

Quantum Mechanical Simulations

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Topics

- ❑ Quantum Monte Carlo
- ❑ Hartree-Fock Self-Consistency Field
- ❑ Density Functional Theory

Quantum Mechanical Methods

□ Approximation methods made to solve the Schrödinger equation

- Time-dependent

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = \mathcal{H} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$$

where

$$\mathcal{H} = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I<J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

- Time-independent

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

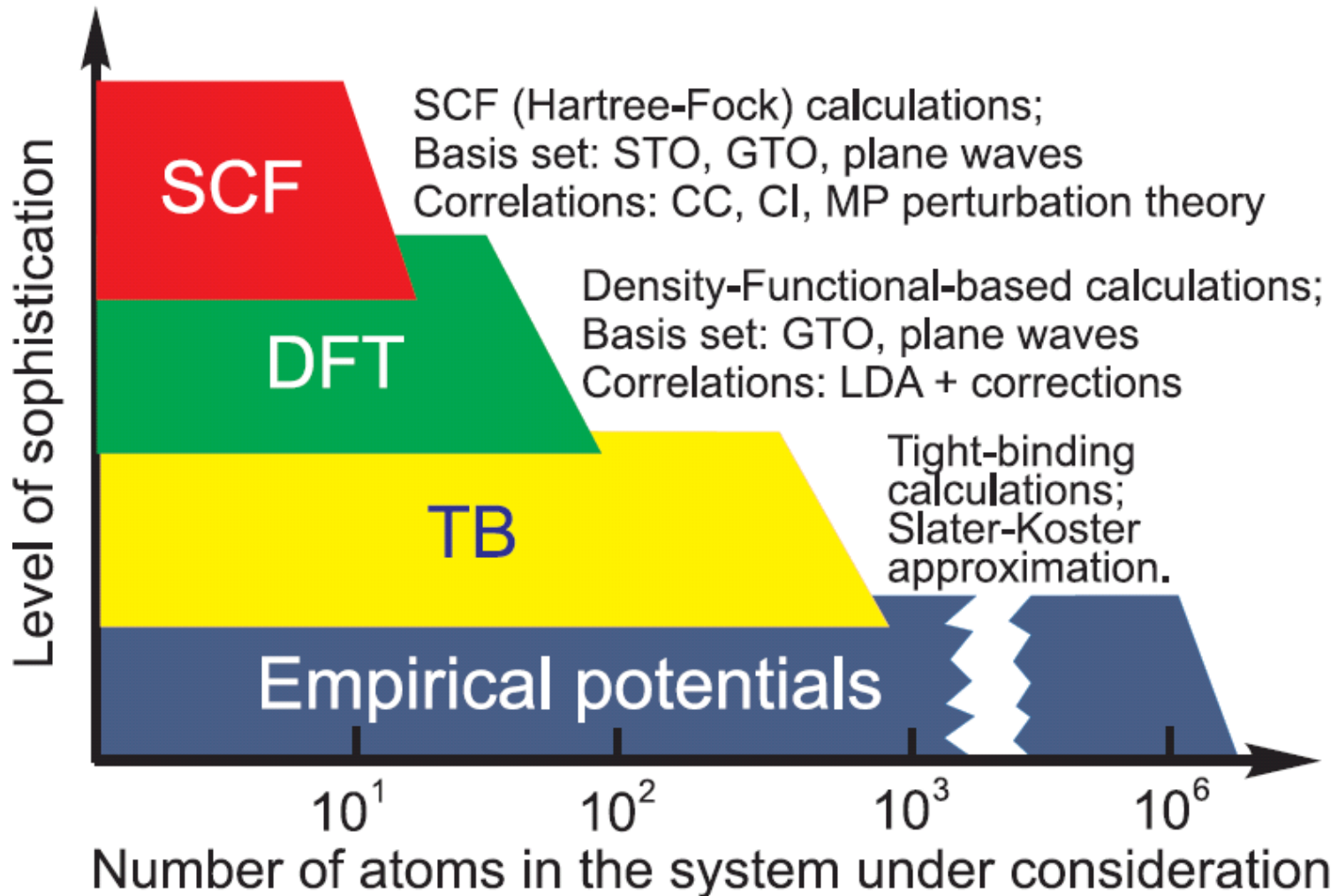
- “Eigenvalue problem”

$$\langle \Psi | \mathcal{H} | \Psi \rangle = E \langle \Psi | \Psi \rangle \quad E = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$$

