rangle \\ &= \langle \psi' | H | \psi' \rangle + \langle \psi' | (V - V') | \psi' \rangle \\ &= E' + \langle \psi' | (V - V') | \psi' \rangle \end{aligned}$$

similarly

$$E' < E + \langle \psi | (V - V') | \psi \rangle$$

then

$$(E + E') < (E' + E) + \langle \psi' | (V - V') | \psi' \rangle + \langle \psi | (V - V') | \psi \rangle \quad (3.4)$$

The last two terms on the right hand side give

$$\int n'(\vec{r}) [V(\vec{r}) - V'(\vec{r})] d\vec{r} - \int n(\vec{r}) [V(\vec{r}) - V'(\vec{r})] d\vec{r} = 0$$

By the assumption  $n(\vec{r}) = n'(\vec{r})$  it follows that  $E + E' < E + E'$ , which is wrong!

The external potential determines a wave function so that the wave function must be a unique functional of the density.

The kinetic energy  $T$  and the electron-electron interaction  $W$  contribute to the Hamiltonian besides the external potential  $V$ . Then, since  $T$  and  $W$  are common for all systems but  $V$  is different for each system, the *universal functional of density* is introduced:

$$F[n(\vec{r})] = \langle \psi | (T + W) | \psi \rangle = \text{const.}$$

The total energy of the system, expressed as a functional, is:

$$E[n(\vec{r})] = \langle \psi | H | \psi \rangle = F[n(\vec{r})] + \int V(\vec{r}) n(\vec{r}) d\vec{r} \quad (3.5)$$

From variational principle:  $E[n(\vec{r})]$  attains minimum for correct  $n(\vec{r})$  since for the same  $V(\vec{r})$  any other density  $n'(\vec{r})$  would lead to:

$$\begin{aligned} E[n'(\vec{r})] &= \langle \psi' | H | \psi \rangle \\ &= F[n'(\vec{r})] + \int V(\vec{r})n'(\vec{r})d\vec{r} \\ &= E[n(\vec{r})] \end{aligned}$$

Using one- and two-particle density:

$$\begin{aligned} E[n(\vec{r})] &= \langle \psi | H | \psi \rangle = -\frac{\hbar^2}{2m_e} \int \nabla_r^2 \gamma(\vec{r}, \vec{r}') \Big|_{\vec{r}=\vec{r}'} d\vec{r} \\ &+ \int \int \frac{e^2}{|\vec{r}-\vec{r}'|} \Gamma(\vec{r}, \vec{r}' | \vec{r}, \vec{r}') d\vec{r} d\vec{r}' + \int V(\vec{r})\gamma(\vec{r}, \vec{r}') d\vec{r} \end{aligned} \quad (3.6)$$

Now equation (3.6) is reduced to a set of single-particle equations.

There is no need to interpret these states as corresponding to electrons; these states represent fictitious fermionic particles, whose density is identical to that of the real electrons.

The fictitious particles can be considered as non-interacting (simplification).

The method is to express the many-body wave function  $\Psi(\{\vec{r}_i\})$  as a Slater determinant, and physical properties in terms of single-particle orbitals  $\phi_i(\vec{r})$  appearing in the Slater determinant.

We then obtain:

$$\begin{aligned} n(\vec{r}) &= \sum_i |\phi_i(\vec{r})|^2 \gamma(\vec{r}, \vec{r}') \\ &= \sum_i \phi_i^*(\vec{r}) \phi_i(\vec{r}') \Gamma(\vec{r}, \vec{r}' | \vec{r}, \vec{r}') \\ &= \frac{1}{2} [n(\vec{r})n(\vec{r}') - |\gamma(\vec{r}, \vec{r}')|^2] \end{aligned}$$

and express the energy functional as:

$$F[n(\vec{r})] = \boxed{T^S[n(\vec{r})]} + \boxed{\frac{e^2}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'} + \boxed{E^{XC}[n(\vec{r})]} \quad (3.7)$$

Kinetic energy      Coulomb interaction      Exchange correlation

Since the fictitious particles are not interacting, the kinetic energy can be written as a sum of single-particle equations:

$$T^S[n(\vec{r})] = \sum_i \left\langle \phi_i \left| -\frac{\hbar^2}{2m_e} \nabla^2 \right| \phi_i \right\rangle \quad \text{kinetic energy} \quad (3.8)$$

As can be seen in Eq. (3.7), the Coulomb term is separated out from the electron-electron interaction term in  $E^{XC}[n(\vec{r})]$ .

$E^{XC}[n(\vec{r})]$  includes all effects of the many-body character of the true electron system.

Consider a variation in density:

$$\delta n(\vec{r}) = \delta \phi_i^*(\vec{r}) \phi_i(\vec{r}) \quad (3.9)$$

with the restriction that the total number of particles does not change:

$$\int \delta n(\vec{r}) d\vec{r} = \int \delta \phi_i^*(\vec{r}) \phi_i(\vec{r}) d\vec{r} = 0 \quad (3.10)$$

With this choice and restriction through a Lagrange multiplier  $\epsilon_i$ , the single-particle equations for the potential energy follow through the variational principle:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V^{eff}(\vec{r}, n(\vec{r})) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \quad \text{Kohn-Sham equation} \quad (3.11)$$

where the effective potential is given by:

$$V^{eff}(\vec{r}, n(\vec{r})) = \boxed{V(\vec{r})} + e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \boxed{\frac{\delta E^{XC}[n(\vec{r})]}{\delta n(\vec{r})}} \quad (3.12)$$

external potential  
due to ions
variational functional  
derivative of exchange  
interaction

Single-particle orbitals  $\phi_i(\vec{r})$  are the Kohn-Sham orbitals. Kohn-Sham Density Functional Theory is in principle exact, but needs an approximation to the exchange-correlation functional.

$V^{eff}$  is a function of density  $n(\vec{r})$  and depends on all single-particle states. The solution of the system can be computed by solving the Kohn-Sham equations by iteration until self-consistency is reached. This is easy; a more difficult issue is the calculation of the exact form of  $E^{XC}[n(\vec{r})]$ , which is unknown.

→ What should  $E^{XC}[n(\vec{r})]$  be to best capture many-body effects?

There are many models, but this is still a field of research.

In most of the commonly used models the exchange-correlation functional is written as

$$E^{XC}[n(\vec{r})] = \int \{ \epsilon^x[n(\vec{r})] + \epsilon^{cor}[n(\vec{r})] \} n(\vec{r}) d\vec{r} \quad (3.13)$$

and the exchange-correlation potential in the Kohn-Sham equations:

$$V^{XC}[n(\vec{r})] = \frac{\delta E^{XC}[n(\vec{r})]}{\delta n(\vec{r})} \quad (3.14)$$

where the pure exchange energy can be

$$\epsilon^x[n(\vec{r})] = -\frac{3}{4} e^2 \left( \frac{3}{\pi} \right)^{1/3} [n(\vec{r})]^{1/3} \quad (3.15)$$

(from Hartree-Fock theory for free electrons, see below.)

Common feature:  $E^{XC}$  depends on  $n(\vec{r})$  in a local fashion.  $n$  is evaluated at one point of space at a time.

The relevant approaches are then referred to as local density approximations (LDA).

But this could be a severe restriction; even at the exchange level, the functional should be non-local, i.e. dependent on  $\vec{r}$  and  $\vec{r}'$  simultaneously because exchange and correlation effects are inherently non-local in an interacting electron system.

It is a much more difficult task to develop non-local exchange-correlation functionals; effort is directed also toward producing expressions for  $E^{XC}$  which depend not only on  $n(\vec{r})$ , but also its gradients → generalized gradient approximation (GGA). The generalized-gradient approximation works better for finite systems, but is still a local approximation to  $E^{XC}$ .

## Hartree-Fock theory for free electrons

Simplest case: the ionic potential forms a uniformly distributed positive background  $\rightarrow$  jellium model  
 electronic states reflect symmetry of potential, which is uniform  $\rightarrow$  plane waves:

$$\phi_i(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\vec{k}_i \cdot \vec{r})} \quad (3.16)$$

$\Omega$  volume of solid

$\vec{k}_i$  wave-vector characterizing  $\phi_i$ ; use  $\phi_i \rightarrow \phi_k$

$\vec{k} = 0, \dots, k_F$  with  $k_F$  the Fermi momentum, related to density  $n = \frac{N}{\Omega}$ .

$n = \frac{k_F^3}{3\pi^2}$  (proof not shown here, integrate over total number of states)

Fermi energy:  $\epsilon_F = \frac{\hbar^2 k_F^2}{2m_e}$

Express  $n$  with regard to  $r_s$  (radius of sphere whose volume corresponds to average volume/electron)

$$\frac{4\pi}{3} r_s^3 = \frac{\Omega}{N} = n^{-1} = \frac{3\pi^2}{k_f^3}$$

If the particles had only kinetic energy, the total energy of the system would be:

$$E^{kin} = \frac{\Omega}{\pi^2} \frac{\hbar^2 k_f^5}{\omega m_e} \rightarrow \frac{E^{kin}}{N} = \frac{3}{5} \epsilon_F \quad (3.17)$$

With electrons as plane waves, the electronic density must be uniform and equal to the ionic density. The two terms, the uniform positive ionic charge and the uniform negative electronic charge of equal density, cancel each other out. The terms remaining are the kinetic energy and the part of  $V_i^{HF}(\vec{r})$  corresponding to the exchange and arises from  $\rho_i^{HF}(\vec{r}, \vec{r}')$ :

$$\left[ -\frac{\hbar^2 \nabla^2}{2m_e} - e^2 \int \frac{\rho_k^{HF}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \right] \phi_k(\vec{r}) = \epsilon_k \phi_k(\vec{r}) \quad (3.18)$$

It can be proven that plane waves are eigenfunctions of this single-particle Hamiltonian.

From that proof, the energy of single-particle state  $\phi_k(\vec{r})$  is:

$$\epsilon_k = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2}{\pi} k_F F(k/k_F) \quad (3.19)$$

where  $F(x) = 1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right|$  rewritten in terms of  $r_s$  and  $\frac{\hbar^2}{2m_e a_0^2} = 1 \text{Ry}$ :

$$\epsilon_k = \left[ \left( \frac{(9\pi/4)^{1/3}}{r_s/a_0} \right)^2 \left( \frac{k}{k_F} \right)^2 - \frac{2}{\pi} \left( \frac{(9\pi/4)^{1/3}}{r_s/a_0} \right) F(k/k_F) \right] \text{Ry} \quad (3.20)$$

The term proportional to  $F(k/k_F)$  gives a lower energy than the non-interacting electrons for all values of  $\vec{k}$ . It follows that electron-electron interaction included at Hartree-Fock level lowers energy of the system, whose total energy is obtained by summing the single-particle energies over  $\vec{k}$  up to  $k_F$ :

$$E^{HF} = \underbrace{2}_{\text{spin}} \sum_{k < k_F} \frac{\hbar^2 k^2}{2m_e} - \underbrace{\frac{e^2 k_F}{m} \sum_{k < k_F} \left[ 1 + \frac{k_F^2 - k^2}{2k k_F} \ln \left| \frac{k_F + k}{k_F - k} \right| \right]}_{\text{electron-electron interaction due to exchange. Spin factor 2 cancelled by 1/2 for double counting effective interaction}} \quad (3.21)$$

$$\frac{E^{HF}}{N} = \frac{3}{5}\epsilon_F - \underbrace{\frac{3e^2k_F}{4\pi}}_{E^X/N} \quad (3.22)$$

In the following we calculate how much the effective electron-electron interaction lowers the energy with regard to kinetic energy.

Using  $\frac{4\pi}{3}r_s^3 = \frac{\Omega}{N} = n^{-1} = \frac{3\pi^2}{k_F^3}$  and the definition of Ry:  $\frac{\hbar^2}{2m_e a_0^2} = \frac{e^2}{2a_0} = 1 \text{ Ry}$ .

$$\frac{E^{HF}}{N} = \left[ \frac{2.21}{(r_s/a_0)^2} - \underbrace{\frac{0.916}{(r_s/a_0)}}_{E^X/N} \right] \text{Ry}$$

Hartree-Fock approximation captures first two terms in exact expansion of energy by Gell-Mann and Brueckner;  $2 < \frac{r_s}{a_0} < 6$  for metals.

Express exchange potential in terms of density:

$$\frac{E^X}{N} = -\frac{0.916}{(r_s/a_0)} \text{Ry}$$

using expressions for  $r_s$  :

$$\frac{E^X}{N} = \frac{3e^2}{4} \left( \frac{3}{\pi} \right)^{1/3} n^{1/3} = -1.477 [a_0^3 n]^{1/3} \text{Ry}$$

For a non-homogeneous distribution of electrons (generalized by Slater), the exchange energy would arise from potential energy in the single-particle Hamiltonian:

$$V^X(\vec{r}) = -\frac{3e^2}{2} \left( \frac{3}{\pi} \right)^{1/3} n^{1/3} = -\frac{3e^2}{2\pi} k_F(\vec{r})$$

where extra factor of 2 is introduced to account for the fact that a variational derivation gives rise to a potential term in the single-particle equations which is twice as large as the corresponding energy term: when one calculates the total energy by summing terms in the single-particle equations, 1/2 is introduced to account for double counting the interactions.

In this equation,  $n, k_F$  are functions of  $\vec{r}$ , i.e. they can be non-homogeneous  $\rightarrow$  use such term to describe exchange contribution in single-particle equation. Since total number of electrons:  $N = \int n \, d\vec{r}$ :

$$E^X[n] = -\frac{3e^2}{4\pi} \int k_F n d\vec{r} = -\frac{3}{4} e^2 \left( \frac{3}{\pi} \right)^{1/3} \int [n]^{1/3} d\vec{r} \quad (3.23)$$

Generalization for when density is not uniform, assuming that same expression holds:

$$E^X[n(\vec{r})] = \int \epsilon^X[n(\vec{r})] n(\vec{r}) d\vec{r} \quad (3.24)$$

$$\boxed{\epsilon^X[n(\vec{r})] = -\frac{3}{4} e^2 \left( \frac{3}{\pi} \right)^{1/3} [n(\vec{r})]^{1/3}} \quad (3.25)$$

This allows to calculate an expression for  $\frac{\delta E^{XC}[n]}{\delta n}$  in the case where we are considering only the exchange aspect of the many-body character:

$$\frac{\delta E^{XC}[n]}{\delta n} = \frac{\partial}{\partial n(\vec{r})} [\epsilon^X[n(\vec{r})] n(\vec{r})] = \frac{4}{3} \epsilon^X[n(\vec{r})] = -e^2 \left( \frac{3}{\pi} \right)^{1/3} [n(\vec{r})]^{1/3} \quad (3.26)$$

Eq. (3.26) shows similarity to Slater's exchange potential

$$V^X(\vec{r}) = -\frac{3e^2}{2} \left(\frac{3}{\pi}\right)^{1/3} [n(\vec{r})]^{1/3} \quad (3.27)$$

Analysis shows that if electrons interacted only through Pauli exclusion principle (only exchange interaction), one could adopt the above exchange potential for the single-particle equations and one would receive an exact solution in terms of  $\phi_i(\vec{r})$ .

General remarks:

- The correlation energy is more complicated to calculate than the exchange energy, because correlation affects both kinetic and potential energies; both effects can be taken into account by a "coupling constant integration".
- The energy state of many electrons in the Hartree-Fock approximation is the best possible wave function made from a single determinant (or a sum of a few determinants in multi-reference Hartree-Fock needed for degenerate states). One improvement of the wave function can be to include correlation. This introduces extra degrees of freedom in the wave function and thus lowers the energy for any state, ground or excited. The amount by which the energy is lowered is the "correlation energy".
- $E^{HF}$  is the lowest possible energy neglecting correlation.
- correlation is more important for electrons of opposite spin; electrons of the same spin are automatically kept apart by the Pauli exclusion principle
- for the ground state: correlation energy is always negative; any approximation should be negative
- Excited states involve differences from ground state (exciton energies); depending upon effects of correlation in both states, the difference is positive or negative.

## 3.1 Exchange and Correlation Functionals

### 3.1.1 Local (Spin) Density Approximation

Kohn-Sham: solids are often close to a homogeneous electron gas.

In the limit, effects of exchange and correlation are local.

→ Local density approximation: exchange-correlation energy is an integral over the whole space with the exchange-correlation energy at each point assumed to be the same as in a homogeneous gas of that density.

Generalization: Local Spin Density Approximation (LSDA) formulated with regard to two spin densities (axis of spin quantization assumed to be the same at all points in space).

$$\begin{aligned} E_{LSDA}^{xc}[n^\uparrow, n^\downarrow] &= \int n(\vec{r}) \epsilon_{hom}^{xc}(n^\uparrow(\vec{r}), n^\downarrow(\vec{r})) dr \\ &= \int n(\vec{r}) [\epsilon_{hom}^x(n^\uparrow(\vec{r}), n^\downarrow(\vec{r})) + \epsilon_{hom}^c(n^\uparrow(\vec{r}), n^\downarrow(\vec{r}))] dr \end{aligned} \quad (3.28)$$

fractional spin polarization:

$$\mathcal{S}(\vec{r}) = \frac{n^\uparrow(\vec{r}) - n^\downarrow(\vec{r})}{n(\vec{r})} \quad (3.29)$$

(for unpolarized systems:  $n^\uparrow(\vec{r}) = n^\downarrow(\vec{r}) = \frac{n(\vec{r})}{2}$ ).



L(S)DA expected to work better for solids close to a homogeneous gas (like a nearly-free-electron metal) and worst for very inhomogeneous cases like atoms where the density must go continuously to zero outside the atom.

Spurious self-interaction term:

The unphysical self-interaction term in Hartree-Fock interaction is cancelled by non-local exchange interaction.

But in local density approximation the exchange cancellation is approximate and the self-interaction terms remain. These are negligible in the homogeneous gas but large in confined systems.

### 3.1.2 Generalized-gradient approximation (GGA)

Improvement over LSDA:

The functional is of the magnitude of the gradient of the density  $|\nabla n|$ .

Sometimes this leads to worse results compared to LSDA because gradients in real materials are so large that low-order expansion of exchange and correlation breaks down.

Generalized form:

$$\begin{aligned} E_{GGA}^{XC}[n^\uparrow, n^\downarrow] &= \int n(\vec{r}) \epsilon^{XC}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|) d\vec{r} \\ &= \int n(\vec{r}) \epsilon_{hom}^X(n) F^{XC}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|) d\vec{r} \end{aligned} \quad (3.30)$$

$F^{XC}$  dimensionless

$\epsilon_{hom}^X(n)$  exchange energy of unpolarized gas

It can be shown, that for exchange

$$E^X[n^\uparrow, n^\downarrow] = \frac{1}{2}(E^X[2n^\uparrow] + E^X[2n^\downarrow]) \quad (3.31)$$

$E^X$  : exchange energy for unpolarized system

→ for exchange  $F^X(n, |\nabla n|)$  only spin-unpolarized electrons can be considered.

Most widely used forms of  $F^X(n, |\nabla n|)$ :

(a) Becker (B88)

(b) Perdew-Wang (PW91)

(c) Perdew-Burke-Enzerhof (PBE)

Most other functionals lead to  $F^X$  that fall within B88 and PBE; qualitative behavior of other functionals appreciated from the behavior of these two.

$F^X \leq 1$  → all generalized-gradient approximations lead to exchange energy lower than local density approximation.

→ more rapidly varying density regions in atoms; greater lowering of exchange energy in atoms than in molecules or solids resulting in reduction in binding energy correcting the local density approximation over binding and improving agreement with experiment.

Correlation is more difficult to cast in terms of functional, but the contribution to total energy is typically smaller than the exchange.

lowest order gradient expansion at high density (Ma & Brueckner):

$$\text{exchange enhancement factor} \quad F^C = \frac{\epsilon_{LDA}^C(n)}{\epsilon_{LDA}^X(n)} (1 - 0.219, 51s_1^2 + \dots) \quad (3.32)$$

$$s_1 = \frac{|\nabla n|}{2k_F n}.$$

for large density gradients the magnitude of correlation energy decreases and vanishes for  $s_1 \rightarrow \infty$ .

### 3.1.3 LDA and GGA expressions for the exchange potential

Local density approximation:

$$\delta E^{XC}[n] = \sum_{\sigma} \int \underbrace{\left[ \epsilon_{hom}^{XC} + n \frac{\partial \epsilon_{hom}^{XC}}{\partial n^{\sigma}} \right]}_{V_{\sigma}^{XC}(\vec{r})} \delta n(\vec{r}, \sigma) d\vec{r} \quad (3.33)$$

Generalized-gradient approximation:

$$\delta E^{XC}[n] = \sum_{\sigma} \int \underbrace{\left[ \epsilon^{XC} + n \frac{\partial \epsilon^{XC}}{\partial n^{\sigma}} + n \frac{\partial \epsilon^{XC}}{\partial \nabla n^{\sigma}} \nabla \right]}_{V_{\sigma}^{XC}(\vec{r})} \delta n(\vec{r}, \sigma) d\vec{r} \quad (3.34)$$

form commonly used; disadvantageous since it requires higher derivatives of density which could lead to numerical problems, e.g. near the nucleus or in the outer regions of atoms where the density is rapidly varying.

Other approach:

use form of operator in  $\delta E^{XC}[n]$  directly by modifying the Kohn-Sham equations:

$$\langle \psi_j | \tilde{V}^{XC} | \psi_i \rangle = \int [\tilde{V}^{XC} \psi_j^* \psi_i + \psi_j^* \vec{V}^{XC} \nabla \psi_i + (\vec{V}^{XC} \nabla \psi_j^*) \psi_i] \quad (3.35)$$

where  $\tilde{V}^{XC} = \epsilon^{EX} + n \left( \frac{\partial \epsilon^{XC}}{\partial n} \right)$  and  $\vec{V}^{XC} = n \left( \frac{\partial \epsilon^{XC}}{\partial \nabla n} \right)$ .

### 3.1.4 Other approximations

1. non-local density formulations:

- Average Density Approximation

$$E_{ADA}^{XC}[n^{\uparrow}, n^{\downarrow}] = \int n(\vec{r}) \epsilon_{hom}^{XC}(\bar{n}^{\uparrow}(\vec{r}), \bar{n}^{\downarrow}(\vec{r})) d^3r \quad (3.36)$$

where  $\bar{n}(\vec{r}) = \int w(n(\vec{r}); |\vec{r} - \vec{r}'|) n(\vec{r}') d^3r$  is the average density.

- Weighted Density Approximation

2. Orbital-dependent functionals  $E^{XC}[\{\psi_i\}]$

- Self-Interaction Corrections

correct for unphysical self-interaction in many functionals for  $E^{XC}$ .

- LDA+U:

Local density- or generalized gradient approximation coupled to additional orbital-dependent interaction (only for highly localized atomic-like orbitals on same site).

Shifts localized orbitals relative to others to correct for local density approximation/generalized-gradient approximation error.

- Optimized Effective Potential

$$E_{OEP}[V] = E[\{\psi_i[V]\}] \quad (3.37)$$

optimization of potential: given a small variation, the system energy remains stationary

- Exact-Exchange

Hartree-Fock exchange

The functional is straightforwardly written in terms of orbitals

$$E_{HF}^X = \frac{1}{2} \sum_{i,j} \int \int \psi_i^*(\vec{r}) \psi_j^*(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_i(\vec{r}) \psi_j(\vec{r}') d\vec{r} d\vec{r}' \quad (3.38)$$

- $X_\alpha$ : Slater local approximation

$V^X = 2\epsilon^X$  rather than  $\frac{4}{3}$  in Kohn Sham. Sometimes better than Kohn Sham

- Meta-generalized-gradient approximation

Curvature of density is introduced, second derivative of kinetic energy

- Hybrid functionals

approximations to exchange-correlation energy in density functional theory: include exact exchange from HF with ab initio (or empirical) exchange and correlation terms.

E.g. B3LYP, HSE, meta-hybrid GGA

In essence the coupling constant integration in XC is basis for constructing combination of orbital-dependent HF with explicit density functional

$$E^{xc}[n] = \int d\lambda \left\langle \psi_\lambda \left| \frac{dV_{int}}{d\lambda} \right| \psi_\lambda \right\rangle - E_H[n] \quad (3.39)$$

for  $\lambda = 0 \rightarrow$  Hartree-Fock exchange

$\lambda = 1$ :  $E^{xc} = \frac{1}{2}(E_{HF}^x + E_{DFA}^{xc})$  with DFA either local density approximation or generalized-gradient approximation functional.

E.g. B3LYP

$$\begin{aligned} E_{B3LYP}^{XC} &= E_{LDA}^{XC} + a_0(E_{HF}^X - E_{LDA}^{XC}) \\ &\quad + a_X(E_{GGA}^X - E_{LDA}^X) \\ &\quad + a_C(E_{GGA}^C - E_{LDA}^C) \end{aligned} \quad (3.40)$$

with  $a_0 = 0.20$ ,  $a_X = 0.72$ ,  $a_C = 0.81$ .

Perdew, Ernzerhof, Burke:

$$E^{XC} = E_{LDA}^{XC} + \frac{1}{4}(E_{HF}^X - E_{DFA}^{XC}) \quad (3.41)$$

- GW approximation: Green's functionals to estimate self-energy

Important: Test functionals for very simple systems, benchmarking.

## 3.2 Pseudo potentials

or effective potentials: approximation for the simplified description of a complex system.

$$\begin{aligned} \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff} \right] \psi_i &= \epsilon_i \psi_i \\ \downarrow \\ \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{eff}^{pseudo} \right] \psi_i^{pseudo} &= \epsilon_i^{pseudo} \psi_i^{pseudo} \end{aligned} \quad (3.42)$$

- replace strong Coulomb potential of the nucleus and the effect of tightly bound core electrons by an effective ionic potential acting on the valence electrons
- pseudo potential generated in a simulation and used to compute properties of other systems (core states remain almost unchanged)
  - (a) orthogonalized plane waves (OPW)
    - smooth part of valence function plus core-like functions
  - (b) Norm-conserving pseudo potentials
    - norm-conserving pseudo functions are normalized and are solutions of a model potential chosen to reproduce valence properties of an all-electron calculation
  - (c) l-dependent norm-conserving pseudo potential
    - each l,m state is treated independently; total potential calculated self-consistently for given approximation for exchange and correlation and given configuration
  - (d) ultra soft pseudo potentials
    - pseudo functions as smooth as possible: smooth and an auxiliary function around each ion core that represents rapidly varying part of density (hard pseudo potentials have higher transferability than soft)
  - (e) projector augmented waves (PAW)
    - transforms rapidly oscillating functions near core into smooth wave functions, also (like ultra soft pseudo potential) uses projectors and auxiliary localized functions.