Quantum Mechanical Methods

- ❑ Quantum Monte Carlo (QMC): scaling with the number of atoms N nearly exponential, and polynomials $O(M^p)$ with respect to the number of electrons M .
- ❑ Hartree-Fock (HF): scaling with $O(N^4)$ or higher (depends on how the correlations are treated)
- ❑ Density-Functional Theory (DFT): scaling with $O(N^3)$
- ❑ Tight-Binding (TB): scaling with $O(N^3)$

Quantum Mechanical Methods



Quantum Monte Carlo (QMC)

- ❑ The most accurate (and *expensive*) approach to calculate electronic property
- ❑ Can compute both ground and excited states
- ❑ Sufficient to address most issues involving inter-atomic forces and chemical properties

Two popular QMC methods

□ Variational quantum Monte Carlo (VMC)

- The expected values are calculated via MC integration over $3N$ dimensional space of electron coordinates $\mathbf{R} = \{r_1, r_2, \dots, r_N\}$

$$E = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \Psi^*(\mathbf{R}) \mathcal{H} \Psi(\mathbf{R}) d\mathbf{R}}{\int \Psi^*(\mathbf{R}) \Psi(\mathbf{R}) d\mathbf{R}}$$

□ Diffusion quantum Monte Carlo (DMC)

- Starting from a trial wave function, the distribution of electrons evolves along a (imaginary) time

VMC

□ Metropolis MC algorithm

- Start the ‘walker’ with a random position \mathbf{R} ;
- Make a trial move to a new position \mathbf{R}' ; with a probability density $T(\mathbf{R}' \leftarrow \mathbf{R})$. That is, the probability that the walker is now in the volume element $d\mathbf{R}'$ is $d\mathbf{R}' \times T(\mathbf{R}' \leftarrow \mathbf{R})$
- Accept the trial move with probability

$$A(\mathbf{R}' \leftarrow \mathbf{R}) = \min \left(1, \frac{T(\mathbf{R} \leftarrow \mathbf{R}') \mathcal{P}(\mathbf{R}')}{T(\mathbf{R}' \leftarrow \mathbf{R}) \mathcal{P}(\mathbf{R})} \right)$$

- repeat

VMC

- ❑ With an enormous number of walkers, after an equilibrium state is achieved, the average number of walkers in the volume element $d\mathbf{R}$ is denoted by $n(\mathbf{R})d\mathbf{R}$
- ❑ Equilibrium means the average number of walkers from $d\mathbf{R}$ to $d\mathbf{R}'$ is the same as that from $d\mathbf{R}'$ to $d\mathbf{R}$
- ❑ Since the probability that the next move of a walker at \mathbf{R} is $d\mathbf{R}'A(\mathbf{R}'\leftarrow\mathbf{R})T(\mathbf{R}'\leftarrow\mathbf{R})$, the average number moving from $d\mathbf{R}$ to $d\mathbf{R}'$ in a single move is $d\mathbf{R}'A(\mathbf{R}'\leftarrow\mathbf{R})T(\mathbf{R}'\leftarrow\mathbf{R})\times n(\mathbf{R})d\mathbf{R}$.

- ❑ Balance:

$$A(\mathbf{R}'\leftarrow\mathbf{R})T(\mathbf{R}'\leftarrow\mathbf{R})n(\mathbf{R})d\mathbf{R}d\mathbf{R}'=A(\mathbf{R}\leftarrow\mathbf{R}')T(\mathbf{R}\leftarrow\mathbf{R}')n(\mathbf{R}')d\mathbf{R}'d\mathbf{R}$$

- ❑ Hence
$$\frac{n(\mathbf{R})}{n(\mathbf{R}')} = \frac{A(\mathbf{R}\leftarrow\mathbf{R}')T(\mathbf{R}\leftarrow\mathbf{R}')}{A(\mathbf{R}'\leftarrow\mathbf{R})T(\mathbf{R}'\leftarrow\mathbf{R})}$$

- ❑ Since the ratio of acceptance in Metropolis algorithm is

$$\frac{A(\mathbf{R}\leftarrow\mathbf{R}')}{A(\mathbf{R}'\leftarrow\mathbf{R})} = \frac{T(\mathbf{R}'\leftarrow\mathbf{R})\mathcal{P}(\mathbf{R})}{T(\mathbf{R}\leftarrow\mathbf{R}')\mathcal{P}(\mathbf{R}')}$$

- ❑ Therefore the equilibrium walker density $n(\mathbf{R})$ is proportional to $\mathcal{P}(\mathbf{R})$

$$\frac{n(\mathbf{R})}{n(\mathbf{R}')} = \frac{\mathcal{P}(\mathbf{R})}{\mathcal{P}(\mathbf{R}')}$$

VMC

- The expected value of \hat{H} evaluated with a trial wave function Ψ_T provides a rigorous upper bound on the exact ground-state energy E_0 as

$$E_V = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} \geq E_0$$

- which is evaluated using the Metropolis MC algorithm in the form

$$E_V = \frac{\int |\Psi_T(\mathbf{R})|^2 \Psi_T^{-1}(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int |\Psi_T(\mathbf{R})|^2 d\mathbf{R}} \quad \text{where } \Psi_T^{-1} \hat{H} \Psi_T = E_L \text{ is "Local energy"}$$

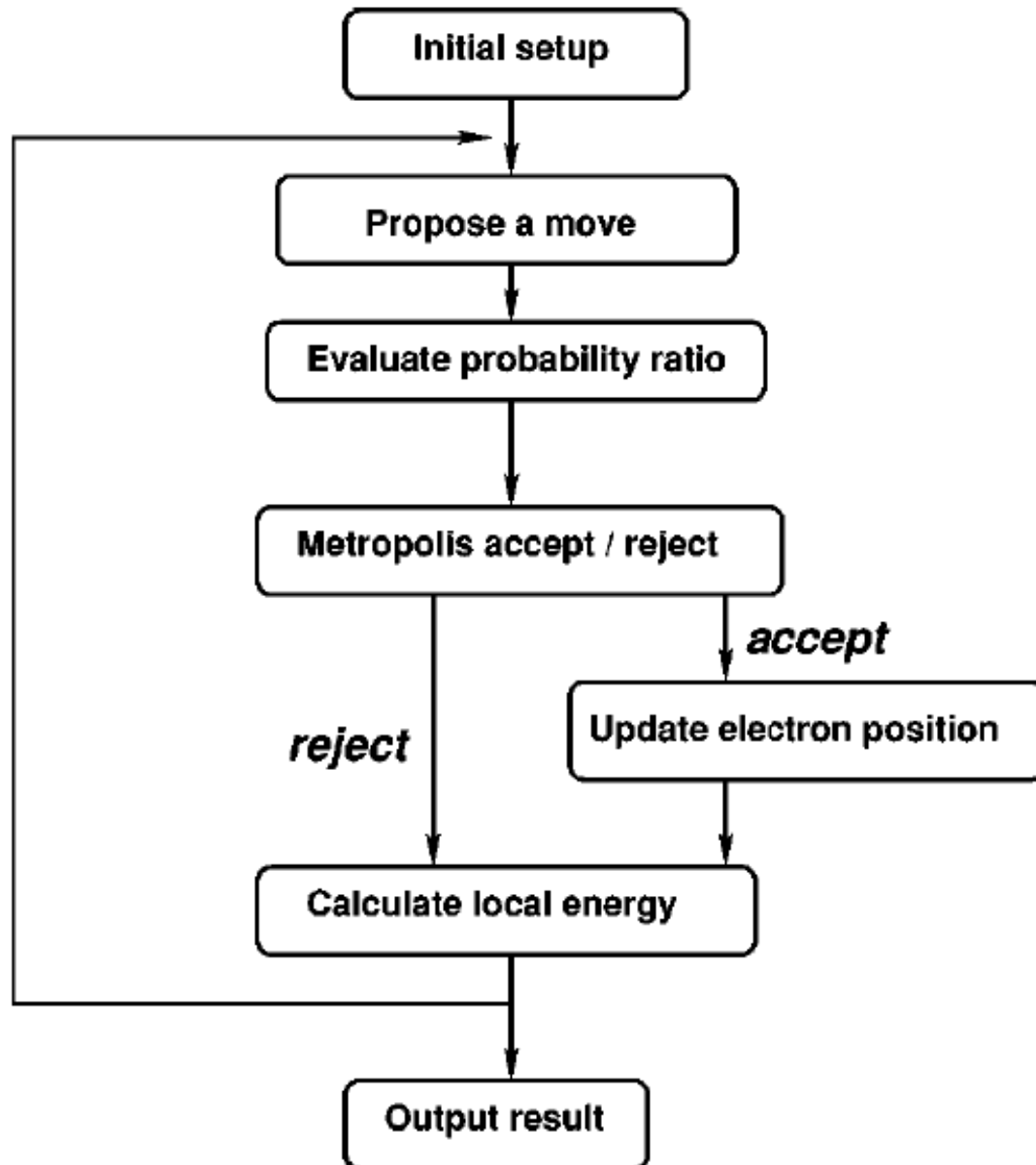
- The configuration-space probability density