Issues: Unscreening, core corrections, transferability, hardness

### 3.3 Elements of solid-state physics

#### 3.3.1 Periodic structures

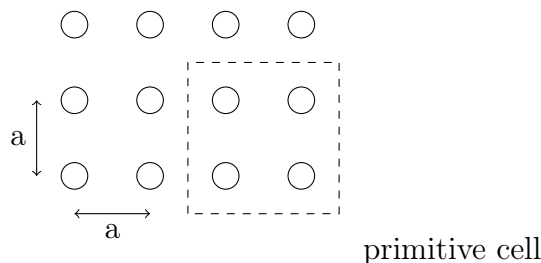


Figure 1: Periodic array of atoms

Crystal can be reconstructed using translation of unit cell: a "building block" periodically duplicated. The smallest building block is the primitive lattice constant: length which describes unit cell. From periodicity the Bloch theorem follows:

$$\begin{aligned}
 [\mathcal{H}, T_R] = 0 &\quad \rightarrow \quad \phi(\vec{r}) = u_{nk}(\vec{r}) \exp(i\vec{k}\vec{r}) \\
 \psi(\vec{r} + \vec{R}) &= \psi(\vec{r}) \exp(i\vec{k}\vec{r})
 \end{aligned}
 \tag{3.43}$$

$T_R$  translation operator

#### 3.3.2 Reciprocal lattice

For crystals/periodic structures, the orbitals are a function of the reciprocal lattice vector  $\vec{k}$ . The Brillouin zone is a uniquely defined primitive cell in reciprocal space.

1<sup>st</sup> Brillouin zone: volume included by taking surfaces at the same distance from one point of the

lattice and its neighbors and construct perpendicular bisectors.

Real space: with basis atom set and basis vectors, crystal can be constructed.

Basis vectors  $\vec{a}_1, \vec{a}_2, \vec{a}_3$  do not have to be orthogonal.

Reciprocal lattice given by vectors:

$$\vec{b}_k = 2\pi \frac{\vec{a}_l \times \vec{a}_m}{\underbrace{\vec{a}_k \cdot (\vec{a}_l \times \vec{a}_m)}_{\text{volume of real space unit cell}}}$$

Bloch wave function distributed throughout crystal

- electron position highly delocalized
- electron momentum should be well defined due to the uncertainty principle
- use k-space instead

### 3.3.3 Band structure

Ranges of energy/energy bands that an electron in the periodic structure may have.

energy bands = allowed bands

energy gaps = forbidden bands

This explains: electrical resistivity, optical absorption (large-scale limit of molecular orbital theory)

A solid creates a large number of closely spaced molecular orbitals, which appear as a band.

The wave vector  $\vec{k}$  takes values within the Brillouin zone corresponding to the crystal structure and conventional names like  $\Gamma, \Delta, \Lambda, \Sigma, M, K$  assign particular directions/points.

For example:

$\Gamma$ -point is the center of k-space ( $\vec{k} = 0$ )

X-point is the edge of the 1<sup>st</sup> Brillouin zone ( $\frac{\pi}{L}$  edge) in  $\langle 100 \rangle$  direction

L-point is the edge in  $\langle 111 \rangle$  direction.

- different potentials exist in different directions
- electron wavelength and crystal momentum  $k = \frac{2\pi}{\lambda}$  differs with direction
- plots of  $E - \vec{k}$  are 4D presented as slices along certain directions
- many different parabolic  $E - \vec{k}$  relations depending on  $\vec{k}$
- all equivalent  $\vec{k}$ -directions give redundant information and are not repeated

Example: Silicon forms a diamond crystal (two inter-penetrating face-centered cubic lattices) with lattice constant  $a = 5.43 \text{ \AA}$ . 2 basis atoms in the primitive cell:

$$(0, 0, 0) \quad \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$$

Unit vectors:

$$\begin{aligned} \vec{a}_1 &= \left(0, \frac{a}{2}, \frac{a}{2}\right) \\ \vec{a}_2 &= \left(\frac{a}{2}, 0, \frac{a}{2}\right) \\ \vec{a}_3 &= \left(\frac{a}{2}, \frac{a}{2}, 0\right) \end{aligned}$$

### 3.3.4 Electron density of states (eDOS)

eDOS: number of states per interval of energy at each energy level which are available to be occupied by electrons.

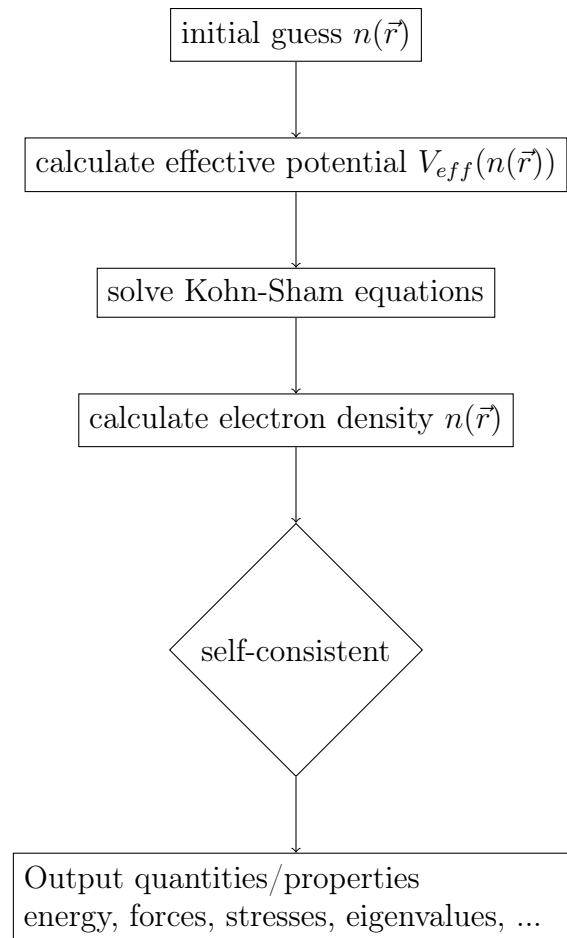
A high eDOS at specific energy means many available states.

In order to count  $N$  allowed states at certain  $\vec{k}$  within  $[\vec{k}, \vec{k} + d\vec{k}]$  many  $\vec{k}$ -points are needed.

A sufficiently dense mesh of integration points is crucial for the convergence of results.

### 3.3.5 k-point sampling

- Monkhorst-Pack  
 $\vec{k}$ -points distributed homogeneously in Brillouin zone
- equivalent  $\vec{k}$ -points  
Comparison of two structures with same unit cell done with same  $\vec{k}$ -vectors
- Chadi-Cohen mesh  
refinement of  $\vec{k}$ -point mesh to obtain higher sampling density based on recursive scheme
- reduced  $\vec{k}$ -points and symmetry  
additional point group symmetries to translational in order to reduce number of  $\vec{k}$ -points
- user-supplied  $\vec{k}$ -points  
specify directly with regard to coordinate axes in reciprocal space (e.g. for band structure calculations)



Deficiencies of local density approximation:

- Kohn-Sham eigenvalues have no physical meaning (Lagrange multipliers)

- exchange-correlation potential decays too fast ( $\exp(-\alpha r)$  instead of  $-\frac{1}{r}$ )
- local density approximation self-exchange and self-correlation do not cancel self-interaction effect  $\approx 1$  eV to 2 eV in solids  
leads to strong hybridization and relaxation since localized d and f states are under-bound
- local density approximation  
lattice constant 1-3% too small  
cohesive energies 5-20% too strongly bound  
bulk modulus 5-20% too strongly bound  
band gaps  $\sim 40\%$  too small
- generalized-gradient approximation (PW91, PBE)  
improves cohesive energies  
often (not always) better for lattice parameters  
important for magnetic systems
- hybrid functionals (B3LYP, HSE)  
improved band gaps

Note: Self-interaction (SI) term

contribution to the energy of a particle due to the interactions of the particle and the system it is part of.

In Hartree-Fock all SIs exactly cancelled by corresponding exchange SIs.

In approximate XC-functionals cancellation is incomplete  $\rightarrow$  SI error.

Post-Hartree-Fock methods usually include factors:

- (a) each energy eigenfunction is not described only by a single Slater determinant
- (b) correlation for electrons with opposite spin included
  - Moller-Plesset treats correlation as perturbation of Fock operator
  - multi-configurational or configurational interaction (CI) or quadratic CI or complete active space SCF
  - self-consistent field: expand true multi-electron wave function in terms of a linear combination of Slater determinants
  - variational Monte Carlo  
modify Hartree-Fock wave function by multiplying by a correlation function
  - alternative to Hartree-Fock  
density-functional theory
  - commonly used are also hybrid functionals  
approximations to exchange-correlation energy functional in density functional theory: include exact exchange from Hartree-Fock with ab initio or empirical exchange and correlation terms, e.g. B3LYP, HSE, meta-hybrid GGA, ...

## 4 Time-dependent systems

### 4.1 Time-dependent Density Functional Theory (TDDFT)

Density functional theory is a ground state method (the Kohn-Sham equations describe fictitious particles, thus lead to independent particle eigenvalues which do not correspond to true electron removal or addition energies, meaning that eigenvalue differences do not correspond to excitation energies.)

TDDFT extends DFT to the treatment of excitations or more general time-dependent phenomena.

How can the Kohn-Sham approach describe excitations? Use again an interacting density. In the full many-body problem, excitations are described in terms of response functions  
 → construct theory to describe the dynamical density response within the Kohn-Sham framework. The electrons feel the time-dependent Kohn-Sham effective potential. The TDDFT scheme is general, but two regimes should be observed:

- time dependent potential is weak, then resort to linear-response theory and calculate e.g. optical absorption spectra
- time dependent potential is strong, a full solution of the Kohn-Sham equations is necessary; example is the treatment of atoms or molecules in strong laser fields, TDDFT can describe non-linear phenomena, like multi-phonon ionization or high-harmonic generation

Note: in the following use Hartree atomic units  $e = \hbar = m = 1$ .

**Runge-Gross theorem** (time-dependent extension of Hohenberg-Kohn approach)

in static problems:  $E[\phi] = \langle \phi | H | \phi \rangle$ .

in time-dependent systems, no variational principle on basis of total energy, since it is not a conserved property, but quantum mechanical action analogous to energy:

$$A[\phi] = \int_{t_0}^{t_1} \left\langle \psi(t) \left| i \frac{\partial}{\partial t} - H(t) \right| \psi(t) \right\rangle dt \quad (4.1)$$

It can be shown that if the potentials  $V(\vec{r}, t)$  and  $V'(\vec{r}, t')$  differ by more than a time dependent function  $c(t)^2$ , they cannot produce the same time-dependent density.

The same holds for the current density operator:

$$\vec{j}(\vec{r}) = \langle \psi(t) | \vec{j}(\vec{r}) | \psi(t) \rangle \quad \text{and} \quad \frac{\partial}{\partial t} n(\vec{r}, t) = -\nabla \cdot \vec{j}(\vec{r}, t) \quad (4.2)$$

Runge-Gross theorem asserts that all observables can be calculated with the knowledge of the one-body density. The external local potential  $V_{KS}$  is chosen such that the density of the Kohn-Sham electrons is the same as the density of the original interacting system.

In time-dependent case, the particles obey the time-dependent Schrödinger equation:

$$i \frac{\partial}{\partial t} \psi_i(\vec{r}, t) = \left[ -\frac{\nabla^2}{2} + V_{KS}(\vec{r}, t) \right] \psi_i(\vec{r}, t) \quad (4.3)$$

and the density  $n(\vec{r}, t) = \sum_i^{\text{occ.}} |\psi_i(\vec{r}, t)|^2$ .

$$V_{KS}(\vec{r}, t) = V_{ext}(\vec{r}, t) + V_{Hartree}(\vec{r}, t) + V_{XC}(\vec{r}, t) \quad \text{with} \quad V_{Hartree}(\vec{r}, t) = \int \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d\vec{r}'$$



In density functional theory,  $V_{XC}$  usually written as a functional derivative of the XC energy, which is calculated from a variational derivation; not straightforward for TDDFT.

van Leeuwen: define a new action functional  $A$  by using Keldish formalism:

$$V_{XC}(\vec{r}, t) = \left. \frac{\delta A_{XC}}{\delta n(\vec{r}, \tau)} \right|_{n(\vec{r}, t)} \quad (4.4)$$

with  $\tau$  the Keldish pseudo-time.

In the exact theory  $V_{XC}[n](\vec{r}, t)$  is a functional of  $n(\vec{r}', t')$  for all earlier times  $t' \leq t$ , but it is difficult to construct functional that include effects of non-locality in time. Using approximations for the functionals is the only fundamental approximation in TDDFT.

Contrary to DFT, development of XC functionals for TDDFT is still at an early stage.

#### 4.1.1 XC functionals in TDDFT

(a) Adiabatic local density approximation (ALDA)

$$V_{ALDA}^{XC}(\vec{r}, t) = V_{hom}^{XC}(n(\vec{r}))|_{n=n(\vec{r}, t)} \quad (4.5)$$

same functional as in local density approximation, but employed at each time with density  $n(\vec{r}, t)$ ;  $V^{XC}$  depends on density only at the same time.

Problems for:

- System near resonance, where functional should include the particular states involved in transition (extension of problem for including orbital dependent effects in density functional theory)
- Extended system where evolution is a functional of current density (extension of problem of polarization in density functional theory)

(b) Time-dependent optimized effective potential  
alternative to orbital-dependent XC functionals

EEX still local, though obtained through solution of extremely non-local and non-linear integral equation:

$$A_{EEX}^X = -\frac{1}{2} \sum_{j,k}^{occ} \int_{t_0}^{t_1} dt \int d^3r \int d^3r' \frac{\psi_j^*(\vec{r}', t) \psi_k(\vec{r}', t) \psi_j(\vec{r}, t) \psi_k^*(\vec{r}, t)}{|\vec{r} - \vec{r}'|}$$

Using the optimized effective potential (OEP) then final form of OEP that determines the EEX potential is:

$$O = \sum_j^{occ} \int_{-\infty}^{t_1} dt' \int d^3r' [V^X(\vec{r}', t') - U_{x_j}(\vec{r}', t')] * \psi_j(\vec{r}, t) \psi_j^*(\vec{r}', t') G_R(\vec{r}t, \vec{r}'t') + cc \quad (4.6)$$

with kernel:

$$iG_R(\vec{r}t, \vec{r}'t') = \sum_{k=1}^{\infty} \psi_k^*(\vec{r}, t) \psi_k(\vec{r}', t') \delta(t - t') \quad (4.7)$$

Eq. (4.7) can be identified with the retarded Green's function of the system. Also:

$$U_{x_j}(\vec{r}, t) = \frac{1}{\psi_j^*(\vec{r}, t)} \frac{\delta A^{XC}[\psi_j]}{\delta \psi_j}$$

Krieger, Li, Iofrate (KLI): simplify above derivation a semi-analytic solution for Eq. (4.6). Both EEX and KLI have correct  $\sim \frac{1}{r}$  asymptotic behavior for neutral finite systems.

- (c) Functional with memory  
 "non-local" in time (includes memory from previous times)

$$\Gamma^{XC}(\vec{r}, t) = \frac{1}{n(\vec{r}, t)} \nabla \int dt' \Pi^{XC}(n(\vec{R}, t'), t - t') \quad (4.8)$$

where  $\Pi^{XC}$  a pressure-like scalar memory function of two variables, determined by requiring it to reproduce the scalar linear response of homogeneous electron gas.

- Linear response  
 external time-dependent potential is small; not necessary to solve full time-dependent Kohn-Sham equations  
 → linear change of density  
 calculation of optical absorption spectrum
- Excitation energies  
 differences between ground-state Kohn-Sham eigenvalues (approximate)  
 taking expectation values of Hamiltonian for different states  
 ensemble density functional theory  
 ⋮  
 TDDFT
- Photo absorption spectra with TDDFT  
 propagating time-dependent Kohn-Sham equations  
 or  
 linear response theory

## 4.2 Approximate solutions of the Schrödinger equation and computational scaling

Post-Hartree-Fock methods

- Semi-empirical (MNDO, AM1, PM3, ...)  
 use single Slater determinant; vary coefficients D  
 use empirical estimates not true integrals  
very cheap; accurate only for molecules similar to those used to develop empirical parameters
- Density functional theory (B3LYP, BLYP, PW91, PBE, ...)  
 slightly empirical  
 similar error to Hartree-Fock  $\mathcal{O}(N^3)$ ,  $\sim 4$  kcal/mol (comparable to MP2 but cheaper)  
 preferred for geometry, 2<sup>nd</sup> derivatives, transition metal containing systems
- Hartree-Fock (HF, SCF)  
 only one many-electron Slater determinant; vary D's  
 all calculations "ab initio" within mean field approximations,  $\mathcal{O}(N^3 - N^4)$ , error 15 kcal/mol
- MP2, MP4 (Moller-Plesset, MBPT)  
 vary D's, set C's to values from perturbation theory  
 MP2  $\mathcal{O}(N^5)$ , error  $\sim 5$  kcal/mol  
 MP4  $\mathcal{O}(N^6)$
- Configurational interaction (CI, CISD, QCISD)  
 vary D's, freeze and vary C's (not all)  
 expensive: CISD -  $\mathcal{O}(N^6)$ , QCISD  $\mathcal{O}(N^{10})$   
 depends on number of orbitals and excitation levels

- MCSCF, CASSCF  
vary finite set of C's and all D's simultaneously  
expensive:  $\mathcal{O}(N^5)$ ; good for systems with states of comparable energies; expertise is needed to select which C's to vary
- CAS-PT2  
determine D's and some C's by CASSCF, then determine more C's by perturbation theory  
as expensive as CASSCF; not very reliable
- Multi-reference configurational interaction (MRCI)  
determine D's and some C's by CASSCF or MCSLF, freeze them and allow many C's to vary  
very expensive; very high accuracy for small systems
- Coupled cluster (CCSD, CCSD(T))  
vary D's, fix them, vary a lot of C's but constrain relations between C's (longer expansion without increasing number of adjustable parameters much)  
constraints force solution to be size-consistent (2 molecules calculated simultaneously have same energy as 2 molecules calculated separately)  
expensive:  $\mathcal{O}(N^7)$ ; often very accurate
- Extrapolations (composite methods) (G2, G3, GBS-q, ...)  
run series of above calculations with different size basis sets, following certain recipes  $\rightarrow$  estimate true  $V(R)$   
error 1-2 kcal/mol, excellent accuracy, faster than CCSD or MRCI

General form of electronic wave function:

$$\Psi_{el}(\vec{r}_1, s_1, \dots, \vec{r}_N, s_N) = \sum_{m_1, \dots, m_N} C_{m_1, \dots, m_N} |\psi_{m_1}(\vec{r}_1, s_1) \dots \psi_{m_N}(\vec{r}_N, s_N)|$$

with

$$\psi_m(\vec{r}, s) = \sum_m D_{mn} X_n(\vec{r}) \otimes s$$

#### 4.2.1 Configuration Interaction (CI)

A post-Hartree-Fock method which is the matrix reformulation of the Schrödinger equation. A non-relativistic multi-electron system within the Born-Oppenheimer approximation is treated (relativistic effects like spin-orbit coupling can also be described).

Configuration : linear combination of Slater determinants for the wave function

Interaction: mixing of different electronic states

Scope : improve the Hartree-Fock theory by increasing the space of all possible many-electron wave functions from a single Slater determinant to a set of many Slater determinants.

Computation is very heavy and needs very long CPU time. Thus, the method is only suitable for very small systems.

N-electron basis functions  $|\psi_i\rangle$  as "excitations" from Hartree-Fock "reference" determinant:

$$\underbrace{|\Psi\rangle}_{\text{electronic ground state}} = c_0 |\psi_0\rangle + \sum_{ra} c_a^r |\psi_a^r\rangle + \sum_{a<b, r<s} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \dots$$

$|\psi_a^r\rangle$  Slater determinant formed by replacing spin-orbital a in  $|\psi_0\rangle$  with spin orbital r; implies usually a single determinant.

Every N-electron Slater determinant can be described by set of  $N$  spin orbitals from which it is formed; this set of orbital occupancies is a configuration.

- Configuration interaction is the matrix mechanics solution of time independent non-relativistic Schrödinger equation  $H\Psi = E\Psi$ .
- Generality of configuration interaction: applies to excited states, open-shell systems, systems with geometries far from equilibrium.
- A complete set of one-particle basis functions is not always necessary (it is also never complete in praxis)
- Reduce size of N-electron basis set:  
if wave functions of given spin and/or spatial symmetry is required, then include only N-electron basis functions of that symmetry, since the Hamiltonian matrix is block diagonal according to spin and space symmetries

Full configuration interaction: calculation using a set of one-particle functions  $\{ \xi_i \}$  and all possible N-electron basis functions  $\{ | \psi_i \rangle \}$  (possibly symmetry restricted).

$|\psi_i\rangle$ : i-th N-electron basis function; usually a single Slater determinant

$\xi_i$ : i-th one-particle basis function (orbital) to expand the Hartree-Fock orbitals,  $\psi_i$ ; denotes an atom spin-orbital

→ Truncating (reducing) configuration interaction space is important to reduce computational cost. Most common approximation: truncation of configuration interaction space expansion according to excitation level relative to the reference state.

Examples:

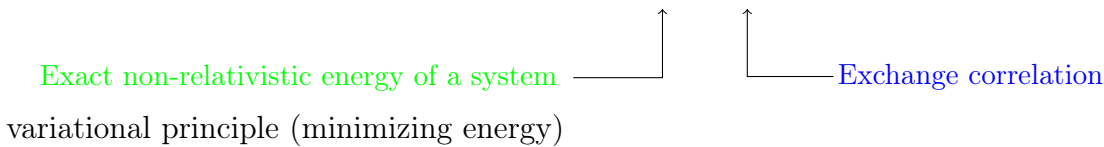
CID - is limited to double excitations only, i.e. includes those N-electron basis functions which represent double excitations

CISD - similarly for single or double excitations.

Hamiltonian operator includes only one- and two-electron terms; only single and double excited configurations can interact directly with reference:  $\sim 95\%$  of the correlation energy in small molecules at their equilibrium geometries

Approximate configuration interaction methods evaluated with regard to the fraction of correlation energy these "recover":

$$E_{corr} = \epsilon_0 - E_{HF} < 0 \tag{4.9}$$



variational principle (minimizing energy)

$$E = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

with

$$|\Psi\rangle = c_0 |\psi_0\rangle + \sum_{ra} c_a^r |\psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs} |\psi_{ab}^{rs}\rangle + \dots$$

Choose basis  $\{|\psi_i\rangle\}$  and solve secular equations  $HC = EC$ .

Outcome: ground state energy and coefficients  $\{c_{0i}\}$

→ Structure of configuration interaction matrix, where  $|S\rangle, |D\rangle, |T\rangle, |Q\rangle$  are blocks of single, double,

triple and quadruple excited determinants.  $H$  is hermitian and if only real orbitals are used, which is usually the case, the Hamiltonian is also symmetric and only the lower triangle is given:

$$H = \begin{matrix} \langle \psi_0 | \\ \langle S | \\ \langle D | \\ \langle T | \\ \langle Q | \end{matrix} \begin{pmatrix} \langle \psi_0 | H | \psi_0 \rangle & & & & \\ & 0 & \langle S | H | S \rangle & & \\ \langle D | H | \psi_0 \rangle & \langle D | H | S \rangle & \langle D | H | D \rangle & & \\ & 0 & \langle T | H | S \rangle & \langle T | H | D \rangle & \langle T | H | T \rangle \\ & 0 & & 0 & \langle Q | H | D \rangle & \langle Q | H | T \rangle & \langle Q | H | Q \rangle \end{pmatrix} \quad (4.10)$$

$\langle S | H | \psi_0 \rangle = 0$  : Brillouin's theorem is valid when reference  $|\psi_0\rangle$  is obtained by Hartree-Fock method. The Hartree-Fock method guarantees that off-diagonal elements of the Fock matrix are zero; matrix element between two Slater determinants differ by one spin orbital.

Off-diagonal blocks  $\langle X | H | Y \rangle$  which are not zero can still be sparse, e.g.  $\langle \psi_{ab}^{rs} | H | \psi_{cdef}^{twvw} \rangle$  which belong to block  $\langle D | H | Q \rangle$  are nonzero only if  $a$  and  $b$  are contained in the set  $\{c, d, e, f\}$  and if  $r$  and  $s$  are contained in the set  $\{t, u, v, w\}$ .

Only doubles interact with Hartree-Fock reference  $\rightarrow$  double excitations expected to make largest contribution to configuration interaction wave functions after the reference state. Although singles, triples, etc. do not interact directly with reference, these can still be part of the configuration interaction wave function (have non-zero coefficients), because these mix with doubles directly or indirectly. Singles are much less important to energy than doubles, but are generally included in configuration interaction, because of their relatively small number and greater importance in describing one-electron properties (dipole moment, etc.).

Quadruple excitations are more important than triples in the energy.

Stretched geometries: CISD, CISDT become poorer

CISDTQ recovers high fraction of correlation energy  $\rightarrow$  could give reliable results for energy differences across potential energy for small molecules

Benchmarks: DZP basis adequate, sometimes also DZ

### 4.2.2 Moller-Plesset perturbation theory

Perturbation methods: problem differs slightly from a problem which has been solved (Rayleigh-Schrödinger perturbation theory). Define:

$$H = H_0 + \lambda H'$$

with perturbation operator  $H'$  assumed small compared to reference  $H_0$ .

$$H_0 \psi_i = E_i^0 \psi_i \quad i = 0, 1, 2, \dots$$

$H_0$  hermitian: solutions form a complete orthonormal set.

$\lambda$  variable determining strength of perturbation; can be varied systematically from  $\lambda = 0$  (unperturbed case) to  $\lambda = 1$  (fully perturbed).

Assume  $i = 0$  (lowest-energy for simplicity).

The perturbed Schrödinger equation is given by:

$$H \Psi(\lambda) = E(\lambda) \Psi(\lambda)$$

$\lambda: H = H_0, \Psi(0) = \psi, E(0) = E^0$

As  $\lambda$  increases, new energy and wave function must change continuously; written as Taylor expansion with regard to  $\lambda$ :

$$\begin{aligned} E(\lambda) &= \lambda^0 E^0 + \lambda^1 E^1 + \lambda^2 E^2 + \dots = \lim_{n \rightarrow \infty} \sum_{i=0}^n \lambda^i E^i \\ \Psi(\lambda) &= \lambda^0 \Psi^0 + \lambda^1 \Psi^1 + \lambda^2 \Psi^2 + \dots = \lim_{n \rightarrow \infty} \sum_{i=0}^n \lambda^i \Psi^i \end{aligned} \quad (4.11)$$

Choose all correction terms orthogonal to reference  $\langle \phi | \phi \rangle = 1$  and overlap between perturbed and unperturbed wave function to be  $\langle \psi^{i \neq 0} | \phi \rangle = 0$ .