$$\mathcal{P}(\mathbf{R}) = |\Psi(\mathbf{R})|^2 / \int |\Psi(\mathbf{R})|^2 d\mathbf{R}$$

- With a sample set of M points

$$E_V \approx \frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m)$$

VMC Algorithm



DMC

- solving an imaginary-time many-body Schrödinger equation

$$-\frac{\partial \Phi(\mathbf{R}, t)}{\partial t} = (\hat{H} - E_T)\Phi(\mathbf{R}, t)$$

where E_T is an energy offset

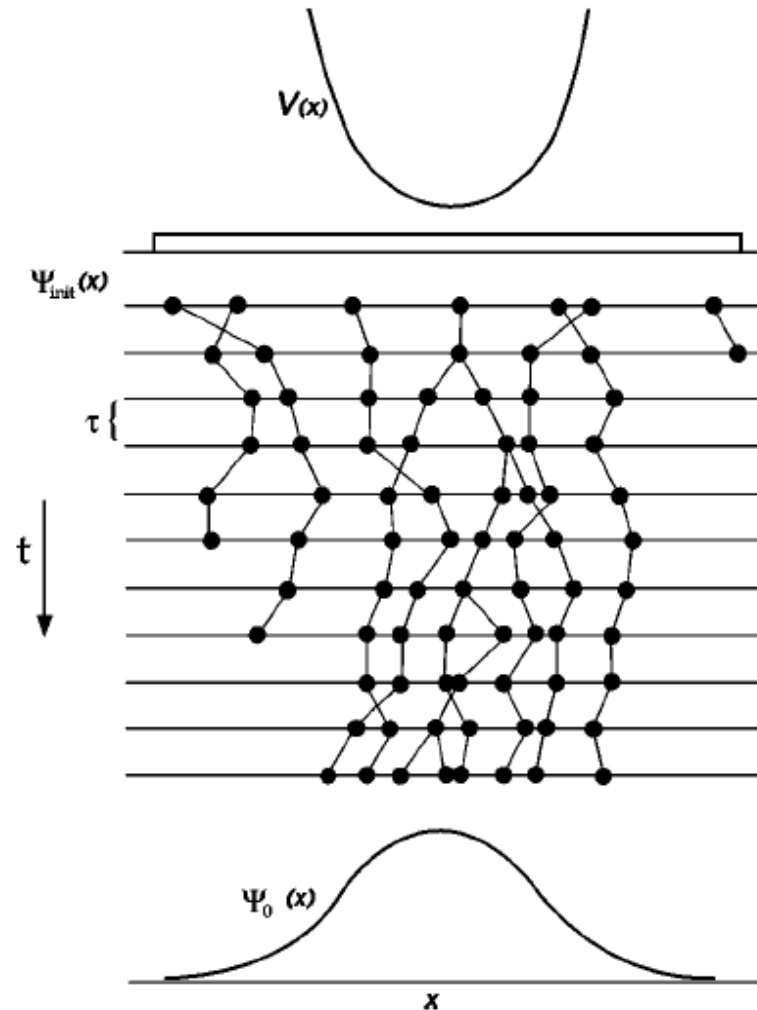
- In the integral form

$$\Phi(\mathbf{R}, t + \tau) = \int G(\mathbf{R} \leftarrow \mathbf{R}', \tau)\Phi(\mathbf{R}', t)d\mathbf{R}'$$

where $G(\mathbf{R} \leftarrow \mathbf{R}', \tau) = \langle \mathbf{R} | \exp(-\tau(\hat{H} - E_T)) | \mathbf{R}' \rangle$ is a Green function