Apply perturbation theory to the calculation of correlation energy:

The most common choice is to take sum of single particle Fock operators as the unperturbed Hamiltonian, and the difference between the full Hamiltonian and Hartree-Fock Hamiltonian as perturbation.

Fock matrix is a matrix approximating the single-electron energy operator of a given quantum system in a given set of basis vectors; approximation to true Hamiltonian operator; electron-electron repulsion included in average way; a one-electron operator which does not include electron correlation energy. Fock operator for restricted cases assuming closed-shell orbitals and single-determinant wave function for  $i$ -th electron:

$$\hat{F}(i) = \hat{h}(i) + \sum_{j=1}^N (\hat{J}_i - \hat{K}_i) \quad (4.12)$$

with  $\hat{h}$  the one-electron Hamiltonian,  $\hat{J}$  the Coulomb operator and  $\hat{K}$  the exchange operator.  $N$  is the total number of occupied orbitals.

$$\hat{F}_i \phi_i(r_i) = \epsilon_i \phi_i(r_i)$$

The sum of Fock operators counts the average electron-electron repulsion twice and the perturbation becomes the exact  $r_{ij}^{-1} = V_{ij}$  operator minus twice the  $V_{ij}^{HF}$  operator:

$$\hat{V}_{ij}^{HF} = \hat{J}_{ij} - \hat{K}_{ij}$$

The operator associated with this difference is the fluctuation potential.

$$\begin{aligned} \hat{J}_i |\phi_i(\vec{r}_i)\rangle &= \langle \phi_j(\vec{r}) | \hat{V}_{ij} | \phi_j(\vec{r}) \rangle |\phi_i(\vec{r}_i)\rangle \\ \hat{K}_j |\phi_i(\vec{r}_i)\rangle &= \langle \phi_j(\vec{r}) | \hat{V}_{ij} | \phi_i(\vec{r}) \rangle |\phi_j(\vec{r}_i)\rangle \\ H_0 &= \sum_{i=1}^N F_i = \sum_{i=1}^N \hat{h}_i + \sum_{i=1}^N \sum_{j=1}^N (\hat{J}_{ij} - \hat{K}_{ik}) \\ &= \sum_{i=1}^N \hat{h}_i + \sum_{i,j} \hat{V}_{ij}^{HF} \end{aligned} \quad (4.13)$$

Perturbation Hamiltonian:

$$\hat{H}' = \hat{H} - \hat{H}_0 = \sum_{i < j} \hat{V}_{ij} - \sum_{i,j} \hat{V}_{ij}^{HF} \quad (4.14)$$

where for a given Slater determinant many-electron wave function  $\phi_0$  expressed in the Hartree-Fock orbital basis  $\{\phi_i\}$ :

$$\left\langle \phi_0 \left| \sum_{i < j} \hat{V}_{ij} \right| \phi_0 \right\rangle = \frac{1}{2} \left\langle \phi_0 \left| \sum_{i,j} V_{ij}^{HF} \right| \phi_0 \right\rangle = \langle V_{ee} \rangle \quad (4.15)$$

The zero-order wave function is the Hartree-Fock determinant, and the zero-order energy is the sum of molecular orbital energies:

$$E^0 = \sum_{i=1}^N \langle \phi_i | \hat{F}_i | \phi_i \rangle = \sum_{i=1}^N \epsilon_i^{HF}$$

First-order energy correction: (average of perturbation operator over the zero-order wave function)

$$\begin{aligned} E^1 &= \langle \phi_0 | \hat{H} | \phi_0 \rangle = \left\langle \phi_0 \left| \sum_{i < j}^N \hat{V}_{ij} \right| \phi_0 \right\rangle - \left\langle \phi_0 \left| \sum_{i,j}^N \hat{V}_{ij}^{HF} \right| \phi_0 \right\rangle \\ &= \langle V_{ee} \rangle - 2 \langle V_{ee} \rangle = - \langle V_{ee} \rangle \end{aligned}$$

→ A correction for double counting of the electron-electron repulsion at zero order (first-order energy, sum of  $E^0$  and  $E^1$  is exactly the Hartree-Fock energy)

→ Notation E(MPn) indicates correction at order  $n$ , and MPn indicates total energy up to order  $n$ :

$$\begin{aligned} \text{MP0:} & & E(\text{MP0}) &= \sum_a^N \epsilon_a^{HF} \\ \text{MP1:} & & E(\text{MP0}) + E(\text{MP1}) &= E(\text{HF}) \end{aligned}$$

→ Electron correlation starts at order 2 with this choice of  $H_0$ : involves sum over double excited Slater determinants (single excited determinants give no contribution to energy) which can be generated by promoting two electrons from occupied orbitals  $a, b$  to virtual orbitals  $r, s$ ; summation restricted, so that each excited state is counted once:

$$E^2 = \sum_{a < b}^{\text{occ}} \sum_{r < s}^{\text{vir}} \frac{\langle \phi_0 | \hat{H}' | \phi_{ab}^{rs} \rangle \langle \phi_{ab}^{rs} | \hat{H}' | \phi_0 \rangle}{E_0 - E_{ab}^{rs}}$$

matrix elements between Hartree-Fock and double excited states by two electron integrals over molecular orbitals; difference in total energy between two Slater determinants becomes a difference in molecular orbital energies

→ 2<sup>nd</sup> order Moller-Plesset correction:

$$E(\text{MP2}) = \sum_{a < b}^{\text{occ}} \sum_{r < s}^{\text{vir}} \frac{[\langle \phi_a \phi_b | \hat{V} | \phi_r \phi_s \rangle - \langle \phi_a \phi_b | \hat{V} | \phi_r \phi_s \rangle]^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

Once the two-electron integrals are available, the 2<sup>nd</sup> order energy correction can be calculated as the sum of such integrals; of the order of  $M^4$  integrals → calculation of energy increases as  $M^4$  with system size.

transformation of integrals from the atomic orbitals to molecular orbital basis grows as  $M^5$ : fairly inexpensive as not all two-electron integrals are required, only those corresponding to combination of two occupied and two virtual molecular orbitals.

100-150 basis functions can be calculated at a cost similar to calculating HF energy.

MP2 ~ 80-90 % of correlation energy (most "cheap" method for including electron correlation)

MP2, MP3, MP4 used; MP5 possible but too "expensive"

ideal case: HF, MP2, MP3, MP4 monotonic convergence towards limiting value with corrections of same sign and numerically smaller as order of perturbation increases, but can be observed that HF, MP2 results differ, MP3 results move back to HF and MP4 moves away again.

Well behaved systems: correct answer between MP3 and MP4

MP2 overshoots correlation effect, but also is often than MP3 if a medium sized basis set is used

→ Main limitations:

assumption that zero-order wave function is reasonable approximation to real wave function, i.e. perturbation operator small; the poorer HF wave function, the larger the correction terms and more terms included for given level of accuracy.

Convergence properties depend on size of basis set; can be slow, rapid, oscillatory, non-existent ...

For open-shell molecules, MPn can be directly applied only to unrestricted Hartree-Fock reference functions, but energies might suffer from spin contamination → errors

### 4.2.3 Coupled Cluster (CC)

Include all corrections of a given type (S,D,T,...) to infinite order, unlike MPn which adds all type of corrections to the reference wave function only up to given order (2,3,4,...)

Coupled Cluster: non-variational, size-extensive, size-consistent (if so, also the reference wave functions)

$$|\psi\rangle = e^{\hat{T}} |\phi_0\rangle$$

$|\phi_0\rangle \equiv$  Slater determinant usually constructed from Hartree-Fock molecular orbitals

$\hat{T} \equiv$  cluster operator, is an excitation operator which, when acting on  $|\phi_0\rangle$ , produces a linear combination of excited Slater determinants.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$$

2<sup>nd</sup> quantization formalism:

$$\hat{T}_1 = \sum_a \sum_r t_a^r \hat{a}_a \hat{r}^\dagger$$

$$\hat{T}_2 = \sum_{a,b} \sum_{r,s} t_{ab}^{rs} \hat{a}_a \hat{a}_b \hat{r}^\dagger \hat{s}^\dagger$$

$a, b$  : occupied orbitals

$r, s$  : unoccupied orbitals

$\hat{T}_1, \hat{T}_2$  convert reference  $|\phi_0\rangle$  into a linear combination of single- and double-excited Slater determinants → solve for  $t_a^r, t_{ab}^{rs}$  necessary to find  $|\psi\rangle$  (approximate solution).

Expand:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots$$

$$= 1 + \hat{T}_1 + \hat{T}_2 + \frac{\hat{T}_1^2}{2!} + \hat{T}_1 \hat{T}_2 + \frac{\hat{T}_2^2}{2!} + \dots$$

In practice series are finite, because the number of orbitals is finite as well as the number of excitations.

Find  $t_{ij}^{ab\dots}$ : expansion terminated at 2<sup>nd</sup> or slightly higher level of excitation; even if system admits more than 4 excitations, the contribution of  $\hat{T}_5, \hat{T}_6$  to  $\hat{T}$  is small.

If highest excitation level is  $n$  (in  $\hat{T}$ ), Slater determinants excited more than  $n$  times may contribute to  $|\psi\rangle$ , because of non-linear nature of exponential form ( $n = 2$  contains  $\hat{T}_1, \hat{T}_2, \hat{T}_2^2$  corresponding to triple and quadruple excitations)

→ CC terminated at  $\hat{T}_n$  usually recovers more correlation energy than configuration interaction with maximum  $n$  excitation.



Coupled Cluster:  $\hat{H}e^{\hat{T}}|\phi_0\rangle = Ee^{\hat{T}}|\phi_0\rangle$

$$\begin{aligned}\langle\phi_0|He^{\hat{T}}|\phi_0\rangle &= E_{cc}\langle\phi_0|e^{\hat{T}}\phi_0\rangle \\ &= E_{cc}\langle\phi_0|(1 + \hat{T}_1 + \hat{T}_2 + \dots)\phi_0\rangle \\ E_{cc} &= \langle\phi_0|He^{\hat{T}}|\phi_0\rangle\end{aligned}$$

If excitations are limited to single and double excited Slater determinants:

$$E_{cc} = E_0 + \sum_a^{\text{occ}} \sum_r^{\text{vir}} t_a^r \langle\phi_0|H|\phi_a^r\rangle + \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} (t_{ab}^{rs} + t_a^r t_b^s - t_a^s t_b^r) \langle\phi_0|H|\phi_{ab}^{rs}\rangle$$

Brillouin theorem: 1<sup>st</sup> matrix elements zero and 2<sup>nd</sup> matrix elements:

$$E_{cc} = E_0 + \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} (t_{ab}^{rs} + t_a^r t_b^s - t_a^s t_b^r) (\langle\phi_a\phi_b|V|\phi_r\phi_s\rangle - \langle\phi_a\phi_b|V|\phi_s\phi_r\rangle)$$

Advantage: Closed set of equations for  $t_{ab}^{rs} \dots$  to be solved iteratively.

Disadvantage: Classification of coupled cluster methods based on highest number of excitations allowed in definition of  $\hat{T}$ , e.g. CCSDT (for single, double, triple excitations):  $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ .

CCSD(T): coupled cluster includes single, doubles fully but triples are calculated with perturbation theory; more accurate and expensive than CCSD.

## 5 Quantum mechanical forces and energy minimization

### 5.1 Calculation of forces in quantum-mechanical approaches

Born-Oppenheimer approximation: ignore coupling between electron motion and nuclei (good if motion of nuclei slow and temperature is low, electronic states at ground state)

Schrödinger equation for ionic motion:

$$[T_N^\dagger + \epsilon_n(\vec{R})]\phi_n^n(\vec{R}) = E\phi_n^n(\vec{R}) \quad (5.1)$$

$\phi_n^n(\vec{R})$  for nuclei at positions  $\vec{R}$  when electrons in state  $\psi_n^e(\vec{r})$ .

$\epsilon_n(\vec{R})$  total electronic energy including interaction among nuclei,  $\hat{V}_{NN}$  is an effective potential energy for nuclei

Nuclei are viewed as point charges, not quantized, and the above Schrödinger equation for nuclei dynamics (5.1) is replaced by:

$$\vec{F}_I = m_I \ddot{\vec{R}}_I = -\frac{\partial \epsilon_n(\vec{R})}{\partial \vec{R}_I} = -\nabla_{\vec{R}} \epsilon_n(\vec{R})$$

which is calculated from total electronic potential.

On density functional theory basis:

$$-\nabla_{\vec{R}} \epsilon_n(\vec{R}) = -\nabla_{\vec{R}} \underbrace{\sum_{J \neq I} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}}_{(1)} - \underbrace{\int n(\vec{r}) \nabla_{\vec{R}} v_I(|\vec{r} - \vec{R}_I|) d\vec{r}}_{(2)}$$

(1) Coulomb repulsion between nuclei

(2) Coulomb attraction exerted on nuclei by electron cloud

$v_I(\vec{r})$  pseudo potential or  $-\frac{Z_I}{r}$  in all-electron approach

$n(\vec{r})$  electronic density of ground state (principal quantum number  $n = 0$ ) or selected excited state ( $n \leq 1$ )

### 5.1.1 Hellmann-Feynman forces

$$\vec{F}_I = -\nabla_R \langle \psi_0 | H_{ee} | \psi_0 \rangle$$

is too expensive and inaccurate for dynamical simulations.

$$\nabla_R \psi_0 H_{ee} | \psi_0 \rangle = \langle \psi_0 | \nabla_R H_{el} | \psi_0 \rangle + \langle \nabla_R \psi_0 | H_{ee} | \psi_0 \rangle + \langle \psi_0 | H_{ee} | \nabla_R \psi_0 \rangle$$

Contributions  $\nabla_R \psi_0$  vanish if the wave function is real. The exact eigenfunctions of the Hamiltonian and nuclear forces become:

$$\vec{F}_I^{HF} = -\langle \psi_0 | \nabla_R H_{el} | \psi_0 \rangle \quad (5.2)$$

Eq. (5.2) is also valid for variational wave functions (e.g. Hartree-Fock or Kohn-Sham).

In general, for a continuous parameter  $\lambda$ :

$$\frac{dE}{d\lambda} = \int \psi^*(\lambda) \frac{dH_\lambda}{d\lambda} \psi(\lambda) d\vec{r}$$

Method: calculate intra-molecular forces and derive equilibrium properties

In practice:

The exact ground state is not known and the Hellman-Feynman are not the exact forces; variation of approximated ground state wave function should be taken into account. But the theorem is often used, as the inclusion of other contributions is more tedious.

### 5.1.2 Ehrenfest Molecular Dynamics

Calculate the Ehrenfest force by solving a coupled set of nuclear and electronic propagation equations:

$$\begin{aligned} M_I \ddot{\vec{R}}_I(t) &= -\nabla_R \langle \psi_0 | H_{el} | \psi_0 \rangle \\ i\hbar \frac{\partial \psi}{\partial t} &= \left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_r^2 + \epsilon(\{\vec{r}_i\}, \{\vec{R}_I\}) \right] \psi \end{aligned} \quad (5.3)$$

Eqs. (5.3) describe the real time-dependent evolution of electronic degrees of freedom; this includes non-adiabatic effects like transitions between different electronic states.

The propagation time step  $\sim 0.1$  as is much smaller ( $10 - 10^2$ ) than in the Born-Oppenheimer case.

### 5.1.3 Born-Oppenheimer Molecular Dynamics

In each MD step, solve static electronic structure given fixed nuclear positions at each time

→ solve time-independent Schrödinger equation with classically propagating nuclei

contrary to Ehrenfest MD, time-dependent electronic structure is a consequence of nuclear motion:

$$\begin{aligned} M_I \ddot{\vec{R}}_I(t) &= -\nabla_R \min_{\psi_0} \{ \langle \psi_0 | H_{el} | \psi_0 \rangle \} \\ E_0 \psi_0 &= H_{el} \psi_0 \end{aligned}$$

for electronic ground state.

Contrary to Ehrenfest Molecular Dynamics, minimum of  $\langle H_{el} \rangle$  is reached in each Molecular Dynamics step; in Ehrenfest Molecular Dynamics, a wave function that minimizes  $\langle H_{el} \rangle$  will stay in minimum as nuclei move.

## 5.2 Geometry optimization/ Energy functional minimization

Algorithms for geometry optimization of periodic or finite systems in electronic structure methods usually take the path of minimizing the energy until convergence (within given accuracy). Examples are: Steepest descent, Conjugate gradient, Newton-Raphson, Hessian, BFGS, L-BFGS,...

### 5.2.1 Steepest descent

To find local minimum of a function, take steps proportional to negative of gradient at given point. Taking steps proportional to the positive gradient will lead to the maximum.

Step length is taken from adaptive scheme or linear search.

- Robust method, but slow convergence towards the end
- Works for any number of dimensions
- Many iterations are necessary to get to local minimum with required accuracy if curvature in different directions is very different (in this case preconditioning should be used, which changes the geometry of space to shape function level sets)
- Line search: find locally optimal step size
- Other methods converge in fewer iterations, but at higher computational cost for each iteration

The aim is to locate the minimum of functional  $F(x)$ , which is assumed to have a minimum.  $x$  is a vector in multidimensional space.

In absence of information about  $F(x)$ : move from point  $x^1$  in the direction of steepest descent  $g^1 = -\left.\frac{\partial F}{\partial x}\right|_{x=x^1}$ .

An assumption is made that the direction of steepest descent at  $x^1$ , obtained from negative of gradient operator  $G$  acting on  $x^1$ , so that:  $g^1 = -Gx^1$ .

To reduce the value of  $F(x)$ , move from  $x^1$  in the direction of steepest descent  $g^1$  to the point  $\bar{x}^1 + b^1 \bar{g}^1$  where  $F(x)$  is at a minimum. Sample  $F(x)$  at some number of points along the line  $x^1 + b^1 g^1$  to find  $b$  at which  $F(\bar{x}^1 + b^1 \bar{g}^1)$  is at a minimum.

Alternatively, if  $G$  is accessible, the minimum of  $F(x)$  can be found by locating the point where the gradient of the function is orthogonal to the search direction, so that  $\bar{g}^1 \cdot G(\bar{x}^1 + b^1 \bar{g}^1) = 0$ .

The procedure only minimizes  $F(x)$  along a particular line in space. To find the global minimum a series of minimizations is needed. Vector  $\bar{x}^1 + b^1 \bar{g}^1$  is starting vector for next iteration; next point is  $x^2$ .

The steps are repeated to generate a series of  $\bar{x}^m$  such that  $F(x)$  decreases for each iteration.

$F(x^l) < F(x^k)$  for  $l > k$  : each iteration reduces the value of  $F(x)$  and moves trial  $x^m$  toward vector that minimizes  $F(x)$ .

- No guarantee that minimum will be reached in finite number of iterations
- Performs poorly when minimum of  $F(x)$  lies in a long narrow valley, as each steepest descent vector is orthogonal to the previous one. So, if initial vector does not lie at the right angles to the axis of the valley, successive vectors will point across rather than along the valley. This leads to a large number of iterations, but can be overcome by the conjugate-gradient technique

### 5.2.2 Conjugate-gradient method (CG)

A steepest descent method with history converges in at most  $n$  steps, where  $n$  is the size of the matrix of the system/ dimensionality of the vector space.

The conjugate-gradient method is used to minimize sum of eigenvalues.

One minimization step is made independent of another in order to not move errors along in the minimization.

#### Example

Assume  $F(x) = \frac{1}{2} \bar{x} G \bar{x}$ .

Minimization of  $F(x)$  along direction  $d^1$  from some starting point  $x^1$ ; minimum will occur at  $\bar{x}^2 = \bar{x}^1 + b^1 \bar{d}^1$ , where  $(\bar{x}^1 + b^1 \bar{d}^1) G \bar{d}^1 = 0$ .

This is obtained by differentiation of  $F(x)$  with regard to  $b^1$  at  $x^2$ . A further minimization along direction  $d^2$  will yield  $\bar{x}^3 = \bar{x}^2 + b^2 \bar{d}^2$ , where  $(\bar{x}^1 + b^1 \bar{d}^1 + b^2 \bar{d}^2) G \bar{d}^2 = 0$ . The best choice, though, of  $b^1$  and  $b^2$  for minimization is obtained from differentiation with regard to both  $b^1, b^2$  at  $\bar{x}^3$ :

$$(\bar{x}^1 + b^1 \bar{d}^1 + b^2 \bar{d}^2) G \bar{d}^1 = 0$$

and

$$(\bar{x}^1 + b^1 \bar{d}^1 + b^2 \bar{d}^2) G \bar{d}^2 = 0$$

In order for all the above to be consistent and the minimization along  $d^1, d^2$  independent:

$$\bar{d}^1 \cdot G \cdot \bar{d}^2 = \bar{d}^2 \cdot G \cdot \bar{d}^1 = 0$$

It follows that  $\bar{d}^1, \bar{d}^2$  conjugate to each other. This can be generalized to

$$\bar{d}^n G \bar{d}^m = 0 \quad , \quad n \neq m$$

- Initial direction negative of gradient at starting point
- Subsequent conjugate direction constructed from a linear combination of new gradient and previous direction that minimized  $F(x)$
- Search direction generated using information about function obtained from all sampling points along conjugate-gradient path
- Instabilities due to large super cell sizes, large plane-wave kinetic energy cutoffs, but
- Preconditioning can be used  
preconditioning means multiplying the steepest-descent vector by preconditioning matrix to produce preconditioned steepest-descent vector, which more accurately represents the error vector; the preconditioned vector is parallel to the error vector
- Relation between error in wave function and steepest-descent direction  
steepest-descent vector a multiple of error vector if all unoccupied eigenstates of Kohn-Sham Hamiltonian are degenerate, but Kohn-Sham Hamiltonian has broad spectrum of eigenvalues extending up to cutoff energy for plane-wave basis set  $\rightarrow$  poor convergence in conjugate gradient method.  
Each step tends to remove components of error vector corresponding to eigenstates in a particular energy range; rate of convergence improved if method conjugates for weighting factors which distinguish error vector and steepest-descent error by preconditioning.

Application to Kohn-Sham equations:

energy functional	$F(x)$
wave functions $\{\psi_i\}$	$\bar{x}$
Hamiltonian $H$	gradient operator $G$

Conjugate Gradient iteration to update all electronic wave functions simultaneously; large amount of data stored  $\rightarrow$  update one band at a time along Conjugate Gradient direction

$$J_i^m = -(H - \lambda_i^m) \psi_i^m \quad ; \quad \lambda_i^m = \langle \psi_i^m | H | \psi_i^m \rangle \quad ,$$

where  $i$  counts the band and  $m$  the iteration.

## 5.3 Molecular Dynamics and electronic structure

Through the Hellmann-Feynman theorem it is possible to perform Molecular Dynamics (MD) simulations using forces calculated from quantum electronic structure. But then a full electronic structure would be needed for each MD step.

Workaround:

### 5.3.1 Car-Parinello method (CPMD)

Within the Car-Parinello method not only nuclear positions, but also electronic states are calculated using Molecular Dynamics algorithms.

The electronic structure does not relax exactly to the ground state of the actual configuration of nuclei, but the calculated electronic structure will follow closely the exact one.

Recall (a) Hartree-Fock and (b) Density Functional Theory:

#### (a) Hartree Fock

Ground state:  $\psi_G(R) = \det[\psi_k(\vec{x}_i)]$  (Slater determinant).  $\psi_k$  denotes the one-electron spin orbital and  $\vec{x}_i$  the combined spin orbital coordinate of particle  $i$ .  $\langle \psi_k | \psi_l \rangle = \delta_{kl}$

For  $h$  the one-electron Hamiltonian and  $g$  the electron-electron Coulomb repulsion, the total energy is:

$$E_{HF} = \sum_k \langle \psi_k | h | \psi_k \rangle + \frac{1}{2} \sum_{kl} [\langle \psi_k \psi_l | g | \psi_k \psi_l \rangle - \langle \psi_k \psi_l | g | \psi_l \psi_k \rangle]$$

Minimization of  $E_{HF}$  with regard to  $\psi_k$  subject to orthonormality constraint requires Fock operator to be satisfied:

$$\mathcal{F}\psi_k = \sum_l \Lambda_{kl}\psi_l$$

with

$$\begin{aligned} \mathcal{F}\psi_k &= \left[ -\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\vec{r} - \vec{f}_n|} \right] \psi_k(\vec{r}) \\ &+ \sum_{l=1}^N \int d\vec{x}' |\psi_l(\vec{x}')|^2 \frac{1}{|\vec{r} - \vec{r}'|} \psi_k(\vec{x}) \\ &- \sum_{l=1}^N \int d\vec{x}' \psi_l^*(\vec{x}') \frac{1}{|\vec{r} - \vec{r}'|} \psi_k(\vec{x}') \psi_l(\vec{x}) \end{aligned}$$

which through unitary transformation of set  $\{\psi_k\}$  transforms to

$$\mathcal{F}\psi_k = \epsilon_k \psi_k$$

where  $\epsilon_k$  are the Fock levels, using

$$\mathcal{F}\psi_k = \frac{\delta E_{HF}}{\delta \psi_k} \rightarrow \frac{\delta E_{HF}}{\delta \psi_k(\vec{x})} = \epsilon_k \psi_k(\vec{x})$$

#### (b) Density Functional Theory

$$n(\vec{r}) = \sum_{k=1}^N |\psi_k(\vec{r})|^2$$

States are ordered according to increasing energy. The form of the kinetic energy functional of density is unknown and a direct expression of total energy as a function of density is also not known. An energy expression is obtained through solutions  $\psi_k$  of Kohn-Sham equations

$$-\frac{1}{2}\nabla^2 \psi_k(\vec{r}) + V_{eff}(\vec{r}) \psi_k(\vec{r}) = \epsilon_k \psi_k(\vec{r})$$

with

$$V_{eff}(\vec{r}) = V_{ion}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}[n](\vec{r})$$

where exchange-correlation potential  $V_{xc}$  is a derivative of  $E_{xc}$  with regard to  $n(\vec{r})$

$$E_{DFT} = - \sum_k \frac{1}{2} \langle \psi_k | \nabla^2 | \psi_k \rangle + \sum_k \langle \psi_k | V_{ion} | \psi_k \rangle + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[n](\vec{r})$$

and

$$\frac{\delta E_{DFT}}{\delta \psi_k(\vec{r})} = \epsilon_k \psi_k(\vec{r})$$

which is similar to the Hartree Fock case (a). The total energy - electronic energy ( $E_{DFT}$  or  $E_{HF}$ ) plus electrostatic energy of nuclei - can be written as a functional depending on  $\psi_k$  and on nuclear coordinates (all collected in a variable  $S$ ):

$$E_{tot} = E_{tot}(\{ \psi_k \}, S)$$

where  $\psi_k$  form an orthonormal set.

In both Hartree Fock and Density Functional Theory  $E_{tot}$  is minimized with regard to  $\psi_k$  according to the variational principle.

Use finite basis set  $\{ \xi_r \}$  to express  $\psi_k$ :

$$\psi_k(\vec{r}) = \sum_r c_{rk} \xi_k(\vec{r})$$

$$\rightarrow E_{tot} = E_{tot}(\{ c_{rk} \}, S).$$

### Carr-Parinello Molecular Dynamics

Use  $E_{tot}$  expression with orthonormality constraint as starting point for equilibrium (minimal energy) conformation by locating minimum of  $E_{tot}$  as function of  $\psi_k$  (or  $c_{rk}$ ) and nuclear coordinates  $S$ .

→ Electronic structure does not have to be calculated exactly for each confirmation of nuclei, as both electronic orbitals and nuclear positions are varied simultaneously to locate the minimum. For this, any minimization algorithm is suitable, e.g. Velocity Verlet or simulated annealing.

Time dependence of nuclear coordinates + fictitious time dependence to electronic wave functions result in a dynamical Lagrangian including  $\psi_k$  and  $S$  with their time derivatives as variables.

→ classical mechanics problem with energy acting as potential

- Add friction term to equations of motion of this classical system, then degrees of freedom will relax after some time with values corresponding to minimum of classical potential. This is the energy of a quantum system at equilibrium configuration of nuclei. It is possible to put the frictional force to zero for a simulation of a system at nonzero temperature.

### Lagrangian of the classical system

$$\mathcal{L}(\{ \psi_k \}, S) = \frac{\mu}{2} \sum_k \dot{\psi}_k^2 + \sum_n \frac{M_n}{2} \frac{\dot{\vec{R}}_n^2}{2} - E_{tot}(\psi_k, S) + \sum_{k,l} \Lambda_{kl} \langle \psi_k | \psi_l \rangle \quad (5.4)$$

$M_n$  actual mass of  $n^{\text{th}}$  nucleus at position  $\vec{R}_n$

$\mu$  small mass. Enough to enable electronic wave functions to adapt reasonably well to the changing nuclear configurations.

$\mu$  is much smaller than  $M_n$ . The choice of  $\mu$  is a trade-off between accuracy and efficiency. The last term of Eq. (5.4) ensures orthonormality of  $\psi_k$  from which  $\Lambda_{kl}$  must always be calculated.

If friction is included in equations of motion, the particular values of neither electronic nor nuclear masses matter. We always end up with zero kinetic energy, at the minimum of the total energy of the system (i.e. potential of Car-Parinello Lagrangian). Different choices of  $\mu$  lead to different rates of convergence toward energy minimum.

$\mu \rightarrow 0$  : Lagrangian coincides with the true Lagrangian of the system.

The Lagrangian can be used for finding the minimum of the total energy, but also to perform real Molecular Dynamics at finite temperature. When the nuclei move, the method might not have produced the minimal energy for the electrons before next nuclear displacement and the electronic structure will lag behind the nuclear motion. This effect will occur in reality. (The Born-Oppenheimer approximation neglects the fact that the electrons do not adapt to the changing nuclear configuration at any time.) , but this retardation effect implied by Car-Parinello Lagrangian does not seem to be related to real physical behavior.

### Euler-Lagrange equations within Car-Parinello Molecular Dynamics

$$\mu \ddot{\psi}_k = -\frac{\partial E_{tot}}{\partial \psi_k} + 2 \sum_l \Lambda_{kl} \psi_l(\vec{r})$$

and

$$M_n \ddot{\vec{f}}_n = -\frac{\partial E_{tot}}{\partial \vec{f}_n} + \underbrace{\sum_{k,l} \Lambda_{kl} \frac{\partial \langle \psi_k | \psi_l \rangle}{\partial \vec{f}_n}}_{\rightarrow 0 \text{ if basis functions do not depend on } S}$$

instead of assigning a kinetic energy whose details don't matter; only  $\mu$  should be small enough, it can be assigned to expansion coefficients:

$$\mu \ddot{C}_{rk} = -\frac{\partial E_{tot}}{\partial C_{rk}} + 2 \sum_l \Lambda_{kl} \sum_s S_{rs} C_{sl}$$

add frictional term to equations of motion and solution becomes stationary; left-hand side vanishes and equation becomes similar to Hartree-Fock/ Density Functional Theory equations, except that  $\epsilon_k$  is replaced by matrix elements  $\Lambda_{kl}$ .

- values of  $\Lambda_{kl}$  depend on time as these are calculated at each Molecular Dynamics step to guarantee orthonormality constraint
- starting nuclear configuration too far from equilibrium:  
likely to end up with local minimum and not global one (then use simulated annealing to hop over local barriers)

Car-Parinello method:

First principles Molecular Dynamics, usually employing plane wave basis sets, pseudo potentials, etc. approximation to Born-Oppenheimer method.

fictitious dynamics to keep electrons close to ground state  $\rightarrow$  no need for self-consistent iterative minimization at each step.

## 5.4 Monte Carlo methods (MC)

### 5.4.1 Classical Monte Carlo

Simulation of classical many-particle systems by introducing artificial dynamics based on random numbers (calculation not of dynamical physical properties but static properties)

## Main Algorithms

- (i) Direct Monte Carlo  
random numbers for calculation of complicated process
- (ii) Monte Carlo integration  
random numbers to calculate integrals
- (iii) Metropolis Monte Carlo  
sequence of distributions of a system generated in a Markov chain → static properties of classical and quantum many-particle system

### (a) Uncorrelated vs. Markov chains

- uncorrelated  
probability of occurrence of sequence of  $N$  objects  $X_1, \dots, X_N$  is statistically uncorrelated:

$$P_N(X_1, \dots, X_N) = P_1(X_1) \dots P_N(X_N)$$

- Markov chain  
defined through transition probability  $T(x \rightarrow x')$  for having object  $x'$  succeed object  $x$  in sequence. Probability of having sequence of objects  $x_i$ :

$$P_N(x_1, \dots, x_N) = P_1(x_1)T(x_1 \rightarrow x_2)T(x_2 \rightarrow x_3) \dots T(x_{N-1} \rightarrow x_N)$$

with normalization  $\sum_{x'} T(x \rightarrow x') = 1$ .

Detailed balance :  $T(x \rightarrow x')\rho(x) = T(x' \rightarrow x)\rho(x')$   
 $\rho(x)$  : occurrence probability of configuration  $x$

$$T(x \rightarrow x') = w_{xx'}A_{xx'}$$

$w_{xx'}$  : trial step probability

$A_{xx'}$  : acceptance probability

Matrix  $w$  symmetric:  $w_{xx'} = w_{x'x}$ . Also  $\sum_{x'} w_{xx'} = 1$  and  $0 \leq w_{xx'} \leq 1$ .

$\forall x, x' : 0 < A_{xx'} < 1$

→ Detailed balance

$$\frac{A_{xx'}}{A_{x'x}} = \frac{\rho(x')}{\rho(x)} \quad (5.5)$$

### (b) Metropolis algorithm

$$T(x \rightarrow x') = w_{xx'}A_{xx'}$$

$$\sum_{x'} w_{xx'} = 1 \quad ; \quad w_{xx'} = w_{x'x}$$

$$w_{xx'} > 0 \quad \forall x, x'$$

$$\text{if } \rho(x') < \rho(x) \quad : A_{xx'} = \frac{\rho(x')}{\rho(x)}$$

$$\text{if } \rho(x') \leq \rho(x) \quad : A_{xx'} = 1$$

That means for  $\rho(x') > \rho(x)$  the new state  $x'$  is always accepted.



### 5.4.2 Quantum Monte Carlo (QMC)

Monte Carlo techniques to calculate properties of collection of interacting quantum mechanical particles.

- Model many-body wave function of choice directly, which overcomes difficulties such as e.g. Hartree-Fock estimate to model cusps in wave function: e.g. use Hartree-Fock approximations as starting point but multiplied by symmetric function designed to enforce cusp conditions.
- Compute ground state wave functions (path integral Monte Carlo, finite-temperature auxiliary field Monte Carlo: calculate density matrix)

Algorithms:

- Variational Monte Carlo  
optimize expectation value by adjusting trial wave function in a variational approach
- Diffusion Monte Carlo  
use similarity of Schrödinger and diffusion equations to calculate properties of quantum system
- Path-integral Monte Carlo  
quantum mechanical problem mapped on classical one
- Reptation Monte Carlo  
zero-temperature related to path integral Monte Carlo
- Stochastic Green's function  
simulate any complicated lattice Hamiltonian with no sign problem (designed for bosons)
- Auxiliary field Monte Carlo  
for lattice problems

Example variational Monte Carlo

Find ground state and first few excited states of quantum Hamiltonian (calculate high-dimensional integrals).

Recall variational method:

(i) Construct trial  $\psi_a(r)$  depending on  $S$  variational parameters  $a = (a_1, a_2, \dots, a_S)$

(ii) Expectation value evaluation

$$\langle E \rangle = \frac{\langle \psi_a | H | \psi_a \rangle}{\langle \psi_a | \psi_a \rangle}$$

(iii) Vary  $a$  with regard to minimization algorithm and return to (i).

The loop stops when minimum energy is reached according to criterion.

Use QMC for step (ii)

In realistic systems many-body the wave functions assume small values in large parts of the configuration space.

This problem can be overcome through the Metropolis algorithm, in which collection of random walkers are pushed towards regions where the wave functions have appreciable values.

Evaluate  $H\psi_t$  for any trial  $\psi_t$  and define the local energy, omitting the  $a$ -dependence

$$E_L(r) = \frac{H\psi_t(r)}{\psi_t(r)}$$

$E_L(r)$  depends on particle positions and is constant if  $\psi_t$  is exact;  $E_L(r)$  varies less the closer  $\psi_t$  approaches the exact wave function. The expectation value is then

$$\langle E \rangle = \frac{\int dr \psi_t^2(r) E_L(r)}{\int dr \psi_t^2(r)}$$

Construct Metropolis walk with stationary distribution  $\rho(r) = \frac{\psi_t^2(r)}{\int dr' \psi_t^2(r')}$ .

Algorithm:

Put  $N$  walkers at random positions  
DO

- Select next walker
- Shift walker to new position (e.g. move a particle within a cube with suitably chosen size  $d$ )
- Calculate  $p = \left[ \frac{\psi_t(r')}{\psi_t(r)} \right]^2$ ;  $r', r$  new and old configuration
- if  $p < 1$  : new position gets accepted with probability  $p$
- if  $p \geq 1$  : new position gets accepted

REPEAT

STOP when precision achieved

→ expectation value of local energy as average over samples generated, excluding a number of initial steps for equilibration

## 5.5 Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM)

**Quantum Mechanics (QM)** very accurate

parameter-free

computationally expensive

small systems at high accuracy (Density Functional Theory and beyond)

larger systems at lower accuracy (semi-empirical)

**Molecular Mechanics (MM)** implicit treatment of electrons

no polarization or electron transfer

bonds, angles, dihedrals through parameterized force field

$$V_{total} = \sum_{\text{bonds}} V_{\text{bonds}} + \sum_{\text{angles}} V_{\text{angles}} + \sum_{\text{dihed.}} V_{\text{dihed.}} + \sum_{\text{impr}} V_{\text{impr}} + \sum_{i \neq j} (V_{\text{vdW}} + V_{\text{el}})$$

no chemical reactions (bonds defined once through force fields), no bond formation/ breaking  
very large systems

### Quantum Mechanics/ Molecular Mechanics (QM/MM)

- combines Quantum Mechanics and Molecular Mechanics
- partition system into electronically important one and remainder which acts as perturbation and is treated classically; reacting part of system treated quantum mechanically
- reduce quantum system size, computational time, memory storage capacity

$$H_{\text{tot}} = H_{\text{QM}} + H_{\text{MM}} + H_{\text{QM/MM}}$$

Original Hamiltonian for Quantum Mechanical system

$$H_{\text{QM}} = -\frac{1}{2} \sum_I \frac{1}{M_I} \nabla_I^2 - \frac{1}{2} \sum \nabla_n^2 + \sum_{I < J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} - \sum_{I,n} \frac{Z_I}{|\vec{R}_I - \vec{r}_n|} + \sum_{n < m} \frac{1}{|\vec{r}_m - \vec{r}_n|}$$

modified to:

$$H_{\text{tot}} = -\frac{1}{2} \sum_I \frac{1}{M_I} \nabla_I^2 - \frac{1}{2} \sum \nabla_n^2 + \sum_{I < J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} - \sum_{I,n} \frac{Z_I}{|\vec{R}_I - \vec{r}_n|} + \sum_{n < m} \frac{1}{|\vec{r}_m - \vec{r}_n|} \\ - \sum_{K,n} \frac{Q_K}{|\vec{R}_K - \vec{r}_n|} + \sum_{K,L} \frac{Q_K Q_L}{|\vec{R}_K - \vec{R}_L|}$$

interaction of electrons in QM  
with charges in MM

electrostatic interaction  
among MM atoms

$K$  and  $L$  run over all Molecular Mechanics atoms with charges  $Q$

### 5.5.1 Boundary treatment

$$H_{\text{QM/MM}} = - \sum_{e,i} \frac{Q_i}{r_{e,i}} + \sum_{m,i} \frac{Z_m Q_i}{r_{m,i}} + H_{\text{vdW}}$$

$i$  over all MM partial charges

$m$  over all QM nuclei

$e$  over all QM electrons

first term : electron interaction between QM electron density and MM partial charges

second term : Coulomb interaction between QM nuclei and MM charges

final term : electron density (thus dispersion) explicitly treated in QM region, but not in MM region

Energy interaction between QM system and single MM partial charge  $Q_i$  is given by:

$$E_{\text{QM/MM}}^i = \langle \psi | H_{\text{QM/MM}}^i | \psi \rangle \\ = \sum_{\mu} \sum_{\nu} P_{\mu\nu} I_{\mu\nu}^i + \sum_m \frac{Z_m Q_i}{r_{m,i}} + E_{\text{vdW}}^i$$

(only one-electron terms required)

→ Deal with bonds

- valence of QM regions satisfied

- MM bond, angle, dihedral terms need partner atom to act on to maintain geometry

QM/MM bond problem avoided if solute QM and explicit solvent with MM.

### 5.5.2 Link atoms

Conventional solution: atoms added along the bond (usually hydrogens or halogens or methyl groups)

link atom satisfies valence of QM region

QM atom used for calculation of all MM bond terms

non-bonded (electrostatic) terms: link atom does not interact with MM atoms

better properties if link atom interacts with entire MM region (HQ link)

poor handling of electron density

→ Improved bond treatments

- local self-consistent (LSCF)  
parameterized frozen orbital along QM/MM bond (not optimized in SCF)
- generalized hybrid orbital (GHO)  
includes QM/MM orbitals in SCF

### 5.5.3 Dynamics

- chemical reactions often simulated by MD, e.g. umbrella sampling
- dynamics of QM/MM system almost identical to those of MM system
  - forces calculated from first energy derivatives on each atom
  - QM nuclei treated identically to MM partial charges
  - system propagated by standard Newtonian dynamics
- QM/MM can also be used with Monte Carlo
  - MM atoms affect QM electron density and SCF is required  $\forall$  MC moves
  - approximate energy change of QM region by 1<sup>st</sup>-order perturbation theory - perturbative QM/MC - as long as moves are far away from QM region

### 5.5.4 Drawbacks of QM/MM

- some parameterization still required for boundary region treatment
- choice of QM size an art, not straightforward
- though QM region polarizes in response to MM partial charges, the reverse is not true (fully polarizable QM/MM methods are being developed)
- free energy of QM system determined through frequency calculation → inaccurate when applied to QM/MM systems (2<sup>nd</sup> derivatives poorly determined, e.g. due to harmonic approximation)

### 5.5.5 Other approaches

#### (i) ONIOM

system into real (full) and model (subset) parts

treat model part at high and real part at low level

$$E(\text{high,real}) \sim E(\text{low,real}) + E(\text{high,model}) - E(\text{low,model})$$

- extension to 3-level system (e.g. core ab-initio, semi-empirical boundary, MM surroundings)
- model system needs to be properly terminated

(ii) empirical valence bond

- any point on reaction surface as combination of two or more valence bond structures
- parameterization from QM or experiments
- carefully set up but effective

(iii) effective fragment potential

- adds fragments to standard QM treatment, fully polarizable and parameterized from separate ab initio calculations
- treatment of bonds between true QM region and fragments still problematic

## 5.6 Tight-binding method (TB)

- semi-empirical method developed as an approach calculation of electronic band structure in solid-state physics
- use of approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site (close to LCAO method)
- good quantitative results
- can be combined with other methods (e.g. MD  $\rightarrow$  TBMD)
- larger number of particles than first-principle
- more accurate than classical methods, but still parameterized

"tight-binding" describes properties of tightly bound electrons in solids. Electrons tightly bound to atom they belong to with limited interactions with states on surrounding atoms  $\rightarrow$  wave function of electron will be rather similar to atomic orbital of free atom it belongs to. Energy of electron will be rather close to ionization energy of electron in free atom or ion.

- one-particle tight-binding Hamiltonian (most important : the inter-atomic matrix elements)
- main contributors Slater & Koster (1954)
- calculations in static regime; if combined with other methods, e.g. random phase approximation (RPA), can be used for dynamic response of systems
- basic approximation for strongly correlated materials; electron-electron interaction e.g. in 3d transition metals need to be considered using many-body physics

Formulation starting point: the Schrödinger equation

$$H |\psi\rangle = \epsilon |\psi\rangle$$

basis functions the atomic-like orbitals  $\{ \phi_a \}$

$$|\psi\rangle = \sum_{i,a}^{N_b} c_{ia} |\phi_a\rangle$$

$N_b = N_0 \cdot N_a$  dimension of space

$N_0$  number of basis functions/atom

$N_a$  number of atoms

$a$  index for atoms

$i$  index for orbitals

$c_{ia} \in \mathbb{C}$  weights of each orbital at each atomic site

orbitals are centered around atoms and decay rapidly  $\rightarrow$  matrix elements of different orbitals non-zero only for on-site terms and between pairs of neighboring atoms (within a cut-off distance)

minimum basis set composed from states of outer shell (e.g. C, 4 orbitals  $|\phi_s\rangle, |\phi_{px}\rangle, |\phi_{py}\rangle, |\phi_{pz}\rangle$ )

In general basis not orthonormal:  $\langle\phi_a|\phi_b\rangle = S_{ab} \neq \delta_{ab}$

$S_{ab}$  the overlap parameters

$c_{ia}$  through variational calculation and minimization of

$$G[\psi] = \int \psi^* H \psi d\vec{r} - \epsilon \int \psi^* \psi d\vec{r}$$
$$\Rightarrow \sum_{j\beta} (H_{i\alpha j\beta} - \epsilon_i S_{\alpha\beta}) c_{j\beta} = 0$$

or in matrix notation

$$Hc = \epsilon Sc$$

elements of Hamiltonian  $H_{i\alpha j\beta} = \langle\psi|H|\psi\rangle c_{i\alpha}^* c_{j\beta} \langle\phi_\alpha|H|\phi_\beta\rangle$

TB reduced to diagonalization of Hamiltonian and calculation of  $c_{i\alpha}, \epsilon_i$ .

simple TB model for total energy for semiconductors:  $E_{\text{tot}} = E_{\text{band}} + E_{\text{rep}}$

$E_{\text{band}}$  sum of one-electron eigenvalues of occupied states (contribution due to outer electrons)

$E_{\text{rep}}$  sum of short range repulsive pair potentials (usually empirical)

$$E_{\text{band}} = 2 \sum_s n_s \epsilon_s = 2 \sum_s n_s \langle\psi_s|H|\psi_s\rangle$$
$$= 2 \sum_s \sum_{i\alpha, j\beta} n_s c_{i\alpha}^* c_{j\beta} H_{i\alpha j\beta}$$
$$= 2 \sum_{i\alpha, j\beta} P_{i\alpha j\beta} H_{i\alpha j\beta} = 2\text{Tr}[\rho H]$$

with  $\rho$  the density matrix.

sum over  $s$  = occupied states

$$E_{\text{rep}} = \frac{1}{2} \sum_{ij} v_R(r_{ij})$$

in empirical TB matrix elements (for  $S, H$ ) not computed, but analytical parameterized expressions as functions of atomic orbitals are used

Example: C, Si only s,p orbitals

only 4 orbitals at each atomic site

$\rightarrow$  4x4 matrix  $\rightarrow$  16 parameters needed

number increases for more orbitals  $\rightarrow$  for more parameters transferability is affected. Include symmetry rules to reduce parameters.

Algorithm:

- atomic positions as input
- calculate Hamiltonian
- diagonalization of Hamiltonian
- eigenvalues and eigenvectors  $\rightarrow$  electronic ground state

### 5.6.1 Two different Hamiltonian as examples

- (a) Mehl & Papaconstantopoulos (1996)  
 $\mathcal{O}(N^2)$  method, no explicit pair potential

$$E_{tot} = E_{band} = \sum_{\text{occ}} \epsilon'_i$$

where  $\epsilon'_i = \epsilon_i + \frac{F[n(\vec{r})]}{N_e}$ ;  $N_e$  the number of electrons.

repulsive energy by functional  $F[n(\vec{r})]$  which depends on system shift in energy

parameters from fits to band structure and total energies from first principle calculations; also extended to other structures

define environment through a pseudo-atomic densities for each atom:  $\rho_i = \sum_j e^{-\lambda^2|\vec{R}_j - \vec{R}_i|} f(|\vec{R}_j - \vec{R}_i|)$

sum over all neighbors of atom  $i$  at  $\vec{R}_i$

$f(R)$  cut-off function

on-site term:

$$h_{il} = a_l + \beta_l p_i^{2/3} + \gamma_l p_i^{4/3} + \xi_l p_i^2$$

$l$  runs over all orbitals

hopping terms for Hamiltonian

$$H_{l\mu}(R) = (a_{l\mu} + \beta_{l\mu} R + c_{l\mu} R^2) \exp[-d_{l\mu}^2 R] f(R)$$

overlap parameters

$$S_{l\mu}(r) = (\delta_{l\mu} + p_{l\mu} + q_{l\mu} R^2 + r_{l\mu} R^3) \exp[-d_{l\mu}^2 R] f(R)$$

for 4 orbitals 41 parameters chosen to reproduce the total energies and shifted eigenvalues of  $\epsilon'$

- (b) environment-dependent tight-binding model (Tong, Wang, Chan, Ho 1996)

- beyond two-center approximation, take into account changes due to bounding environment
- parameters obtained by fitting to electronic band structures and cohesive energies with volume
- hopping parameters  $h(r_{ij}) = a_1 R_{ij}^{-a_2} \exp[-a_3 R_{ij}^{a_4}]$
- scaling the distance between two atoms according to their effective coordination number (interaction for highly-coordinated atoms weaker)

$$R_{ij} = r_{ij} \left\{ 1 + \frac{\delta}{2} \left[ \frac{g_i - g_0}{g_0} + \frac{g_i - g_0}{g_0} \right] \right\}$$

$g_i$  effective coordination number

$g_0$  coordination number of reference atom in reference structure :  $g_i = \sum_j (1 - \delta_{ij})$

- screening function to weaken the interaction strength between two atoms if other atoms are located between them

$$S_{ij} = \frac{\exp(\chi_{ij}) - \exp(-\chi_{ij})}{\exp(\chi_{ij}) + \exp(-\chi_{ij})}$$

$$\chi_{ij} = \beta_1 \sum_j \exp \left[ -\beta_2 \left( \frac{r_{il} - r_{jl}}{r_{ij}} \right)^{\beta_3} \right]$$

$\rho_{ij} \rightarrow 0$  if  $i, j$  nearest neighbors

$\rho_{ij} \rightarrow 1$  elsewhere

nearest neighbor interactions dominate

( $R_{ij} = r_{ij}$  and  $S_{ij} = 0 \rightarrow$  two-center approximation)

- diagonal matrix elements (also environment dependent)

$$\epsilon_{\lambda i} = \epsilon_{\lambda 0} + \sum_j \Delta\epsilon_{\lambda}(r_{ij})$$

$\Delta\epsilon_{\lambda}(r_{ij})$  same expression as  $h(r_{ij})$

$\lambda$  over all orbitals

$$E_{\text{rep}} = \sum_i f \left( \sum_j \phi(r_{ij}) \right)$$

with

$$\phi(r_{ij}) = \phi_0 \left( \frac{d_0}{r_{ij}} \right)^m \exp \left\{ m \left[ - \left( \frac{r_{ij}}{d_c} \right)^{m_c} + \left( \frac{d_0}{d_c} \right)^{m_c} \right] \right\}$$

- all fitting parameters can differ for different hopping integrals and pairwise repulsive potentials

density matrix related to variational density matrix  $\tilde{\rho} = 3\rho^2 - 2\rho^3$

off-diagonal elements of  $\rho$  beyond cut-off are set to zero, assuming  $\rho$  well localized

## 6 Molecular Dynamics (MD)

- Physical quantities of a many-particle system can be found as ensemble average
- Experimental systems too large to be determined by summing over all accessible states in a computer
- Molecular Dynamics and Monte Carlo to determine physical quantities as statistical averages over a restricted set of states.

In Molecular Dynamics : system moves in space along its physical trajectory as determined by equations of motion

In Monte Carlo : system follows a directed random walk

In a quantum mechanical approach a full treatment of all interactions is extremely computationally expensive. Thus, Quantum Mechanics is practical only for short time scales, small length scales, few particles and low temperature.

Molecular Dynamics takes over for longer time and length scales, so called "macroscopic" systems.

Quantum Mechanics  $\xrightarrow{\hbar \rightarrow 0}$  classical limit

Molecular Dynamics : N particles (classical) [in rectangular volume  $L_1 \times L_2 \times L_3$ ] interacting with each other.

Simplify: interaction force as a sum over pair forces  $\vec{F}(\vec{r})$  whose magnitude depends only on distance  $r$  between particle pairs and is directed between them:

$$\vec{F}_i(R) = \sum_{j \neq i}^N F(|\vec{r}_i - \vec{r}_j|) \hat{r}_{ij}$$

the internal force (due to interaction between particles) acting on particle  $i$ .

$R$  position coordinates  $\vec{r}_i$  of all particles

$\hat{r}_{ij}$  unit vector pointing along  $\vec{r}_j - \vec{r}_i$

Neglecting external forces

$$\frac{d^2 \vec{r}_i(t)}{dt^2} = \frac{\vec{F}_i(R)}{m_i}$$

$m_i$  mass of particle  $i$

The equation above is solved numerically for the collection of particles in Molecular Dynamics.



## 6.1 Boundary conditions

system size in simulations smaller than in experiments

not a big problem if correlation length much smaller than the system size, but need to use finite-size scaling methods if correlation length exceeds system size

finiteness of system through a boundary

most common correction: periodic boundary conditions (PBC)

for PBC behavior of system most similar to that of system of same size embedded in an infinite system.

With PBC the system of interest is surrounded by similar systems with exactly the same configuration of particles at any time.

The interaction between two particles  $i, j$  is then

$$\vec{F}_{PBC}(\vec{r}_i - \vec{r}_j) = \sum_{\vec{n}} \vec{F} \left( \left| r_i - r_j + \sum_{\mu=1}^3 L_{\mu} n_{\mu} \right| \right)$$

$L_{\mu}$  vectors along edges of rectangular system volume

sum over all vectors  $\vec{n}$  with integer coefficients  $n_{\mu}$

$\vec{F}$  is directed along line of connecting particle  $i$  and image particle  $j$

- time-consuming: calculation terms of infinite sum until convergence
- time-average evaluated over finite time
- relevant: number of integration steps and time steps
- correlation time of system smaller than total simulation time
- numerical integration not infinitely accurate  $\rightarrow$  optimum choice between speed and accuracy: the longer the integration time step, the more inaccurate the results (system would follow a trajectory in phase space deviating from that in reality), i.e. physical quantities measured in simulation
- MD: direct simulation of many-particle system but carried out with care (benchmarking always needed)

## 6.2 Forces in Molecular Dynamics

Interactions between particles are approximated through classical pair potentials between particle centers  $\rightarrow$  "effective potentials"

Use of these effective potentials allow Molecular Dynamics calculations also for  $10^6$  particles

$$\vec{F} = - \frac{dV(\vec{R})}{d\vec{R}}$$

- Advantages of force fields (FF)
  - $N$  particle system:  $\mathcal{O}(N^2) \rightarrow$  fast computation
  - with proper optimization (cut-offs etc.) also  $\mathcal{O}(N)$
- Disadvantages of force fields
  - force field is parameterized, this inherently carries errors
  - force field can be applied only to known pairs, for which it was parameterized

- quality of parameters needs to be evaluated (often difficult to be estimated)
  - force field ignores orbital interactions and often polarizability
  - force field neglects multi-body effects as not all interactions can be represented through pair potentials
- e.g. chemical reactions not possible to be directly described (covalent bond breaking would need different parameters)

### 6.2.1 Force Fields in simulations involving biomolecules

Biomolecules resemble "Lego"; they consist of distinct units (e.g. DNA is a sequence of nucleobases, proteins consist of amino acids, etc.)

Assumption: atom-atom interactions can be described by the same potential with different parameters.

Potential form typically used for biomolecules

$$E_{\text{tot}} = E_{\text{bond}} + E_{\text{ang}} + E_{\text{tor}} + E_{\text{vdW}} + E_{\text{cb}}$$

$$E_{\text{bond}} = \sum_{\text{bonds}} S_{ij} (r_{ij} - \bar{r}_{ij})^2$$

$\bar{r}_{ij}$  equilibrium covalent bond distance

$$E_{\text{ang}} = \sum_{i,j,k \in S_{AB}} K_{ijk} (\cos \theta_{ijk} - \cos \bar{\theta}_{ijk})$$

$S_{AB}$  covalent bond angle

$\bar{\theta}_{ijk}$  equilibrium bond angle

$$E_{\text{tor}} = \sum_{i,j,k,l \in S_{DA}} \sum_n \frac{V_{nijkl}}{2} [1 \pm \cos(n\tau_{ijkl})]$$

$S_{DA}$  dihedral angle

van der Waals interactions through Lennard-Jones potential

$$E_{\text{vdW}} = \sum_{i,j \in S_{NB}} \left( -\frac{A_{ij}}{r_{ij}^6} + \frac{B_{ij}}{r_{ij}^{12}} \right)$$

Coulomb interaction of partial charges

$$E_{\text{cb}} = \sum_{i,j \in S_{NB}} \left( \frac{q_i q_j}{\epsilon(r_{ij}) r_{ij}} \right)$$

Interaction potential includes bonded and non-bonded interactions. The force field parameterization is based on experimental data and quantum mechanical calculations:

e.g. Methane → Fitting parameters not unique : take into account system, fitted properties where Force Field should be applicable, desired properties, accuracy, efficiency, etc.

property	fit to
bond-lengths, angles	X-Rays, QM
force constants	IR, QM
torsion angles, constants	QM
partial charges	QM, experimental data
Lennard-Jones	QM, experimental data

## 6.3 Water models in classical simulations

### 6.3.1 Water

- Transparent, odorless, tasteless and ubiquitous
- Really simple: two H atoms attached to single O atom
- Extraordinary substance:
  - Importance as a solvent, a solute, a reactant and a biomolecule, structuring proteins, nucleic acids and cells
  - About 2/3 of human body, 93.3% of blood
- A hundred times as many water molecules in our bodies as the sum of all the other molecules put together life cannot evolve or continue without liquid water (solvation of biomolecules (DNA), ions, proteins)
- But poorly understood: small size but complex with enormous capabilities

### 6.3.2 History

- 1932 - Spectroscopic proofs of the V-shaped water molecule
- 1933 - Bernal and Fowler [J.Chem. Phys. 1, 515 (1933)] propose 1st realistic interaction potential for water
- 1953 - Metropolis et al [J. Chem. Phys. 21, 1087 (1953)] presents the 1st Monte Carlo sampling scheme
- 1957 - Adler and Wainwright [J.Chem. Phys. 27, 1208 (1957)] performed 1st MD simulation
- 1969 - Baker and Watts [J.Chem. Phys. Lett. 3, 144 (1969)] 1st computer simulations of water
- 1976 - Lie et al, [J. Chem. Phys. 64, 2314 (1976)] 1st pair potential from ab initio calculations for water
- 1981 - Berendsen et al [intermolecular Forces, Reidel Publ.] construct the 1st "accurate" and simple pair potential for liquid water
- 1993 - Laasonen et al [J. Chem. Phys. 99, 9080 (1993)] 1st ab initio calculations for liquid water

### 6.3.3 Water molecule: H<sub>2</sub>O

Tiny and V-shaped; molecular diameter about 2.75 Å. liquid state, in spite of 80% of the electrons involved in bonding, the three atoms do not stay together as the hydrogen atoms are constantly exchanging between water molecules due to (de)protonation.

Many different classical water models

Modelling parameters:

- number of charges
- interactions
- dipole moment

### 6.3.4 Why is water such a good solvent?

- Polar substance
  - good for dissolving salts, ions...
  - Large relative dielectric constant ( $\approx 80$ )
- Hydrogen bonds
  - network former, liquid water has structure
  - an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one,
  - a high cohesiveness and, thus, surface tension

### 6.3.5 Hydrogen Bonds

In water, the strength of hydrogen bonds are about 5 kcal/mol  $\approx 8.4 k_B T$ . What do we get, if we calculate the electrostatic energy of an H-O pair?

$$\frac{E}{k_B T} = l_B \frac{q_1 q_2}{r} = 7.1 \frac{0.8 \cdot 0.4}{1.8} \approx 1.25 k_B T$$

Question : Why so low ?

Answer: In this model, van der Waals contribution need to be taken into account! Effective interactions...

### 6.3.6 Water parameterization

- Each model developed to fit well with one particular physical structure or parameter (e.g., the density anomaly, radial distribution function, critical parameters)
- The more fitting parameters that are required by the model (and some require over 50), the better the fit
- Some models show a lack of robustness due to their sensitivity to the precise model parameters, system size or simulation method
- Some are polarizable, others reproduce 'average' structures

- Note: Water molecules in liquid water are all non-equivalent (differ in molecular orbitals, precise geometry, molecular vibrations) due to hydrogen bonding status (influenced by arrangements of surrounding water molecules)

Water models: mainly 4 structures, 3-5 interaction points

a, b, c : planar

d : tetrahedral

$q_2$ : mid-point in c

lone-pairs in d

### 6.3.7 Water model types

- Rigid models:
  - fixed atom positions (match known geometry of water)
  - only non-bonded interactions
- Flexible models:
  - Atoms on "springs"
  - include bond stretching and angle bending
  - Reproduce vibration spectra
- Polarizable models:
  - include explicit polarization term (enhances ability to reproduce water in different phases and interaction between them)
  - first attempt (Barnes et al, Nature (1979))
  - examples: SPC/FQ, Tip4p/FQ (computationally only 1.1 times the corresponding rigid model).

#### Potentials

ab initio determined from calculations of dimers, trimers or higher order clusters empirical (e.g. Lennard-Jones) developed to reproduce experimental data in gas or liquid phase.

#### Most common water models

- SPC (Berendsen et al, Interaction Models for Water in Relation to Protein Hydration, in Intermolecular Forces, ed. B. Pullman, p. 331, D. Reidel Publishing Company, Dordrecht, 1981)
- SPC/E (Berendsen et al, J. Phys. Chem. 91, 6269 (1987))
- TIP3P (Jorgensen et al, J. Am. Chem. Soc. 105, 1407 (1983))
- TIP4P (Jorgensen et al, J. Am. Chem. Soc. 105, 1407 (1983))
- TIP5P (Mahoney & Jorgensen, J. Chem. Phys. 112, 8910 (2000))

## Force fields

Some water models developed in a specific force field and often adapted to other force fields:

SPC, SPC/E - GROMOS

Tip3p - AMBER (modified Tip3p for CHARMM)

Tip4p, Tip5p - OPLS

## Simple water models

Rigid molecule interacting via non-bonded interactions with other molecules:

$$E_{ab} = \sum \sum \frac{k_c q_i q_j}{r_{ij}} + A \frac{1}{r_{00}^{12}} - B \frac{1}{r_{00}^6}$$

$k_c$  electric constant  $\frac{1}{4\pi\epsilon_0} \approx 332.1 \text{ \AA kcal/mol}$

$q_{i/j}$  partial charges

Variation of the location and size of partial charges:

Difference in physical properties like diffusion constant, dielectric constant, density, heat of vaporization, ...

**3-site** Each atom gets a point charge assigned and Oxygen atom also has its own Lennard-Jones parameters. Popular in MD (simple & efficient)

**4-site** The negative charge sits on a dummy atom M instead of on the position of the O. This improves the electrostatic distribution around the water molecule.

**5-site** The negative charges are split and sit on the L-L (lone pairs) of oxygen with a tetrahedral-like geometry. a lone pair is a valence electron pair without bonding or sharing with other atoms

**6-site** combines all sites of 4-site and 5-site

## Computational cost

Number of inter-atomic distances

$$T_{CPU} \propto N$$

3-site	3 x 3 = 9 distances for each pair of water molecules
4-site	3 x 3 charge - charge + 1 x LJ (O-O) = 10 distances
5-site	4 x 4 charge - charge + 1 x LJ (O-O) = 17 distances
6-site	5 x 5 charge - charge + 1 x LJ (O-O) = 26 distances

In Molecular Dynamics simulations most molecules are rigid → need constraint algorithms → can use larger time steps

Some models also exist in flexible variants:

- flex.SPC
- TIP4PF
- ...

Different models reproduce different properties correctly, but never all:  
Diffusion, dielectric constant, density, phase behavior, etc....

Common 3-site models

...

- model known geometry of water molecule
- SPC uses ideal tetraeder shape of  $109.47^\circ$  (Simple Point Charge)
- TIP3P uses slightly modified CHARMM force field (transferable intermolecular potential functions, see W.L. Jorgensen, JACS 103, 33 (1981))

Water models - efficiency

...

$\mu$  dipole moment

$\epsilon$  dielectric constant

$E_{conf}$  average configurational energy

SPC/E water model

Add average polarization energy:

$$E_{pol} = \frac{1}{2} \frac{\sum (\mu - \mu_0)^2}{\alpha_i}$$

$\alpha_i$  constant isotropic polarizability  $\approx 1.608 \times 10^{-40}$  F m

$\mu$  2.35 D effective dipole moment of polarized water

$\mu_0$  1.85 D dipole moment of isolated water (1.85 D from experiment).

Since the charges are constant this results in a constant correction of 1.25 kcal/mol in the total interaction energy

$$E_{ab} = E_{Coul} + E_{LJ} + E_{pol}$$

This results in a better density and diffusion constant description than the SPC model.

Water models - efficiency

In reality: water is flexible and polarizable  $\rightarrow$  models which do not include these properties are not expected to make predictions of high accuracy.

Predictability becomes worse as temperature is lowered.

Phase diagram of water

...

Solid phase: water exhibits one of the most complex phase diagrams with 13 different (known) solid structures. From the simple water models (SPC, SPC/E, TIP3P, TIP4P and TIP5P) only TIP4P provides a qualitatively correct phase diagram on water.

### 6.3.8 Physical properties of water: complexities

#### Density

Many potentials are fitted to reproduce the experimental liquid density, which is the case for most of the models that show good agreement. When the density is not used as a fitting parameter, as in the case with ab initio potentials (for example MCY, MCYL and NEMO) the results are rather poor.

#### Diffusion coefficient

Water mobility is an indicator of the influence of the hydrogen bonds on the molecular motion. Diffusivity is overestimated by many of the common water rigid models.

#### Comparison of physical properties

...

#### Beyond the most common water models

**F3C** Levitt et al . A water model calibrated for simulation of Molecular Dynamics of proteins and nucleic acids in solution.

**DEC** Guillot & Guissani [J. Chem. Phys. 114, 6720 (2001)]. A water model that employs diffuse charges, in addition to the usual point charges, on the oxygen and hydrogen atoms, to account for charge penetration effects.

**TIP4P/FLEX** Lawrence & Skinner [Chem. Phys. Lett. 369, 472 (2003)]. Model that well describes the absorption spectra for liquid water.

**MB model** Silverstein, Haymet & Dill [JACS 120, 3166 (1998)] (resembles Mercedes-Benz logo). Reproduces features of water in 2-D systems (better for educational purposes than for real simulations).

**Coarse-grained models** one- and two-site models, where each site represents a number of water molecules [e.g. Izvekov & Voth. J. Chem. Phys. 123, 134105 (2005)].

#### Aquaporin Channel

Simplified view:

- excess water left out
- lipids not shown
- channel shown as ribbon

### 6.3.9 Notes

- No water model available is able to reproduce all the water properties with good accuracy. All empirical models are parameterized and the ab initio models do also not behave well
- But, it is possible to describe the force field of water using simple empirical models, and make predictions
- It is worth considering which models to use when performing any simulation including water. Computational cost vs. accuracy.



### 6.3.10 Implicit water models

- Represent the solvent and counter-ions as a continuous medium
- Simulations with implicit water can usually be run more quickly than explicit simulations
- Usually not interested in the distribution of individual water molecules in the solvent-solute interface.

Common implicit water model:

- Solvent accessible surface area models
- Poisson-Boltzmann equation
- Generalized Born models

## 7 Implicit solvent models

### 7.1 Implicit solvation

- Solvent molecules are not explicitly taken into account
- Solvent is modelled as a continuous medium
- Used when distributions of individual water molecules are not of interest
- The continuous medium has specific solvation and dielectric properties
- Faster computations
- Errors in statistical averaging arising from incomplete sampling of solvent conformations
- Types of models : accessible surface area, continuum electrostatics, Born models
- Accessible surface area based on experimental relations between Gibbs free energy of transfer and surface area of solute; operates directly with free energy of solvation unlike electrostatic methods which include only enthalpic component of free energy
- Implicit averaging over solvent degrees of freedom eliminates the "noise", i.e. a number of local minima arising from small variations in solvent structure

#### 7.1.1 Solvent accessible surface area (SASA)

The free energy of solvent is

$$\Delta G^{solv} = \sum_i \sigma_i ASA_i$$

$i$  sum over all atoms

$ASA_i$  surface area of atom  $i$  accessible to solvent (generate by center of sphere/probe rolling on van der Waals surface of atoms)

$\sigma_i$  atom-specific surface tension parameter (estimated from empirical hydration free energies of compounds in water)  
(contribution to free energy of solvation of atom  $i$  per surface area)

Within SASA:

atoms and solvent molecules modelled as spheres

$ASA_i$  : area of points on surface of sphere of radius  $R$  which can contact the center of a spherical solvent molecule that intersects no other atom.

$R$  : sum of van der Waals radius of atom and radius of solvent molecule (water : 1.4 Å)

Algorithms to estimate ASA

(i) Shrake-Rupley algorithm (1973)

- discretize molecular surface
- 92 points distributed uniformly along a sphere centered at each atom with radius  $R$  (choice of this probe radius affects observed surface area; smaller  $R$  detects more surface details and gives larger surface; typical value 1.4 Å, close to the radius of water molecule)
- ASA estimated by calculating the proportion of points that can be contacted by a solvent molecule that intersects no other atoms
- similar methods use polyhedra to approximate the surface
- numerical evaluation of gradients of discretized ASA estimates

(ii) Linear combination of pairwise overlaps (1999)

analytical expression based on inclusion-exclusion-like formula

$$A_i \approx P_1 S_i + P_2 \sum_{j \in N(i)} A_{ij} + \sum_{j \neq k} (P_3 + P_4 A_{ij}) A_{jk}$$

$S_i$  surface area of atom  $i$

$A_{ij}$  surface area of sphere  $i$  inside a sphere  $j$

$N(i)$  neighbor list of atom  $i$

$P_{1-4}$  calculated through least square regression

relative error : 0.1-7.8%

Limitations of SASA

- solvation free energies are not linearly related to surface area (SASA overestimates hydration free energies)
- solvation free energy calculated using SASA ignores electrostatic effects of solvent
- no interactions between solvent and polar atoms in the interior of the molecule considered

### 7.1.2 Continuum electrostatic models

- effects of solvent on electrostatics of molecule
- simplest approach: use a distance-dependent dielectric function:

$$\epsilon(\vec{r}) = \frac{D_s + D_0}{1 + k e^{-k(D_s + D_0)|\vec{r}|}} - D_0$$

$\epsilon(\vec{r})$  mimics electrostatic screening due to presence of solvent.

ignore the fact that the solute molecule influences distribution of solvent molecules [solvent molecules often excluded from interior of solute; counter-ions and polar solvent molecules may condense around charged atoms]

- model distribution of solvent around molecule  $\rightarrow$  more accurate results:

Potential of mean force  $\tilde{V}_i(\vec{r})$

equilibrium: total charge density of solvent and dissolved salt described by Boltzmann distribution:

$$\rho_{solvent}(\vec{r}) = \sum_i q_i c_i e^{-\tilde{V}_i(\vec{r})/k_B T} \quad (7.1)$$

$q_i$  charge of  $i$ -th ion

$c_i$  concentration of  $i$ -th ion

Potential of mean force (PMF) for ion  $i$ :

$$\tilde{V}_i(\vec{r}) \approx q_i \phi(\vec{r})$$

Potential of mean force associated to bulk electrostatic field  $\phi(\vec{r})$  which is in turn related to charge distribution of solvent and solute, through Poisson's equation

$$\nabla[\epsilon(\vec{r})\nabla\phi(\vec{r})] = -4\pi\rho_{solute}(\vec{r}) - 4\pi\rho_{solvent}(\vec{r}) \quad (7.2)$$

Combine Eq. (7.1) and (7.2) to derive the Poisson-Boltzmann equation (PBE):

$$\nabla[\epsilon(\vec{r})\nabla\phi(\vec{r})] = -4\pi\rho_{solute}(\vec{r}) - 4\pi\sum_i q_i c_i e^{-\tilde{V}_i(\vec{r})/k_B T}$$

[Many numerical Poisson-Boltzmann solvers have been developed, but performance is poorer than that of the generalized Born approximation]

For a solvent consisting of two oppositely charged ions with the same concentration  $c$ , the Poisson-Boltzmann equation becomes:

$$\begin{aligned} \nabla[\epsilon(\vec{r})\nabla\phi(\vec{r})] &= -4\pi\rho_{solute}(\vec{r}) - 4\pi qc(e^{q\phi(\vec{r})/k_B T} - e^{-q\phi(\vec{r})/k_B T}) \\ &= -4\pi\rho_{solute}(\vec{r}) - 8\pi qc \sinh(q\phi(\vec{r})/k_B T) \end{aligned}$$

**linearized Poisson-Boltzmann equation (LPBE)** PBE usually linearized around 0. Linearization possible when  $q_i\phi(\vec{r}) \ll k_B T$ . The purpose of linearization is to solve PBE more efficiently. Assume  $\sum_i c_i q_i = 0$  and  $\gamma^2 = \frac{8\pi}{k_B T} \sum_i c_i q_i^2$ . Then:

$$\begin{aligned} \nabla[\epsilon(\vec{r})\nabla\phi(\vec{r})] &= -4\pi\rho_{solute}(\vec{r}) - 4\pi\sum_i q_i c_i (1 - q_i\phi(\vec{r})/k_B T) \\ &= -4\pi\rho_{solute}(\vec{r}) + \gamma^2\phi(\vec{r}) \end{aligned}$$

linearization of PBE leads to Debye-Hückel theory (an analytical solution)

consider a single spherical ion in an electrolyte with a radius  $a$ , a uniform surface charge  $q$ , constant interior  $\epsilon_i$  and solvent  $\epsilon_s$  permittivities.

Then rewrite LPBE as

$$\nabla\phi(\vec{r}) = \begin{cases} \frac{\epsilon_s}{\epsilon_i} \kappa^2 \phi(\vec{r}) & , \quad |\vec{r}| < a \\ \kappa^2 \phi(\vec{r}) & , \quad |\vec{r}| > a \end{cases}$$

with  $\kappa^2 = \frac{\gamma^2}{\epsilon_s}$ .

For  $|\vec{r}| \neq a$  a unique solution exists:

$$\phi(\vec{r}) = \begin{cases} \frac{q}{4\pi} \left[ \frac{1}{\epsilon_i |\vec{r}|} - \frac{1}{\epsilon_i a} + \frac{1}{\epsilon_s a(1+\kappa a)} \right] & , \quad |\vec{r}| < a \\ \frac{\exp(\kappa a)}{1+\kappa a} \frac{q \exp(-\kappa |\vec{r}|)}{\epsilon_i |\vec{r}|} & , \quad |\vec{r}| \leq a \end{cases}$$

for  $|\vec{r}| \leq a$ : exponential screening of ion by counter-ions in solvent.

$\kappa^{-1}$  : Debye screening length (inversely proportional to square root of ionic strength)

$$\kappa^{-1} = \lambda_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{\sum_{j=1}^N n_j q_j^2}}$$

Numerical solutions of PBE, LPBE:

- repetitive solution of PBE needed for energy minimization and MD
- solutions smooth in space and time are to be used in MD
- boundary conditions accurately defined
- dielectric function changes rapidly at solvent-solute interface

For solving numerically PBE, LPBE finite-difference, finite-element and boundary-element approaches have been developed.

### 7.1.3 Generalized Born model

The Generalized Born model is an approximation to the Poisson-Boltzmann equation. The solvation free energy is approximated through:

$$\Delta G_{GB} = - \left(1 - \frac{1}{\epsilon_w}\right) \sum_i \frac{q_i^2}{2\alpha_i} - \frac{1}{2} \left(1 - \frac{1}{\epsilon_w}\right) \sum_{i \neq j} \frac{q_i q_j}{f^{PB}(r_{ij}, \alpha_i, \alpha_j)}$$

$q_i$  particle charge

$\alpha_i$  effective Born radius of atom  $i$

$\epsilon_w$  dielectric constant of water

$$f^{PB}(r_{ij}, \alpha_i, \alpha_j) = \sqrt{r_{ij}^2 + \alpha_i \alpha_j \exp(-r_{ij}^2 / 4\alpha_i \alpha_j)}$$

- GB corresponds to solvation in an infinite volume of solvent
- GB often used with Solvent Accessible Surface Area estimate of the non-polar solvation energy (GBSA)
- GBSA more crude approximation for solvation energy than Poisson-Boltzmann equation
- GB models the solute as a set of spheres whose internal dielectric constant differs from that of external solvent
- effective Born radii should be well calculated; denote distance from atom to molecular surface (SAS) (degree of "burial" inside the solute)  $\rightarrow$  approximation (most of the atoms will not be surrounded by spherical cavities)
- effective Born radius chosen so that  $-\left(1 - \frac{1}{\epsilon_w}\right) \frac{q_i^2}{2\alpha_i}$  is the electrostatic solvation energy of an isolated charge surrounded by a spherical shell that excludes the solvent

- effective Born radii can be estimated numerically but often evaluated using an approximate analytical expression (Hawkins et al., 1996):

$$\begin{aligned}\alpha_i^{-1} &\approx \rho_i^{-1} - \sum_{j \neq i} \int_{\rho_i}^{\infty} \frac{1}{r^2} H_{ij}(\vec{r}, \rho_j) dr \\ &= \rho_i^{-1} - \sum_{j \neq i} g(r_{ij}, \rho_i, \rho_j)\end{aligned}$$

$\rho_i$  intrinsic radius of atom  $i$  (in isolation)

$H_{ij}(r, \rho_j)$  fraction of area of a sphere of radius  $r$  centered at atom  $i$  which is shielded by atom  $j$ .

The 2nd term in GB  $\sum_{i \neq j} \frac{q_i q_j}{f^{PB}(r_{ij}, \alpha_i, \alpha_j)}$  is the pairwise contribution of the charges of the molecule to the solvation energy.  $f^{GB}$  interpolation function, chosen so that

$$\lim_{r_{ij} \rightarrow 0} f^{GB}(r_{ij}, \alpha_i, \alpha_j) = \sqrt{\alpha_i \alpha_j}$$

$$\lim_{r_{ij} \rightarrow \infty} r_{ij}^{-1} f^{GB}(r_{ij}, \alpha_i, \alpha_j) = 1$$

#### 7.1.4 Ad-hoc fast solvation models

Strategies:

- calculation of a per-atom solvent accessible surface area  
For each group of atom types, a different parameter scales its contribution to solvation
- Gaussian-shaped solvent exclusion

$$\Delta G_i^{solv} = \Delta G^{ref} - \sum_j \int_{V_j}^{\infty} f_i(r) dr$$

reference  $\Delta G^{ref}$  corresponds to a suitably chosen small molecule in which a group is fully solvent-exposed.

$V_j$  Volume of group

$j$  sum over all groups

#### 7.1.5 Hybrid solution models

Include layer of sphere of water molecules around solute and model bulk with implicit solvent. Viscosity, hydrophobic effect, hydrogen-bonds with solvent are not accounted for.

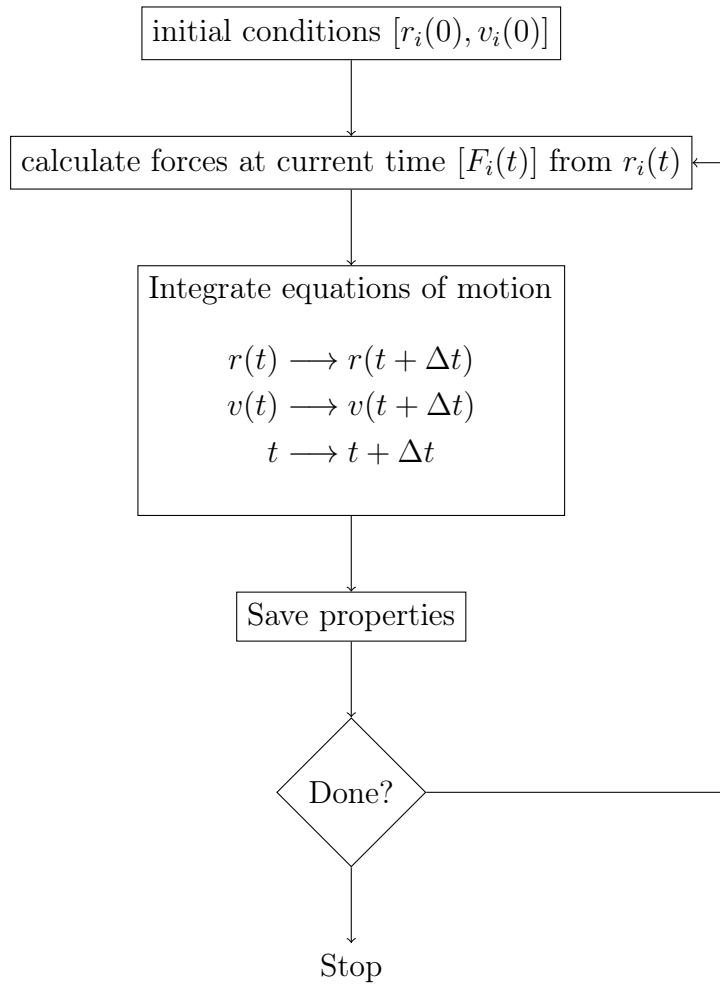
- mean electrostatic free energy estimated without entropic effects due to solute-imposed constraints on organization of water
- viscosity typically absent; water molecules impart viscosity by randomly colliding and impeding motion of solutes through their van der Waals repulsion
- average energetic contribution of hydrogen bonds reproduced

Main concept of implicit solvent models:

non-polar atoms of a solute tend to cluster together or occupy non-polar media

ionization of charged groups neglected (ionizable groups remain charged in the non-polar environment → overestimation of electrostatic energy)

overcome using different solvation parameters for charged atoms



## 7.2 Basics of MD simulations

A simple minimal MD code Properties: relate microscopic phenomena/structure and macroscopic properties

MD: follow dynamics (motion) of all atoms in system (material, biomolecule, etc.). In order to do this solve numerically classical (Newton's) equations of motion:

$$\vec{F}_i = m_i \vec{a}_i$$

or

$$\begin{cases} \dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \\ \dot{\vec{p}}_i = \vec{F}_i \end{cases}$$

Forces on atoms arise from the interaction with other atoms:

$$\vec{F}_i = -\nabla E(\{\vec{r}_j\})$$

$E(\{\vec{r}_j\})$  the total potential energy from QM or inter-atomic potential

Hamilton's picture: a Hamiltonian can be defined for the system:

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) = V(\{\vec{r}_i\}(t)) + \sum_{i=1}^{3N} \frac{p_i^2(t)}{2m_i}$$

$i$  denotes atom and Cartesian component.

From the Hamiltonian the equations of motion can be derived

$$\vec{r}_i = \frac{\partial H}{\partial \vec{p}_i} \quad \vec{p}_i = -\frac{\partial H}{\partial \vec{r}_i}$$

The equations can be solved analytically only for very few specific cases

Knowledge of  $H$  can link microscopic states to macroscopic properties or given a thermodynamic state of the system what are the probabilities of finding a system in various microscopic states.

To enable this link, statistical mechanics approaches are used and specific statistical ensembles. From the statistical ensembles, the following three are the most common ones:

Example: MD at constant temperature

Micro-canonical	Canonical	Isobaric/Isothermal
probability distributions $P(\{\vec{r}_i\} \{\vec{p}_i\})$		
$\frac{1}{\Omega(E, V, N)}$	$\frac{e^{-H(\{\vec{r}_i\} \{\vec{p}_i\})/k_B T}}{Z(T, V, N)}$	$\frac{e^{-[H(\{\vec{r}_i\} \{\vec{p}_i\}) - PV]/k_B T}}{Z_P(T, P, N)}$
partition functions		
$\Omega(E, V, N)$ $= \sum \delta[E - H(\{\vec{r}_i\} \{\vec{p}_i\})]$	$Z(T, V, N)$ $= \sum_{\text{micro}} e^{-E/k_B T}$	$Z(T, P, N)$ $= \sum_V \sum_{\text{micro}} e^{-[E - PV]/k_B T}$
free energies (atomistic $\rightarrow$ macroscopic properties)		
$S(E, V, N) = k_B \ln \Omega$	$F(T, V, N) = -k_B T \ln Z$	$G(T, P, N) = -k_B T \ln Z_P$

canonical (NVT) averages  $\longleftrightarrow$  time averages

From an (NVT) MD simulation it is expected that the average kinetic energy corresponds to the desired temperature (recall equipartition of energy  $\langle K \rangle = \frac{3N}{2} k_B T$ ) and that the dynamics of the system is consistent with the canonical distribution.

Different thermostats have been developed for (NVT) MD simulations:

## 7.3 Thermostats

Ensure that desired temperature is applied to system

### 7.3.1 Andersen thermostat (1980)

Coupling of system with heat bath:

stochastic collisions between randomly selected particles with the bath that result in a new velocity consistent with the desired temperature:

- (i) integrate equations of motion for time  $\Delta t$

- (ii) number of atoms that were involved in collisions during  $\Delta t$  is  $\nu\Delta t$  with  $\nu$  the coupling constant; these are selected randomly
- (iii) assign new velocities to selected atoms from a Maxwell-Boltzmann distribution at temperature  $T$

The thermostat leads to a canonical distribution but the collisions affect the atomic dynamics (e.g. diffusion coefficients)

### 7.3.2 Berendsen thermostat (1984)

The equations of motion are modified to obtain the desired temperature

$$\begin{aligned}\dot{\vec{r}}_i &= \frac{\vec{p}_i(t)}{m_i} \\ \dot{\vec{p}}_i &= \vec{F}_i(t) - \gamma(t)\vec{p}_i(t) \\ \dot{\gamma}(t) &= \nu \frac{T(t) - T_0}{T(t)}\end{aligned}$$

characteristics of thermostat:

- direct feedback to control temperature
- $\gamma$  is a heat flow variable (negative or positive)
- $\gamma$  is defined in terms of instantaneous temperature  $T$  and thermostat temperature  $T_0$
- MD temperature converges to desired temperature

but thermostat does not lead to a canonical distribution, which is remedied by the Nosé-Hoover approach

### 7.3.3 Nosé-Hoover thermostat (1984-1985)

Equations of motion are again modified:

$$\begin{aligned}\dot{\vec{r}}_i &= \frac{\vec{p}_i(t)}{m_i} \\ \dot{\vec{p}}_i &= \vec{F}_i(t) - \nu\gamma(t)\vec{p}_i(t) \\ \dot{\gamma}(t) &= \nu \frac{T(t) - T}{T}\end{aligned}$$

characteristics of thermostat:

- heat flow variable has its own equation of motion: integral feedback
- enables kinetic energy fluctuations
- leads to canonical distribution
- time reversible

but approaching the equilibrium can lead to fluctuations and persistent, non-canonical oscillations can occur if care is not taken.



## 7.4 Integration & search schemes in MD

Newton's equations of motion  $\vec{F}_i(\vec{r}_i) = m_i \frac{d^2 \vec{r}_i}{dt^2}$  can be solved analytically only for  $N < 3$ , where  $N$  is the number of particles in the system. For  $N > 3$  the equations can be solved only numerically by integrating the equations of motion in small steps. Specific algorithms have been developed for the integration. Examples of these algorithms - the most common ones - are given.

Another issue also in MD simulations is the "search problem"; i.e. searching for the global energy minimum of a system. A system can have a very large number of degrees of freedom. These can relate to harmonic, anharmonic, chaotic, or diffusive motions. Correlations are almost always present and cover time and spatial scales from fs and nm to ms and  $\mu\text{m}$ . In this respect the potential function defines a very rugged energy hyper-surface. The energy surface has energy wells and mountains of a wide range of depths and heights and spatial extent. Searching the regions of the system which mostly contribute to the free energy (looking for a global minimum of a high-dimensional function) is difficult. A global minimum can be described only by a statistical mechanics ensemble of configurations in which the weight is given by the Boltzmann factor

$$P(x) \sim \exp\left(-\frac{V(x)}{k_B T}\right)$$

The equilibrium properties of the system are dominated by the parts of configuration space with a low  $V(x)$ . High-energy regions of the energy hyper-surface do not contribute configuration relevant to the state of the system, unless they are numerous (high entropy).

## 7.5 Search & sample configuration space techniques

Search techniques depend on potential  $V(x)$  as well as the number and types of degrees of freedom. The "probability search" techniques also depend on the Boltzmann probabilities  $P(x)$ .

Basic search methods are either *systematic* or *heuristic*.

### (a) Systematic (exhaustive) search methods

Scan the complete (or a significant fraction of) configuration space. Exclude particular subspaces which do not contain desired solution only if there is no reduction in the quality of the result. Exclusion is usually based on a priori (physical/chemical nature) knowledge about structure of space or energy hyper-surface. Applied to small systems (exponential growth of computing time as degrees of freedom increase)

### (b) Heuristic search methods

The aim is to generate a representative (according to Boltzmann weighting) set of system configurations by visiting a very small fraction of configuration space. There are 3 types of heuristic schemes

(i) Non-step : generate series of independent system configurations. E.g. distance-geometry metric

matrix method : uncorrelated

series of random configurations cast into a distance-based form

(ii) Step : build complete system configuration from configurations of fragments of system in step-wise manner

E.g. build-up Gibson-Scheragen, combinatorial programming techniques, Monte Carlo chain growing method (configurational bias Monte Carlo)

(iii) Step methods generating a new configuration of complete system from previous configuration (energy minimization, Metropolis Monte Carlo, MD, stochastic dynamics); classified with regard to the way step direction and step size are chosen.

Energy minimization : based only on energy values and random steps (simplex schemes) or on energy and energy gradient values (steepest descent and conjugate-gradient schemes) or on 2nd derivatives of energy (Hessian matrix schemes).

MC : randomly chosen step direction; step size limited by Boltzmann acceptance criterion: if  $\Delta V < 0$  (change in system energy) step in configuration space is accepted, if  $\Delta V > 0$  step is accepted with probability  $e^{-\Delta V/k_B T}$

MD : step determined by force ( $\propto -\frac{\partial V}{\partial x}$ ) and inertia of degrees of freedom ( $\rightarrow$  short time memory of path followed until current step).

SD : random component added to force, the size of which is determined by the system temperature, atomic masses and friction coefficients.

Also search procedures based on stepping through configuration space using a combination of the above (energy, gradient, Hessian, memory, randomness).

Efficiency of search methods restricted by  $V(x)$  to be explored to find low-energy regions. Occurrence of high-energy barriers between local minima means that radius of convergence of step methods is small  $\rightarrow$  need to enhance search and sampling power of search methods. For this, three types of search and sampling enhancement techniques exist:

(a) Deformation or smoothing of potential energy surface

- omit high-resolution diffraction intensities for structure when calculating electron density from these through Fourier transform
- gradually introduce distance restraints connecting atoms at longer distances in the potential energy function (variable-target function method)
- soften repulsive short-range interaction between overlapping atoms (reduce energy barriers)
- deformation of energy surface during simulation based on diffusion equation is made proportional to local curvature (2nd derivative) of surface
- once local minimum found, it is removed from potential energy surface through suitable local deformation of energy surface
- time average to soften geometric constraints from experimental data
- circumvent energy barriers by extension of dimensionality of configuration space beyond 3D Cartesian
- constraints to freeze highest-frequency degrees of freedom (e.g. bond length constraints  $\rightarrow 4\times$  longer time step)
- coarse graining

(b) Scaling system parameters

- temperature annealing
- atomic mass scaling (enhanced relative inertia  $\rightarrow$  overcome barriers)
- mean-field approximation

(c) Multi-copy search and sample

- genetic algorithms (configurations created and deleted)
- replica-exchange (multiple system copies at different temperatures)
- SWARM : Combine collection (swarm) of copies of system each with own trajectory into cooperative multi copy system which searches configurational space.

## 7.6 Algorithms

### (a) Verlet algorithm

Start with a Taylor expansion:

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{\vec{F}(t)}{2m}\Delta t^2 + \frac{\Delta t^3 \dots}{3!}\ddot{\vec{r}} + \mathcal{O}(\Delta t^4)$$

similarly

$$\vec{r}(t - \Delta t) = \vec{r}(t) - \vec{v}(t)\Delta t + \frac{\vec{F}(t)}{2m}\Delta t^2 - \frac{\Delta t^3 \dots}{3!}\ddot{\vec{r}} + \mathcal{O}(\Delta t^4)$$

sum both equations to obtain:

$$\vec{r}(t + \Delta t) + \vec{r}(t - \Delta t) = 2\vec{r}(t) + \frac{\vec{F}(t)}{m}\Delta t^2 + \mathcal{O}(\Delta t^4)$$

or

$$\vec{r}(t + \Delta t) \approx 2\vec{r}(t) - \vec{r}(t - \Delta t) + \frac{\vec{F}(t)}{m}\Delta t^2$$

To start integration: specify  $\vec{r}(t)$  and  $\vec{v}(t)$ . The Verlet algorithm does not use velocities to compute new positions.

The velocities are derived from the trajectory and used only to calculate kinetic energy and instantaneous temperature

$$\begin{aligned} \vec{r}(t + \Delta t) - \vec{r}(t - \Delta t) &= 2\vec{v}(t)\Delta t + \mathcal{O}(\Delta t^3) \\ \rightarrow \vec{v}(t) &= \frac{\vec{r}(t + \Delta t) - \vec{r}(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \end{aligned}$$

Advantages

- fast
- time reversible (if velocities are reversed at a given time, the algorithm traces back its steps)
- symplectic (conserves volume in phase space as Hamiltonian dynamics does)
- good short-term energy conservation and small long-term energy drift
- trajectory very close to the constant energy hyper-surface in phase space (note  $S = k_B \ln \Omega(E, V, N)$ )

Disadvantages

velocities do not enter directly (difficult in case of  $T = \text{const.}$  simulations)

### (b) Leap-frog algorithm

Use Euler method to numerically solve differential equations. For Newton's equations of motion:

$$\begin{aligned} x(t + \Delta t) &= x(t) + v(t)\Delta t \\ v(t + \Delta t) &= v(t) + \frac{F(t)\Delta t}{m} \end{aligned}$$

A better approximation is to replace  $v$  by its value at midpoint of the time interval

$$x(t + \Delta t) = x(t) + v\left(t + \frac{\Delta t}{2}\right)\Delta t$$

to propagate  $v$  a similar midpoint rule is used:

$$v\left(t + \frac{3\Delta t}{2}\right) = v\left(t + \frac{\Delta t}{2}\right) + \frac{F(t + \Delta t)\Delta t}{m}$$

Leap-frog algorithm: generate positions and velocities shifted by  $\frac{\Delta t}{2}$ . First, update the positions, then recalculate forces and finally update velocities...

How to start a leap-frog algorithm if only  $r(0)$  and  $v(0)$  are given?

simple way: do single half step:

$$v\left(\frac{\Delta t}{2}\right) = v(0) + \frac{1}{2} \frac{F(t)\Delta t}{m}$$

(c) Velocity Verlet algorithm

Velocities might also be needed at the same time points as the positions in order to correctly calculate kinetic energy, potential energy and total energy at the same time. One way to do this is to split the leap-frog algorithm into two half steps, which is called the velocity Verlet algorithm:

$$\begin{aligned} v\left(t + \frac{\Delta t}{2}\right) &= v(t) + \frac{1}{2} \frac{F(t)\Delta t}{m} \\ r\left(t + \frac{\Delta t}{2}\right) &= r(t) + v\left(t + \frac{\Delta t}{2}\right) \Delta t \\ v(t + \Delta t) &= v\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2} \frac{F(t + \Delta t)\Delta t}{m} \end{aligned}$$

This scheme is equivalent to the leap-frog scheme. Forces are still only calculated once per time step.

The scheme can be simplified by inserting previous equation for  $v\left(t + \frac{\Delta t}{2}\right)$  into that for  $v(t + \Delta t)$

$$\begin{aligned} v(t + \Delta t) &= v(t) + \frac{1}{2} \frac{F(t)\Delta t}{m} + \frac{1}{2} \frac{F(t + \Delta t)\Delta t}{m} \\ v(t + \Delta t) &= v(t) + \frac{\Delta t}{2m}(F(t) + F(t + \Delta t)) \end{aligned}$$

The complete Velocity Verlet algorithm is often written as:

$$\begin{aligned} r(t + \Delta t) &= r(t) + v\left(t + \frac{\Delta t}{2}\right) \Delta t \\ v(t + \Delta t) &= v(t) + \frac{\Delta t}{2m}(F(t) + F(t + \Delta t)) \end{aligned}$$

The algorithm gives positions and velocities at the same time points.

(d) Higher order algorithms

- Include higher order terms in Taylor expansion for  $r$  and  $v$ : Beemavis algorithm, Gear Predictor-Corrector, Forest-Ruth
- Better conservation of energy, longer time steps
- Often not symplectic
- Often require several force calculations per step

Characteristics of the three main algorithms:

- The Leap-Frog and Velocity Verlet algorithms are less susceptible to round-off errors than the Verlet method (terms of order  $\Delta t$  vs  $\Delta t^2$ )
- The algorithms are time reversible
- The Leap-Frog and Velocity Verlet algorithms conserve the angular momentum
- The algorithms are symplectic (area conserving)

## 8 MD simulations of biomolecules

### 8.1 General remarks on MD

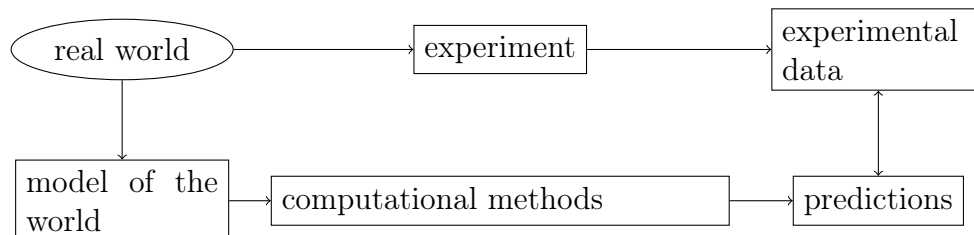
Time and length scales in biomolecular simulations:

2001 biomolecules in water  $\sim 10^6$  atoms for 1 ns

2010 1 ms simulation of a small protein in water

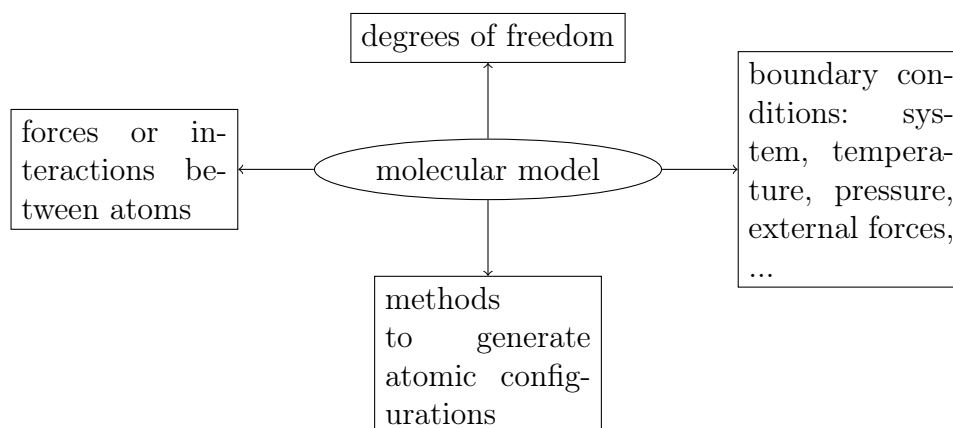
2029 ... 1 ms simulation of biomolecules in water?

Molecular simulations:



Strategy in molecular simulations:

Balance between choices made with regard to degrees of freedom, force fields, sampling and boundary conditions.



Choices depend on 3 factors (see von Gunsteren et al, *Angewandte Chemie*, 45; 4064 (2006))

#### 8.1.1 Convergence

Time-scales are relevant to various systems (dynamics of biomolecules or materials' processes) from fs to s or longer. Current Molecular Dynamics cover up to tens of hundreds of ns. Are these time scales long enough to generate reliable trajectories, properties, etc.?

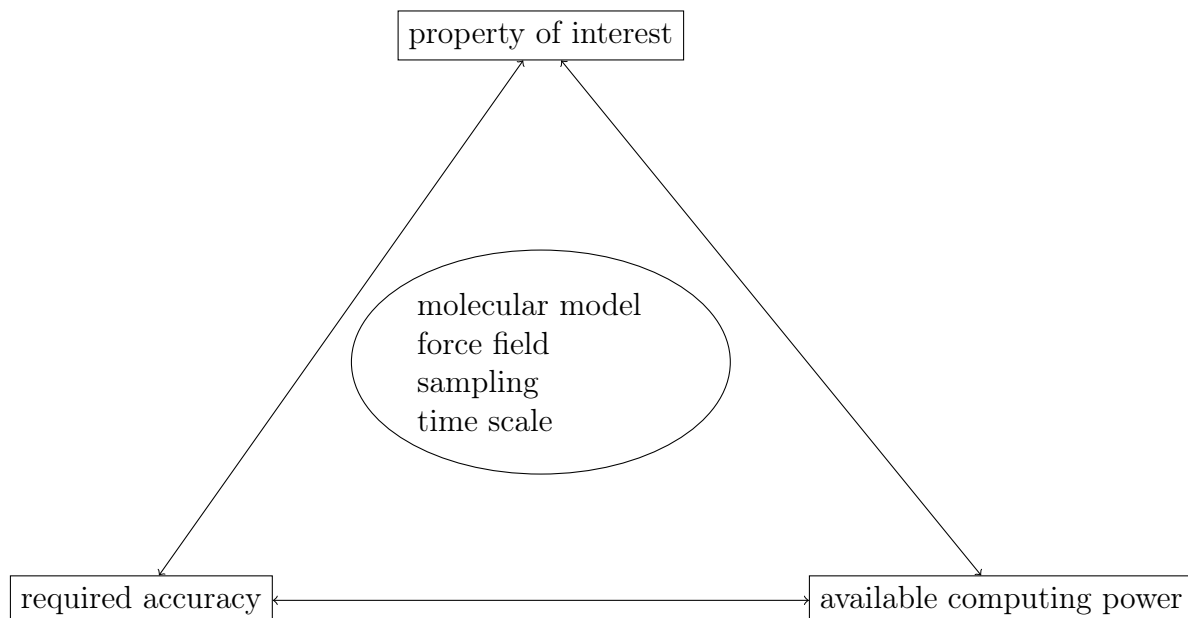
Reliable results may be expected if:

$$\begin{aligned} \tau_{\text{equil}} &> \tau_{\text{relax}}(Q) \\ \tau_{\text{sample}} &\ll \tau_{\text{relax}}(Q) \end{aligned}$$

, where  $Q$  is a property of the system,  $\tau_{\text{equil}}$  is the equilibration time of the simulation and  $\tau_{\text{relax}}$  is the relaxation time of property  $Q$ .  $\tau_{\text{sample}}$  is the sampling time.

Choice of  $\tau_{\text{relax}}(Q)$

1. equilibrium simulations: monitor time dependence of  $Q(t)$ , average  $\langle Q(t) \rangle$ , or fluctuations  $\langle (Q(t) - \langle Q(t) \rangle)^2 \rangle^{1/2}$  or autocorrelation function  $\langle Q(t')Q(t'+t) \rangle$ .  $\tau_{\text{relax}}(Q)$  is defined from the decay time of the autocorrelation function or build-up rate of trajectory/ property averages



2. start simulation from non-equilibrium initial state,  $\tau_{\text{relax}}(Q)$  given from rate of relaxation of  $Q(t)$  toward equilibrium and measured over many non-equilibrium trajectories
3. if Molecular Dynamics simulations starting from a different initial condition do not converge to the same averages for  $Q$ , then  $\tau_{\text{relax}}(Q)$  is longer than the simulation time

### 8.1.2 Basic problems of classical modelling

- i. force-field
  - (a) very small (free) energy differences, many interactions
  - (b) entropic effects
  - (c) wide range of atoms/molecules
- ii. search problem
  - (a) convergence
  - (b) alleviating factors (state of system contains much fewer conformations significantly populated at equilibrium than possible conformations for the system)
  - (c) aggregating factors (inclusion of degrees of freedom in sampling necessary for good results)
- iii. ensemble problem
  - (a) averaging
  - (b) entropy
  - (c) non-linear averaging
- iv. experimental problem
  - (a) averaging
  - (b) insufficient data
  - (c) insufficient accuracy of data

Table 1: Levels of modelling

Method	Degrees of freedom	Properties/Processes	Time scale
quantum dynamics	atoms, nuclei, electrons	excited states, relaxation, reaction dynamics	ps
quantum mechanics (ab initio, DFT, valence bond, semi-empirical)	atoms, nuclei, electrons	ground/excited states, reaction mechanisms	no time scale
classical statistical mechanics (MD,MC,force-fields)	atoms, nuclei	ensembles, averages, system properties/dynamics (e.g. folding)	ns
statistical mechanics (database analysis)	group of atoms, residues, molecules	structural homology and similarity	no time scale
continuum methods (hydrodynamics, electrostatics, finite element,...)	electrical continuum, velocity continuum	rheological crack propagation	supra-molecular
kinetic equations	population of species	population dynamics, materials failure (fracture)	macroscopic

### 8.1.3 Levels of modelling

## 8.2 Classical interactions

### 8.2.1 Biomolecular systems - Force Fields

A biomolecular Force Field consists of energy terms representing covalent interactions between atoms (bond-stretching, bond-angle bending, improper/proper dihedral-angle torsion) and non-bonded interactions between atoms in different molecules or the same molecules (but which are separated by more than two or three covalent bonds).

Force Field development issues:

- Free energy differences guiding biophysical processes are  $\sim 1 - 10 k_B T$ , which results from a summation over many atom pairs ( $N = 1000$  atoms  $\rightarrow \frac{1}{2}N(N-1) = 5 \cdot 10^4$  pairs contributing to non-bonded interactions).  
To reach accuracy in total non-bonded energy, the accuracy of individual energy terms should be higher
- account for entropic effects in free energy ( $F = U - TS$ ,  $T \neq 0$ );  $U$  and  $S$  work together or against each other depending on relative strengths of non-bonded interactions in the system. The Force Field is calibrated for simulations above 0 K.
- Force Field transferability  
do not apply to a variety of molecules, for which it was not developed

Examples of functional forms of a Force Field

(a) CHARMM (Chemistry at HARvard Molecular Mechanics)

$$\begin{aligned} V(r) = & \sum_{\text{bonds}} K_b(b - b_0)^2 && \text{bond stretching} \\ & + \sum_{\text{angles}} K_\theta(\theta - \theta_0)^2 && \text{bond-angle bending} \\ & + \sum_{\text{dihedrals}} K_x(1 + \cos(n_x - \delta)) && \text{dihedral angle torsion} \\ & + \sum_{\text{Urey-Bradley}} K_{UB}(S - S_0)^2 && \text{interaction based on distance between atoms sep-} \\ & && \text{arated by two bonds - 1,3 interaction} \\ & + \sum_{\text{improper}} K_\varphi(\varphi - \varphi_0)^2 && \text{improper dihedral angles torsion} \\ & + \sum_{\text{non-bonded pairs}} \left( \epsilon_{ij} \left[ \left( \frac{R_{ij}^{\text{min}}}{r_{ij}} \right)^{12} - \left( \frac{R_{ij}^{\text{min}}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\epsilon_0 n y} \right) && \text{non-bonded interactions} \\ & && \text{(LJ + Coulomb)} \end{aligned}$$

$K_b, K_\theta, K_x, K_{UB}, K_\varphi$  constants

$b, \theta, S, x, \varphi$  bond length, bond angle, Urey-Bradley 1-3 distance, dihedral torsion angle and improper dihedral angle, respectively

Subscript 0 denotes equilibrium values.

Dihedral term:  $n_x$  denotes multiplicity,  $\delta$  the phase which dictates the location of minima and maxima.  $\delta$  can be set to any value, and combined with expansion of dihedral term into Fourier series via  $n_x$ , allows for extended flexibility of dihedral term.

Non-bonded (external) interactions:

$\epsilon$  LJ well depth

$R^{\text{min}}$  distance at LJ minimum interaction energy

$q_i$  partial atomic charge

$\epsilon_D$  dielectric constant. =1 for explicit solvent.

$r_{ij}$  distance between atoms  $i$  and  $j$

CHARMM : extensive optimization of every term in Force Field, with little emphasis on transferability.

Maximum agreement with quantum mechanical target data for model compounds and experimental target data for model compounds and macromolecules.

CHARMM27 : emphasis on balancing local small molecule based properties with global condensed phase or macro-molecular properties during parameter optimization.

Parameter development for novel molecules is achieved by following specific (published) protocols.

Force Field development in CHARMM :

Self-consistency among different terms in potential energy by iterative optimization of parameters. Initial values of inter-molecular parameters (Coulomb, LJ) based on reproduction of ab initio interaction calculations on rigid monomers. Given these, the intra-molecular parameters (bond-length, Urey-Bradley, bond angle, improper/proper dihedral terms) are determined by using vibrational and structural data for the model compounds. The resulting structures are used for optimization of inter-molecular parameters relative to interaction energies and condensed-phase properties of model compounds. With improved interaction parameters, the structures,



vibrational spectra and energy surfaces of model compounds are re-optimized by adjusting the internal (bonded) parameters. The iterative process is repeated until convergence of parameters is achieved.

(b) GROMOS (Groningen Molecular Simulation)

The potential energy function consists of the following terms:

$$\begin{aligned}
 V^{\text{bonds}}(\vec{r}; K_b, b_0) &= \sum_{n=1}^{N_b} \frac{1}{4} K_{b_n} [b_n^2 - b_{0_n}^2]^2 && \text{bond stretching} \\
 V^{\text{angle}}(\vec{r}; K_\theta, \theta_0) &= \sum_{n=1}^{N_\theta} \frac{1}{2} K_{\theta_n} [\cos(\theta_n) - \cos(\theta_{0_n})]^2 && \text{bond angle bending} \\
 V^{\text{har}}(\vec{r}; K_\chi, \chi_0) &= \sum_{n=1}^{N_\chi} \frac{1}{2} K_{\chi_n} [\chi_n - \chi_{0_n}]^2 && \text{improper dihedral angle torsion} \\
 V^{\text{trig}}(\vec{r}; K_\varphi, \delta, m) &= \sum_{n=1}^{N_\varphi} K_{\varphi_n} [q + \cos(\delta_n) \cos(m_n \varphi_n)] && \text{proper dihedral angle torsion} \\
 V^{\text{LJ}}(\vec{r}; C_{12}, C_6) &= \sum_{i \neq j} \left[ \frac{C_{12}(i, j)}{r_{ij}^{12}} - \frac{C_6(i, j)}{r_{ij}^6} \right] && \text{van der Waals forces (LJ)} \\
 V^{\text{C}}(\vec{r}; q) &= \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0\epsilon_1} \frac{1}{r_{ij}} && \text{electrostatic interactions} \\
 V^{\text{RF}}(\vec{r}; q) &= \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon_0\epsilon_1} \frac{-\frac{1}{2} C_{rf} r_{ij}^2}{R_{rf}^3} && \text{distance independent interaction from RF}
 \end{aligned}$$

The dipolar reaction field (RF) is induced by charge distribution inside cut-off sphere through continuous dielectric medium outside this sphere.

The Force Field covers a variety of molecules and includes 52 types of bonds, 54 types of bond angles, 3 types of improper (harmonic) dihedral angles, 41 types of proper torsional (trigonometric) dihedral angles, van der Waals interactions of 53 types of atoms and different sets of atomic charges for typical polar/charged groups of atoms in molecules, for which GROMOS was developed.

Functional form chosen such that terms are easily computed: non-bonded interactions contain only pair terms and more complex 3-/4-body terms are much fewer than non-bonded pair terms. Solvent part of Force Field: only non-bonded terms; intra-molecular degrees of freedom of solvent molecules are kept frozen. Major computational effort: evaluation of non-bonded interactions.

### Calibration of GROMOS Force Field

A bio-molecular system is usually in condensed phase; data from condensed phase are used when possible. Maximize transferability by using only data for small molecules; when using data from large molecules, properties of groups of atoms may depend on particular environment.

Strategy:

geometric parameters for covalent interaction terms from crystal structures of small molecules; vibrational force constants from infrared spectroscopic data on small molecules in gas phase

- non-bonded  $C_6, C_{12}, q$  from fitting heats of vaporization, densities of pure liquids, free energies of solvation of small solutes in polar and apolar solvents (from MD simulations to data from experiments)
- Dielectric permittivities and diffusion properties of liquids used as secondary data for parameterization

- electron densities from QM only for initial guess of partial atomic charges (as they depend strongly on environment as a result of polarization effects)
- torsional angle parameters derived by fitting torsional-energy profiles to QM data leaving set of non-bounded parameters the same

Force Field: consistent set of parameters for both solute molecules and solvent. Changing a subset of parameters by taking these from another Force Field or model may introduce inaccuracy and inconsistencies.

structural data (exp.)	$\longleftrightarrow$	$b_0, \theta_0, \chi_0$ (geometries)
spectroscopic data (exp.)	$\longleftrightarrow$	$K_b, K_\theta, K_\chi$ (vibrational forces)
thermodynamic data (exp.)	$\longleftrightarrow$	$C_{12}(i, j), C_6(i, j), q_i$ final (heat of vaporization, free energy of solvation, ...)
dielectric data (exp.)	$\longleftrightarrow$	charges $q_i$ (dielectric permittivity)
transport data (exp.)	$\longleftrightarrow$	$C_{12}(i, j), C_6(i, j), q_i$ (diffusion and viscosity coefficients)
electron densities (theory)	$\longleftrightarrow$	charges $q_i$ initial (atom charge)
energy profiles (theory)	$\longleftrightarrow$	$K_\varphi, \delta, m$ (rotational profile)

Benchmark : test Force Field by applying it to systems containing different, larger molecules in condensed phase. Comparison of simulated properties with available experimental data. For solid-state (materials) systems, interactions are modelled differently, i.e. through simpler pair-wise potentials.

## 9 Hydrodynamic methods

### 9.1 Mesoscopic particle methods

Mesoscale :

- links atomistics with macroscopic behavior
- computationally less demanding (reaches larger length and time scales)

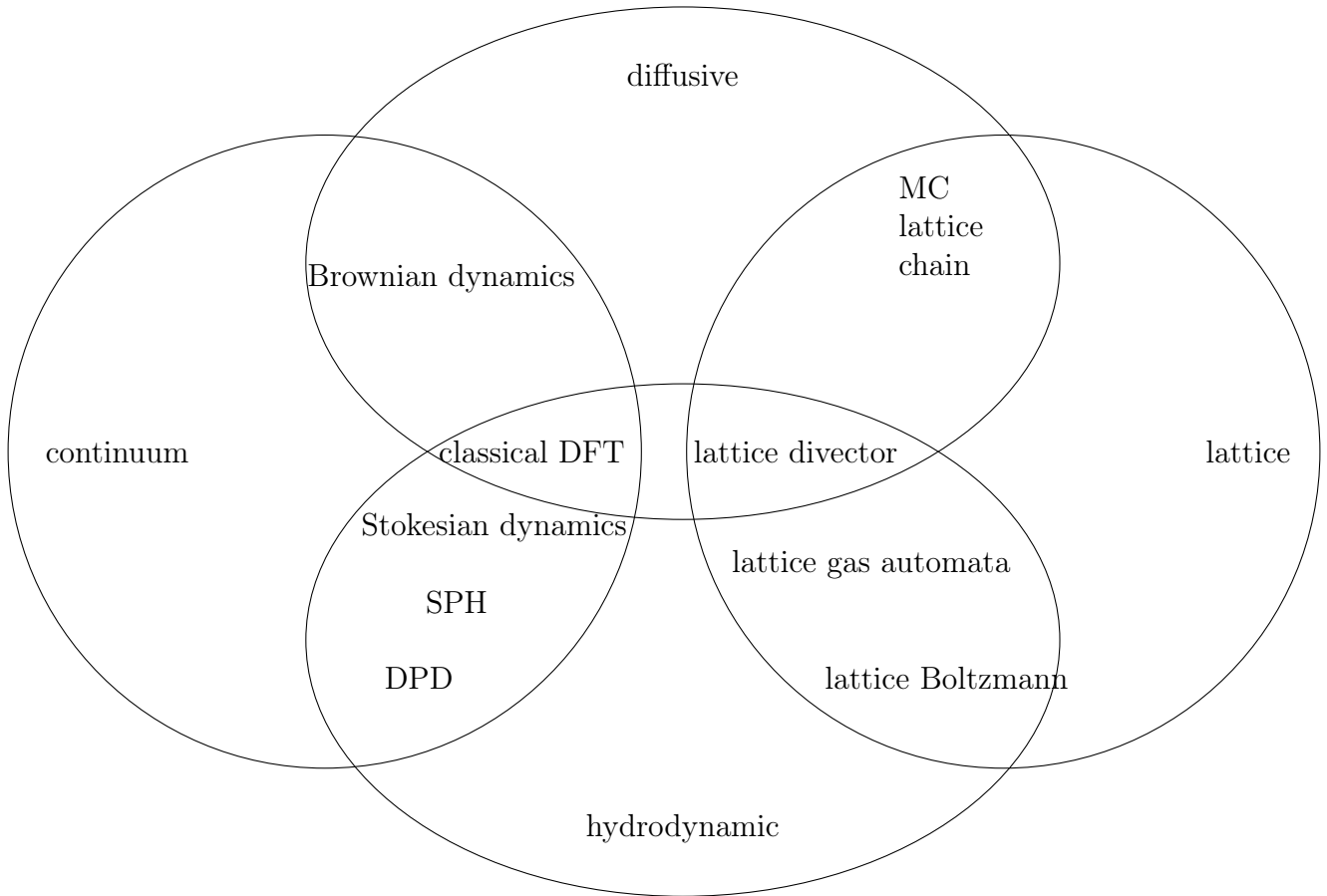
Applications of mesoscale modelling:

- block-copolymers, surfactants
- dislocations in metals
- biomedical materials
- any type of self-organizing material

Definition of mesoscale: if at that length and associated time scale one can assume that the degrees of freedom pertaining to a smaller scale will be in equilibrium when seen from that scale.

Mesoscale modelling techniques: SPH : smooth particle hydrodynamics

DPD : dissipative particle dynamics



Particle methods : "particles" defined by a set of attributes whose physical meaning depends on specific spatio-temporal scales. Particles can be atoms, molecules (direct simulation of discrete components), volumes of fluid, moving mesh nodes (Lagrangian simulation of continuum equations).

## A. Continuum methods

### 9.1.1 Brownian Dynamics (BD)

- Brownian motion of particles is of a stochastic nature - random kicks between particles
- Brownian motion an experimental evidence for the kinetic theory of gases
- kinetic theory: describes a gas as a large number of small particles all of which are in constant, random motion

The mean kinetic energy of a Brownian particle is given by the equi-partition theorem:

$$\frac{1}{2}m\langle v \rangle = \frac{3}{2}k_B T \quad (9.1)$$

Einstein relation (motion of a Brownian particle as a stationary random walk):

$$\langle x^2 \rangle = Nl^2 = \frac{l^2 t}{\tau} \quad (9.2)$$

$N$  number of steps of length  $l$  in a random walk with mean time  $\tau$  between collisions

**Langevin approach** : particle moves in a dissipative medium, i.e. experiences frictional forces. The thermal, or "kicking", forces of the surrounding particles, are represented by an average time-dependent force. The Langevin equation for a system of  $N$  Brownian particles is:

$$\dot{p}_i = m_i \dot{v}_i = F_i(r) + \sum_j \chi_{ij} v_j + \sum_j a_{ij} f_j \quad (9.3)$$

$p_i$  momentum

$\chi_{ij}$  hydrodynamic friction tensor

$F_i$  sum of inter-particle and external forces

$\sum_j a_{ij} f_j$  randomly fluctuating force exerted on a particle by surrounding (fluid) environment. Negligible for particles larger than 1 fm

Properties of the fluctuating force:

- zero time average

$$\langle f_i \rangle = 0$$

- independently applied on  $i, j$  particles of different positions at different times

$$\langle f_i(t) f_j(t') \rangle = 2\delta_{ij} \delta(t - t')$$

- related to friction coefficient

$$\chi_{ij} = \frac{1}{k_B T} \sum_k a_{ik} a_{jk}$$

The time evolution equation is derived through integration of Langevin equation:

$$r_i(t + \Delta t) = r_i(t) + \sum_j \frac{D_{ij}(t)}{k_B T} F_j \Delta t + (\nabla D) \Delta t + \Delta r_i^G$$

where  $\Delta r_i^G$  are the random replacements selected from a  $3N$  Gaussian distribution with zero mean and covariance matrix:

$$\langle \Delta r_i^G \rangle = 0 \quad , \quad \langle \Delta r_i^G \Delta r_j^G \rangle = 2D_{ij} \Delta t$$

The Oseen tensor is given by:

$$D_{ij} = \frac{k_B T}{8\pi\eta} \left( \frac{\mathbb{I}}{r} + \frac{\mathbf{r}\mathbf{r}^T}{|\mathbf{r}|^3} \right)$$

where  $\nabla D = 0$ . For  $F_j \approx 0$ , random motion is dominant in multi-particle dynamics.

Langevin equation with inter-particle (conservative) forces  $f^P$ , drag forces  $f^H = -\chi\mu$  and random Brownian forces  $f^B$ :

$$m \frac{dv}{dt} = f^P + f^H + f^B(t)$$
$$f^H = -\chi v$$

$$\langle f^B(t) \rangle = 0$$

$$\langle f^B(0) f^B(t) \rangle = 6\chi k_B T \delta(t)$$

Stokesian dynamics

Langevin Eq. for system of  $N$  force-free non Brownian particles:

$$\dot{p}_i = m_i \dot{v}_i = - \sum_j \chi_{ij} (v_j - v) = F^H$$

with  $F^H$  the hydrodynamic forces and torques.

Simulation of fluids:

- microscopic description

fluid as a collection of atoms/molecules interacting through classical (or quantum mechanical) potentials  $V(r)$ , following Newton's equation of motion

$$\dot{\vec{r}}_i = \vec{v}_i \dot{\vec{r}}_i = -\nabla_i V(\vec{r}_1, \dots, \vec{r}_N)$$

- mesoscopic description

statistical description of fluid given by one-particle phase-space distribution functions  $f(t, \vec{r}, \vec{v})$  density

$$\langle n(\vec{r}, t) \rangle = \int f(t, \vec{r}, \vec{v}) dV$$

macroscopic velocity

$$\langle v(\vec{r}, t) \rangle = \frac{1}{\langle n \rangle} \int f(t, \vec{r}, \vec{v}) \vec{v} dV$$

kinetic theory:

$$\frac{df}{dt} = \underbrace{\partial_t f + \vec{v} \nabla f}_{\text{free streaming operator}} + \underbrace{C(f)}_{\text{collision operator}}$$

free streaming term: local change in  $f$  is due to independent motion of particles only and is zero in the absence of collisions; rate of change of distribution is due to collisions

- continuum picture

a volume element of the fluid is large enough to neglect underlying microscopic structure but small enough to be treated mathematically as infinitesimal. E.g. conservation of mass:

$$\oint_{\Sigma} \rho \underbrace{\vec{v} d\vec{S}}_{\text{flux of mass}} = -\partial_t \underbrace{\int_{\Sigma} \phi dV}_{\text{mass}} = \int_{\Sigma} \nabla(\rho \vec{v}) dV$$

$$\xrightarrow{\Sigma \rightarrow 0} \boxed{\partial_t \rho + \nabla(\rho \vec{v}) = 0} \quad \text{continuity equation}$$

geometrical considerations: continuum assumption + conservation laws

discretization: approximate equations using suitable discretization techniques and numerical solving

### 9.1.2 Dissipative Particle Dynamics (DPD)

- off-lattice mesoscopic simulation scheme
- set of particles moving in continuous space and discrete time
- simulates dynamic and rheological properties of simple and complex fluids
- particles represent whole molecules or fluid regions  
→ coarse-grained entities reproducing the mesoscopic dynamics correctly
- stochastic method, off-lattice version of lattice gas automata
- describes collection of molecules moving coherently
- coarse graining of molecular mechanics
- dissipation-fluctuation theorem enforced  
canonical ensemble (MD-type) but with preserved hydrodynamics

Original Dissipative Particle Dynamics model: collection of soft repelling, frictional and noisy balls.  
3 types of forces between dissipative particles:

- (i) conservative : derived from a soft potential which tries to capture effects of "pressure" between different particles
- (ii) frictional : describes viscous resistance in real fluids
- (iii) stochastic : describes degrees of freedom eliminated in the coarse graining process (responsible for Brownian motion of particles)

Fundamental variables are  $\vec{r}$  and  $\vec{p}$

$$d\vec{r}_i = \vec{v}_i dt$$

$$m_i d\vec{v}_i = \sum_{i \neq j} F_{ij}^c(r_{ij}) dt - \gamma \sum_{i \neq j} w(r_{ij}) (\hat{e}_{ij} \vec{v}_{ij}) dt + \sigma \sum_{i \neq j} w^{1/2}(r_{ij}) \hat{e}_{ij} dW_{ij}$$

$F_{ij}^c$  conservative, repulsive force between dissipative particles  $i$  and  $j$

$\gamma$  friction coefficient which governs overall magnitude of dissipative force

$\sigma$  noise amplitude which defines the intensity of the stochastic force

$w$  weight function which provides the range of interaction for dissipative particles  $\rightarrow$  local nature, i.e. particles interact only with neighbors

$dW_{ij} = dW_{ji}$ . Satisfies  $dW_{ij} dW_{i'j'} = (\delta_{ii'} \delta_{jj'} + \delta_{ij'} \delta_{i'j})$

- The equations are translationally, rotationally and Galileo invariant
- The total momentum is preserved  $d(\sum_i \vec{p}_i)/dt = 0$ . (3 types of forces satisfy Newton's third law)
- DPD captures mass/momentum conservation responsible for hydrodynamic behavior of a fluid at large scales
- all forces pair-wise between particle center of mass  $\rightarrow$  linear/angular momentum conserved
- DPD explores mesoscopic time scales because all terms are soft and short ranged
- softness of potential prevents energy from diverging for long time steps
- stochastic and frictional forces related through fluctuation-dissipation theorem  $\rightarrow$  random energy kick for all particles with associated viscous drag to remove equal amount of energy from system
- versatile, construct simple models for complex fluids
- Newtonian fluid made complex by adding additional interactions

## B. Lattice methods

The Navier-Stokes equation

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho \vec{v} \cdot \nabla \vec{v} = -\nabla p + \mu \nabla^2 \vec{v} + (\mu + \lambda) \nabla(\nabla \cdot \vec{v}) \quad (9.4)$$

$\rho$  density

$p$  pressure

$\lambda, \mu$  Lamé parameters

and the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \vec{v}) = 0 \quad (9.5)$$

can be solved by discretization on a grid.

Lattice gas: discrete particles moving on a lattice from site to site, colliding.

### 9.1.3 Lattice Boltzmann Method (LBM)

- fluid represented as a dilute gas of particles
- particles move freely most of the time except for two-body collisions
- such a dilute gas is described through the Boltzmann equation
- Navier-Stokes equation is derived (in a certain limit) from the Boltzmann equation

(i) Simple, a-thermal Lattice Boltzmann Method model:

Macroscopic variables are defined as functions of particle distribution functions (probability).

Local stress tensor:

$$\Pi_{m,n} = \sum_{i=0}^{\beta-1} \vec{e}_{i,m} \vec{e}_{i,n} (f_i - f_i^{eq})$$

Macroscopic fluid density:

$$\rho = \sum_{i=0}^{\beta-1} f_i$$

Macroscopic velocity:

$$\vec{u} = \frac{1}{\rho} \sum_{i=0}^{\beta-1} f_i \vec{e}_i$$

$f$  discretized probability distributions which represent the central link to the Lattice Boltzmann Method. Discrete-velocity analogue of continuous space single-particle probability distribution functions  $f(\vec{x}, \vec{v}, t) d^3x d^3v$  (probability to find particle in volume  $d^3x$  with a velocity in the range  $[\vec{v}, \vec{v} + d\vec{v}]$ )

$f_i$  probability for site  $\vec{x}$  to have a particle heading in direction  $i$  at time  $t$ .  $f_i$  "reside" on a lattice for which many choices exist

Lattices classified as  $D_\alpha Q_\beta$

$\alpha$  space dimensionality

$\beta$  number of discrete velocities (with particles at rest within the momentum discretization)

restrictions apply to ensure that particular discretization can be used to simulate the Navier-Stokes equations.

Most commonly used lattices:  $D2Q9$  /  $D3Q19$ .

Algorithm: for each time step and every mesh point stream particles and let particles collide.

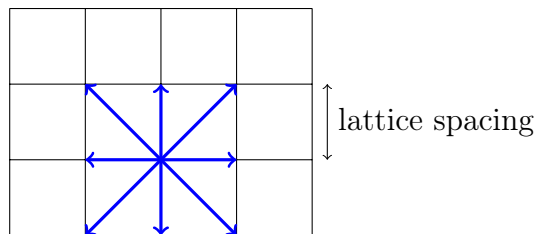


Figure 2:  $D2Q9$

At each lattice point update:

$$f_i(\vec{x} + \vec{e}_i \Delta t, t + \Delta t) = f_i(\vec{x}, t) - \frac{|f_i(\vec{x}, t) - f_i^{eq}(\vec{x}, t)|}{\tau} \quad (9.6)$$

with  $i \in [0, \beta - 1]$  spanning the momentum space and  $\tau$  a relaxation parameter related to fluid viscosity.

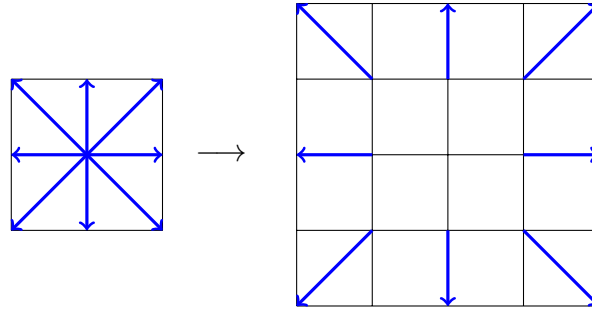
Equation (9.6) is true for lattice points within the fluid domain, but not for boundaries.

Two steps: streaming and collisions handled separately.

streaming step distributions translated to neighboring sites according to discrete velocity directions

collision step re-distribution of the distribution functions towards the local discretized Maxwell distribution function so that local mass and momentum are invariant

In the streaming process, the magnitude of the distribution functions remains unchanged, but move to neighboring nodes according to their direction.



The equilibrium distribution can be obtained from the local Maxwell-Boltzmann Eq.

$$f_i^{eq}(\vec{x}) = w_i p(\vec{x}) \left[ 1 + 3 \frac{\vec{e}_i \vec{u}}{c^2} + \frac{q}{2} \frac{(\vec{e}_i \vec{u})^2}{c^4} - \frac{3 \vec{u}^2}{2 c^2} \right]$$

where for  $D2Q9$  the weights are:

$$\begin{aligned} w_i(0, 0) &= \frac{4}{9} \\ w_i(1, 4) &= \frac{1}{9} \\ w_i(5, 8) &= \frac{1}{36} \end{aligned}$$

Collision:

Local density and velocity is conserved, but the distribution functions change according to the "relaxation" / local Maxwell rule.

Fluid viscosity

$$\begin{aligned} v = c_s^2(\tau - 1/2) &\Rightarrow \tau = \frac{v}{c_s^2} + \frac{1}{2} \\ \tau_{D2Q9} &= 3v + \frac{1}{2} \end{aligned}$$

Boundary conditions:

- periodic  
domain folded along direction of periodic boundary pair
- no-slip  
most often used in Lattice Boltzmann Method, simple bounce back rule; incoming distribution function at a wall node is reflected back to original fluid nodes, with direction rotated by ?
- bounce-back  
allow to introduce obstacle into fluid domain  
incoming particles: populations with velocities pointing to opposite direction (collision) + propagation



(ii) Bhatnager, Gross and Krook (BGK)

If the system is not in equilibrium, it will relax towards equilibrium and the relaxation process can be very complicated. Relaxation is affected by collision term in the Boltzmann equation, which is written as

$$\left(\frac{df}{dt}\right)_{\text{collision}} = \int d^3v_2 d\Omega (f_{1'}f_{2'} - f_1f_2)v_{rel} \cdot \sigma(v_{rel}, \Omega)$$

$\sigma$  differential scattering cross section for two particle collisions:  $v_1 + v_2 \rightarrow v_{1'} + v_{2'}$

$v_{rel} = v_1 - v_2$  is the relative velocity

$\Omega$  scattering direction in CM

Viscous effects: from collisions between particles energy of fluid motion is transformed to internal particle motion in fluid.

Simple approximation for collision term (collision operator by BGK, 1954):

$$\left(\frac{df}{dt}\right)_{\text{collision}} = -\frac{f - f^{eq}}{\tau} \tag{9.7}$$

$\tau$  relaxation time constant

The approximation implies that the distribution relaxes exponentially to equilibrium with time constant  $\tau$ ; this is related to viscosity.

Time evolution of a system in equilibrium with no collisions

$$f_i(\vec{r} + c_i\delta t, t + \delta t) = f_i(\vec{r}, t)$$

Time evolution

$$f_i(\vec{r} + c_i, t + 1) = f_i(\vec{r}, t) - \frac{f_i - f_i^{eq}}{\tau}$$

### Coupling the Lattice Boltzmann Method with Molecular Dynamics

- Ahlrichs-Dünweg (1998) Coupling through frictional coefficient (= tunable parameter).

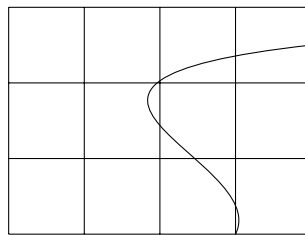


Figure 3: A polymer in a LBE flow

Polymer: chain of monomers interacting through Lennard-Jones potential for free monomers

$$V_{LJ}(r) = \epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

and spring-like potential for "chained" monomers:

$$V_k = \frac{1}{2}k(r_p^2 - r_{p+1}^2)$$

$r$  separation between two monomers of radius  $\sigma$

$k$  spring constant

Each monomer obeys Newton/Hamilton equations for point-like particles:

$$\begin{aligned}\frac{d\vec{x}_p}{dt} &= \frac{\vec{p}_p}{m} \\ \frac{d\vec{p}_p}{dt} &= \vec{F}_p\end{aligned}$$

Key: evaluation of force  $\vec{F}_p$  exerted by fluid on  $p$ -th monomer.

Simple model:

$$\vec{F}_p = -\eta(\vec{u}_p - \vec{U}_p)$$

$\vec{U}_p$  local flow speed at monomer position evaluated by simple interpolation from grid points

Reaction on fluid: interpolate force on each of the grid nodes surrounding the monomer and bias corresponding populations (impart momentum to Lattice Boltzmann Equation populations)

## 10 Inter-atomic potentials

- accuracy
- transferability
- efficiency (simple mathematical forms)

How to obtain a potential function for a particular system?

- (a) assume functional form for potential function and choose parameters to reproduce a set of experimental results  
→ empirical potential functions, e.g. Morse, Lennard-Jones,...
- (b) use quantum mechanical argument to derive analytical semi-empirical potential, e.g. bond-order potentials of Tersoff and Brenner, embedded atom method (EAM),...
- (c) perform direct electronic-structure calculations of forces; ab initio MD, e.g. Car-Parinello

Different types of chemical bonds:

- (i) primary bonds ("strong")
  - ionic (ceramics, quartz,...)  
non directional (interacting point charges)
  - covalent (silicon,...)  
directional (bond angles, torsion)
  - metallic (copper, nickel,... -high melting point)  
non-directional (electron gas)
- (ii) secondary bonds ("weak")
  - van der Waals (wax,... -low melting point)
  - hydrogen bonds (proteins,...)

Total energy of a system

$N$  atoms with interactions described by empirical potentials:

$$U(\vec{r}_1, \dots, \vec{r}_N) = \sum_i U_1(\vec{r}_i) + \sum_i \sum_{j>i} U_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

$U_1$  one body term due to external field or boundary conditions

$U_2$  two body term (pair potential): interaction depends on spacing of two atoms; not affected by the presence of other atoms

$U_3$  three body term maps the modified interaction between a pair of atoms due to the presence of a third atom

→ separate potentials into pair potentials (only  $U_2$  present) and many-body potentials ( $U_3$  and higher terms).

Differences between bonds

Bonds depend on their environment.

Examples:

(i) hydrocarbons

(ii) surface vs. bulk

According to pair potentials, the bonding energy of center atom in a six times coordinated molecule is 6 and the bonding energy of a once coordinated molecule. This is a contradiction with regard to experimental and quantum mechanical results.

An important quantity is the coordination  $Z$ , which denotes the number of immediate neighbors.

For pair potentials  $\sim Z$

For metals  $\sim \sqrt{Z}$

In metals bonds become weaker as more atoms are added to the central atom.

Pair potentials:

- limited transferability. Parameters used for molecules cannot be used for crystals, parameters for specific types of crystals cannot be used to describe the range of crystal structures.
- e.g. difference between fcc and bcc crystals cannot be captured using a pair potential
- do not include bond directionality

... unless bond order potentials are used or reactive force fields.

## 10.1 Simple pair-potential models

- simplest many-body system: ideal gas of non-interacting particles (not very relevant)
- real gas: particles have a size (short range repulsion) + possible short range attraction

(i) hard-sphere potential

$$V(r_{ij}) = \begin{cases} \infty & r_{ij} < \sigma \\ 0 & r_{ij} \geq \sigma \end{cases}$$

(ii) square-well potential

$$V(r_{ij}) = \begin{cases} 0 & r_{ij} < \sigma_1 \\ -\epsilon & \sigma_1 \leq r_{ij} < \sigma_2 \\ 0 & \sigma_2 \leq r_{ij} \end{cases}$$

(iii) soft-sphere potential

$$V(r_{ij}) = \epsilon \left( \frac{\sigma}{r_{ij}} \right)^v = ar_{ij}^{-v}$$

(iv) Lennard-Jones potential

$$V(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

(v) Morse potential

$$V(r_{ij}) = D(e^{-2a(r_{ij}-r_0)} - 2e^{-a(r_{ij}-r_0)})$$

(vi) Buckingham potential

$$V(r_{ij}) = Ae^{-\frac{r_{ij}}{\sigma}} - C \left( \frac{\sigma}{r_{ij}} \right)^6$$

(vii) harmonic approximation (no bond breaking)

$$V(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij} - r_0)^2$$

no dissociation energy

describes bond stretching

no chemical reactions: set of parameters only valid for particular bond

## 10.2 Bond order potentials

Pair potentials applied to covalent bonds, which depend on atomic environment.

Concept of bond order: number of chemical bonds between a pair of atoms (e.g. H-C  $\equiv$  C-H, bond order between C is 3 and one for C-H bond)

Mathematical definition of bond order:

$$\frac{\text{number of bonding } e^- - \text{number of anti-bonding } e^-}{2}$$

Magnitude of bond order associated with bond length (Pauling)

$$s_{ij} = \exp\left(\frac{d_i - d_{ij}}{b}\right)$$

where  $d_i$  is the simple bond length and  $d_{ij}$  is the experimentally measured bond length;  $b$  depends on atoms.

Bond order does not need to be an integer. E.g. for molecules with non-classical bonding or molecules which have resonance. (benzene: the delocalized molecular orbitals contain 6  $\pi$  electrons over 6 carbons, yielding half a  $\pi$  bond together with a  $\sigma$  bond for each pair of carbon atoms  $\rightarrow$  calculated bond order is 1.5)

Schematic representation of the bond order of two interacting atoms

bond length

$\downarrow$

bond order

$\downarrow$

energy

bond length

$\downarrow$

energy

conventional potential, e.g. Morse, Lennard-Jones,...

more general description of chemical bonding;  
all energy terms depend on bond order

(1) Tersoff potential (1988)

The Tersoff potential is based on theory by Abel (1985) regarding the influence of the local environment on the bond order. Initially it was developed for group IV elements (Si, Ge, C); now parameterizations for H, N, B, ... also exist.

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij}$$

$$V_{ij} = f_c(r_{ij}) [a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

$i$  and  $j$  run over all atoms.

Repulsive pair potential which includes the orthogonalization energy when wave functions overlap

$$f_R(r_{ij}) = A \exp(-\lambda_1 r_{ij})$$

Attractive pair potential associated with bonding

$$f_A(r_{ij}) = -B \exp(-\lambda r_{ij})$$

$f_C(r_{ij})$  : smoothing function; cut-off to limit potential range and thus limit computational cost. Novel feature:  $b_{ij}$  : measure of bond order modelled by a monotonically decreasing function of coordination of atoms  $i$  and  $j$ .

$a_{ij}$  : range-limiting term (limit range of interaction to the first neighboring shell)

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-n/2} \quad \text{dependent on local coordinates}$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) g(\vartheta_{ijk}) \exp[\lambda_3 (r_{ij} - r_{ik})^3]$$

$g(\vartheta)$  : a function of the bond angle  $\vartheta_{ijk}$  between  $i$ ,  $j$  and  $k$ . This function implicitly accounts for 3 body terms.

$\zeta_{ij}$  : counts the number of other bonds to atom  $i$  besides the  $ij$  bond

$\zeta_{ij} \rightarrow Z - 1$  with  $Z$  the coordination number when only the first shell of neighbors falls within the cut-off.

(According to Abel a first approximation could be by  $\sim Z^{-\delta}$ , where  $\delta$  depends on the system)

Tersoff potential: efficient modelling of single- and multicomponent systems containing carbon, silicon or germanium.

Development was based on cohesive energies and elastic constants.

$b_{ij}$  : modulates strength of attractive part by coordination or bond order.

Problems: over-binding of radicals (overestimates density for specific hybridizations) and poor treatment of conjugacy.

(2) Brenner potential (1990) Based on Tersoff potential but corrects the inherent over-binding of radicals and also includes non-local effects. Parameterized for hydrocarbons.

Correction for over-binding of radicals and conjugacy (overlap of two p-orbitals, bridging the interjacent single bonds):

$$E = \sum_i \sum_{j > i} [V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij})]$$

with  $\bar{B}_{ij} = \frac{B_{ij} + B_{ji}}{2}$ .

$B_{ij}$  : empirical bond order function given by average of terms associated with each atom in a bond plus a correction.

$$B_{ij} = f(r_{ij}, \vartheta_{ijk}, N_i^{(H)}, N_i^{(C)})$$

$N_i^{(H/C)}$  number of hydrogen/carbon atoms bonded to atom  $i$

Parameterized with binding energies, lattice constants, ...  
 → reactive empirical bond order (REBO) potential.

Shortcomings: absence of non-bonding interactions, lacks torsional parameter for hindered rotation about single bonds. Morse-type terms ( $V_R, V_A$ ) go to finite values when atomic distance decreases

(3) Adaptive inter-molecular reactive bond-order potential (AIREBO) (Stuart, et al, 2000)

- overcomes drawbacks of REBO potentials. Both repulsive and attractive pair interaction functions in REBO are modified to fit bond properties; long-range atomic interactions and single bond torsional interactions are included. Parameterized for hydrocarbons.
- transferable (compared to REBO) empirical potential capable of simulating chemical reactions in different environments

$$E = E^{REBO} + E^{LJ} + E^{tors}$$

The Lennard-Jones term can be switched off depending on distance and bonding environment an also includes a bond order term.

$$E^{tors} = \frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i, j} \sum_{l \neq i, j, k} w_{ij}(r_{ij}) w_{kl}(r_{kl}) V^{tors}(w_{ijkl})$$

$w_{ijkl}$  dihedral angle

$w_{ij}$  bond weights ensure that torsional energy associated with a given dihedral angle will be removed smoothly as any of the constituent bonds are broken

Example for a three body potential

Stillinger-Weber potential (1985)

- one of the early potentials for diamond lattices
- first parameterized for silicon

$$V(\vec{r}_1, \dots, \vec{r}_N) = \sum_i \sum_{j > i} V_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j > i} \sum_{k > j} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k)$$

$$V_2(\vec{r}_i, \vec{r}_j) = \begin{cases} \epsilon A (B r_{ij}^{-p} - r_{ij}^{-q}) \exp(r_{ij} - a)^{-1} & r < a \\ 0 & r \leq a \end{cases}$$

$a$  cut-off

$$V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \epsilon [h(\vec{r}_{ij}, \vec{r}_{ik}, \vartheta_{jik}) + h(\vec{r}_{ji}, \vec{r}_{jk}, \vartheta_{ijk}) + h(\vec{r}_{ki}, \vec{r}_{ij}, \vartheta_{ikj})]$$

$$h(\vec{r}_{ij}, \vec{r}_{ik}, \vartheta_{ijk}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \left( \cos \vartheta_{ijk} + \frac{1}{3} \right)^2$$

If  $\cos \vartheta_{jik} = -\frac{1}{3}$  ( $\vartheta_{jik} = 109.47^\circ$ ) the diamond lattice is in the energetically favorable structure.

Stillinger-Weber: simple, realistic description of crystalline silicon.

Transferability issues: 3-body term defines only one equilibrium configuration, this makes it difficult to extend to elements like carbon with 3 hybridizations (3 equilibrium angles  $180^\circ$ ,  $120^\circ$  and  $109.47^\circ$ ). Built-in tetrahedral angle leads to low coordination (liquid silicon), wrong surface structure, ...

## 10.3 Multi-body potentials

(1) Reactive Force Field (Reax FF) (von Duin et al, 2001)

$$E_{\text{system}} = \underbrace{E_{\text{bond}} + E_{\text{vdW}} + E_{\text{Coul}}}_{\text{2-body}} + \underbrace{E_{\text{val,angle}}}_{\text{3-body}} + \underbrace{E_{\text{tors}}}_{\text{4-body}} + \underbrace{E_{\text{over}}}_{\text{multi-body}} + E_{\text{under}} + E_{\text{pen}} + E_{\text{conj}}$$

- terms describe individual chemical bonds
- all expressions in terms of bond order
- all interactions calculated between all atoms
- no atom type (e.g. hybridization), only element type is considered
- parameterized for hydrocarbons
- fundamental assumption : bond order between a pair of atoms is obtained directly from inter-atomic distance; contributions from  $\sigma$ ,  $\pi$  and  $\pi\pi$  bonds

$$\begin{aligned} \text{BO}_{ij} &= \text{BO}_{ij}^{\sigma} + \text{BO}_{ij}^{\pi} + \text{BO}_{ij}^{\pi\pi} \\ &= \exp \left[ P_{bo1} \left( \frac{r_{ij}}{r_0^{\sigma}} \right)^{P_{bo1}} \right] + \exp \left[ P_{bo2} \left( \frac{r_{ij}}{r_0^{\pi}} \right)^{P_{bo2}} \right] + \exp \left[ P_{bo3} \left( \frac{r_{ij}}{r_0^{\pi\pi}} \right)^{P_{bo3}} \right] \end{aligned}$$

Over-coordination : differences between total bond order around atom and number of bonding electrons  $v_{el}$

$$\Delta_i = \sum_{\Delta=1}^{\# \text{ bonds}} \text{BO}'_{ij} - v_{el}$$

with  $\text{BO}'_{ij}$  the uncorrected bond orders.

Bond order correction:

$$\text{BO}_{ij} = \text{BO}'_{ij} f_1(\Delta'_i, \Delta'_j) f_4(\Delta'_i, \text{BO}'_{ij}) f_5(\Delta'_j, \text{BO}'_{ij})$$

$E_{\text{bond}}$  bond energy =  $-D_e \text{BO}_{ij} [P_{bo1} (1 - \text{BO}_{ij}^{P_{bo1}})]$

$E_{\text{over}}$  imposes energy penalty for over-coordinated atom

$E_{\text{under}}$  consider energy contribution for resonances of  $n$  electron between attached under-coordinated atomic centers

$E_{\text{val,angle}}$  valence angle

$E_{\text{tors}}$  torsion angle

$E_{\text{conj}}$  accounts for conjugation effects to molecular energy

$E_{\text{vdW}}$  non-bonded van der Waals

$E_{\text{Coul}}$  electronic interactions

$E_{\text{pen}}$  penalty in order to produce stability of system with two double bonds sharing atom in a valence angle

A more general reactive force field potential energy function:

$$\begin{aligned} E_{\text{system}} = & E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} \\ & + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{c2}} \\ & + E_{\text{triple}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{h-bond}} \\ & + E_{\text{vdW}} + E_{\text{Coul}} \end{aligned}$$

$E_{\text{coa}}$  angle conjugation

$E_{\text{c2}}$   $C_2$  correction

$E_{\text{triple}}$  triple-bond related

$E_{\text{h-bond}}$  Hydrogen-bonded

For specific materials/systems:

- covalent

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coul}}$$

- metal alloys

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{vdW}} + E_{\text{Coul}}$$

- metals

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{vdW}}$$

- ionic material

$$E_{\text{system}} = E_{\text{vdW}} + E_{\text{Coul}}$$

- noble gases

$$E_{\text{system}} = E_{\text{vdW}}$$

- reactive force field parameterization extends to a lot of different elements and materials (metals, ceramics, polymers,...)
- all reactive force field descriptions use the same potential functions → interface between different material types possible
- geometry dependent charge calculation scheme with reactive force field → polarization effects
- describes properly bond dissociation → chemical reactions

Reactive potentials:

- molecular model to describe chemical reactions
- continuous energy landscape during reactions
- only element types
- computationally efficient (finite range of interactions → treat large systems  $> 10^5$  atoms)
- parameters with physical meaning



## 10.4 Embedded Atom Method (EAM)

- Classical potential for metallic systems

Pair potentials cannot adequately describe metallic systems because:

- (a) they do not have environmental dependence; strength of "individual bond" should decrease as the local environment becomes too crowded due to Pauli's principle, but pair potentials do not depend on environment and cannot account for this decrease
- (b) they do not account for directional nature of bonds; covalent contributions (d orbitals) of transition metals cannot be described. Pair potentials work better for metals in which cohesion is provided by s and p electrons

Metallic bond: electrostatic attractive forces between delocalized electrons (conduction electrons) gathered in an electron cloud and the positively charged metal ions. The conduction electrons "divide" their density equally over all atoms and the atoms function as neutral (non-charged) entities. The conduction electrons move between nuclei, generating a binding force to hold atoms together: electron gas model (positive ions in electron sea).

Mostly non-directional bonding.

- dependence of strength of individual bonds on local environment especially important for simulation of surfaces and defects
- EAM: description of bonding in metallic systems based on concept of local density, i.e. environment of an atom, the electron density imposed by other atoms, influences the bond strength
- each atom features a certain distribution of electron density

EAM concept: include electron density effects.

Total energy of a system of  $N$  atoms:  $E_{tot} = \sum_i E_i$ .

$$E_i = \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) + F_i(\rho_i)$$

$F_i(\rho_i)$  embedding energy as a function of electron density; describes how local electron contributes to potential energy

$\rho_i = \sum_{j \neq i} \Pi_{\rho,j}(r_{ij})$  local density  
 $\equiv$  contribution to electron density at atom  $i$  due to electron density of atom  $j$  evaluated at distance  $r_{ij}$ .

The exact functional form of  $F$ ,  $\Pi$ ,  $\phi$  depend on the system and method.

The embedding energy  $F$  is the energy associated with placing an atom in the electron environment described by  $e$ .

The pair potential  $\phi$  describes electrostatic contributions.

- The embedding energy is a measure of the number of available states to delocalize onto (inherently a many-body effect)
- As the electrons get more states to spread out over, their kinetic energy decreases ( $\rightarrow$  bounding energy due to electron delocalization)
- When an impurity is added to a metal, the energy is lowered due to delocalization of the electrons from impurity into solid

- Increase of coordination decreases the strength of each of the individual bonds and increases the bond length

In order to use Embedded Atom Method potential in Molecular Dynamics, the forces are needed

$$\begin{aligned}
 \vec{F}_i &= -\nabla_{\vec{r}_i} E_{tot} = -\nabla_{\vec{r}_i} \sum_i E_i \\
 &= -\nabla_{\vec{r}_i} \left[ F_i(\rho_i) + \sum_{j \neq i} F_j(\rho_j) + \sum_{j \neq i} \phi_{ij}(r_{ij}) \right] \\
 &= -\sum_{j \neq i} \left[ \left. \frac{\partial F_i(\rho)}{\partial \rho} \right|_{\rho=\rho_i} + \left. \frac{\partial \Pi_j(r)}{\partial r} \right|_{r=r_{ij}} + \left. \frac{\partial F_j(\rho)}{\partial \rho} \right|_{\rho=\rho_j} \cdot \left. \frac{\partial \Pi_i(r)}{\partial r} \right|_{r=r_{ij}} + \left. \frac{\partial \phi_{ij}(r)}{\partial r} \right|_{r=r_{ij}} \right] \cdot \frac{\vec{r}_i - \vec{r}_j}{r_{ij}}
 \end{aligned}$$

Only inter-particle distances  $r_{ij}$  are needed to calculate energy and forces.

EAM potentials:

- numerically efficient ( $\approx 10^9$  particles)
- state of the art approach to model metals
- very good potentials for nickel, aluminum, copper,...
- environment-dependent pair potential
- describes differences between bulk and surfaces
- lack of explicit 3-body terms makes the use of EAM potentials for metals where covalent effects are important, challenging (i.e. transition metals)

$F(\rho)$  can be a linear function of  $\rho$ : in this case we have only a pair potential.

Curvature of  $F(\rho)$  imposes many-body effects. For  $F(\rho)$  with positive curvature and a positively decreasing  $\Pi$ , the effective potential becomes more repulsive as density increases.

- various EAM type potentials for fcc, bcc, hcp metals
- bcc and hcp EAM potentials are more difficult to develop:
  - hcp structure should have lower energy than fcc
  - bcc should have a more "open" rather than close-packed structure

## 10.5 Elements of coarse-graining

- Reduce degrees of freedom to decrease computational effort
- reduction of degrees of freedom such that information relevant to desired properties is not lost
- typically coarse-grained particles are represented by beads
- one bead - depending on coarse-graining level - maps a number ( $10^n$ ,  $n = 1, \dots$ ) of particles (atoms, molecules, residues,...)
- simulations are being carried out with the coarse-grained particles (beads) together with the relevant coarse-grained potentials
- the coarse-grained beads in the simulations implicitly include the information regarding the particles which have been coarse-grained
- The results from the simulations can be mapped back to the particles

### 10.5.1 Multiscale Modelling

- Bridge spatial and temporal scales
- couple different computational schemes
- concurrent (within the same simulation) and sequential (results from one scheme complement those from a scheme at another level) multiscale approaches
- develop new, faster algorithms
- novel applications in medical and biological applications
- efficient mathematical treatment of boundaries; seamless coupling of different computational methods, i.e. of the various time and length scales

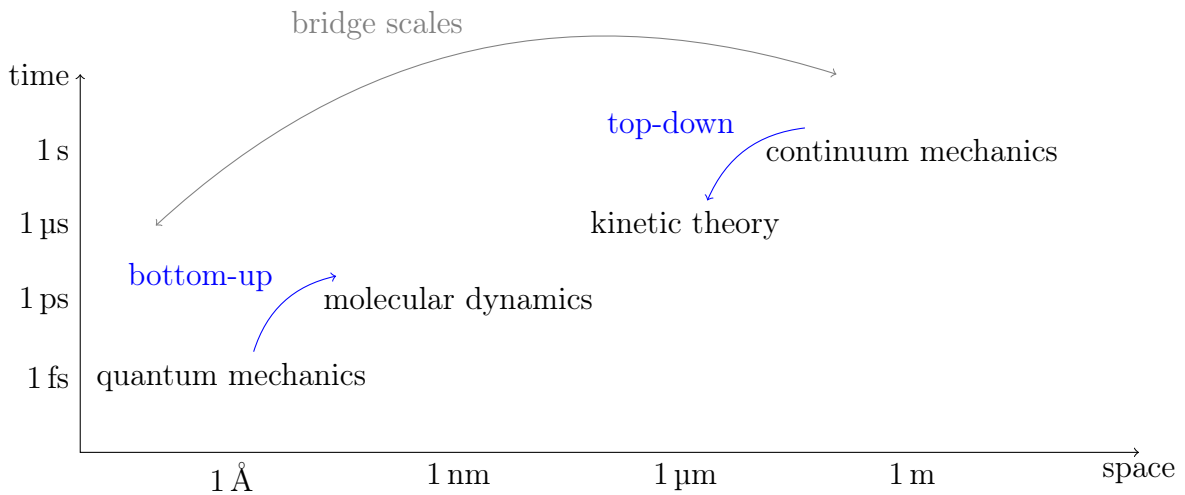


Figure 4: Commonly used models of physics at different scales

Table 2: The multi-physics hierarchy

<u>Gases, plasmas</u>	<u>Liquids</u>	<u>Solids</u>
Gas dynamics	hydrodynamics (Navier-Stokes)	elasticity models plasticity models dislocation dynamics
kinetic theory	kinetic theory Brownian dynamics	kinetic Monte Carlo
particle models	Molecular Dynamics	Molecular Dynamics
Quantum mechanics	Quantum mechanics	Quantum mechanics

- Multiscale approaches are tackled with analytical and numerical methods
- Classical multiscale algorithms:
  - multi grid method
  - fast multiple method

- domain decomposition methods
  - adaptive mesh refinement
  - multi-resolution representation
- there is a hierarchy of physical models. Each model can model a physical system at different level; each model is a refinement of the models at higher level of hierarchy:
1. Continuum mechanics (Euler and Navier-Stokes equations)
  2. Kinetic theory (Boltzmann equation)
  3. Molecular dynamics (Newton's equation)
  4. Quantum mechanics (Schrödinger equation)

Inside each level of hierarchy, there are sub-hierarchies, i.e. models of different complexity and detail

## References

- [1] Michael P Allen and Dominic J Tildesley. *Computer simulation of liquids*. Oxford university press, 1989.
- [2] Daan Frenkel and Berend Smit. *Understanding molecular simulation: from algorithms to applications*. Access Online via Elsevier, 2001.
- [3] Efthimios Kaxiras. *Atomic and electronic structure of solids*. Cambridge University Press, 2003.
- [4] David P Landau and Kurt Binder. *A guide to Monte Carlo simulations in statistical physics*. Cambridge university press, 2009.
- [5] Andrew R. Leach. *Molecular modelling: principles and applications*. Pearson Education, 2001.
- [6] F Martin and Hendrik Zipse. Charge distribution in the water molecule—a comparison of methods. *Journal of computational chemistry*, 26(1):97–105, 2005.
- [7] MEJ Newman and GT Barkema. *Monte carlo methods in statistical physics* oxford university press. 1999.
- [8] Dennis C Rapaport. *The art of molecular dynamics simulation*. Cambridge university press, 2004.
- [9] Martin Oliver Steinhauser. *Computational multiscale modeling of fluids and solids: theory and applications*. Springer, 2007.
- [10] Sauro Succi. *The lattice Boltzmann equation: for fluid dynamics and beyond*. Oxford university press, 2001.
- [11] Jos Thijssen. *Computational physics*. Cambridge University Press, 2007.
- [12] Mark Tuckerman. *Statistical Mechanics and Molecular Simulations*. Oxford University Press, 2008.