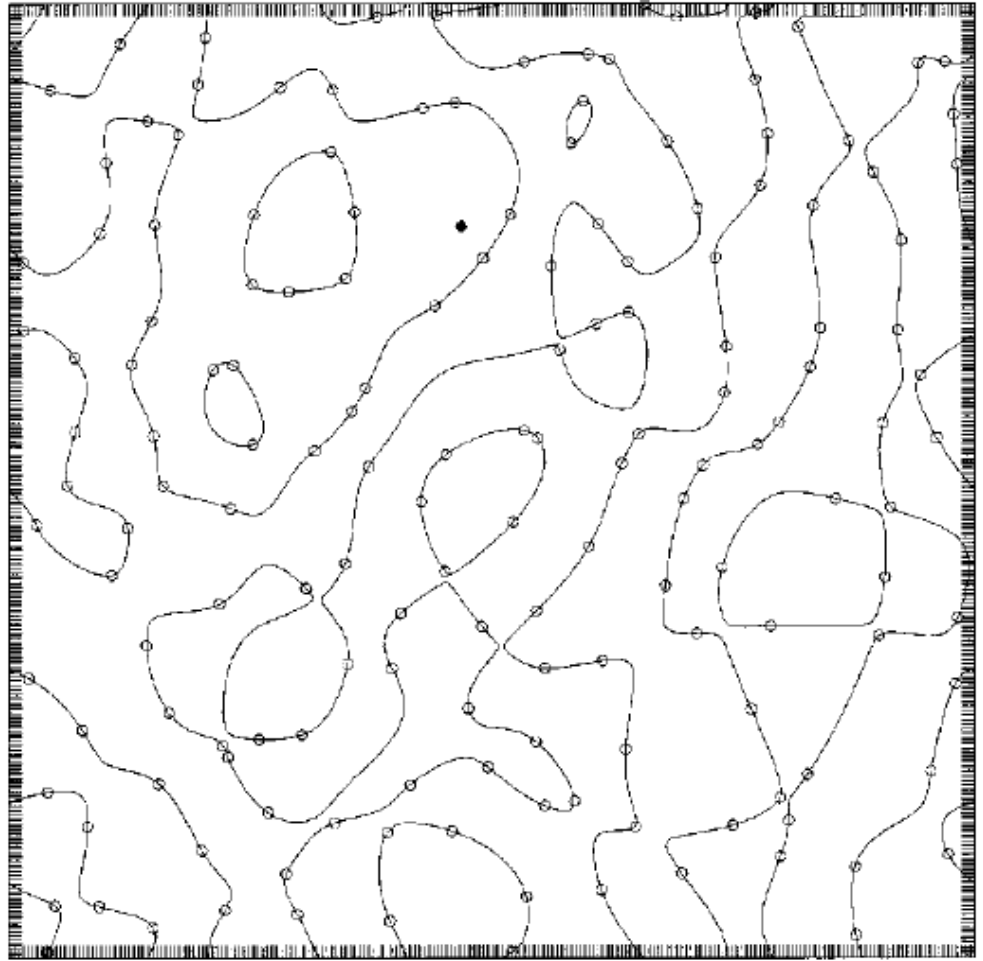
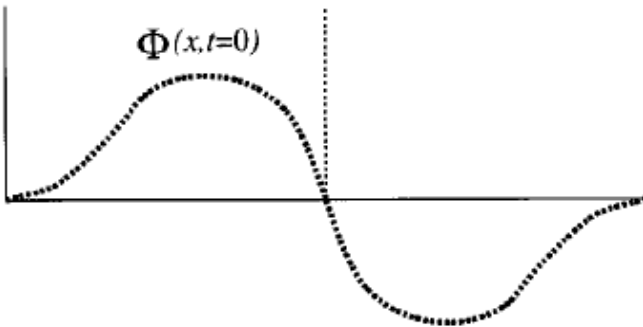
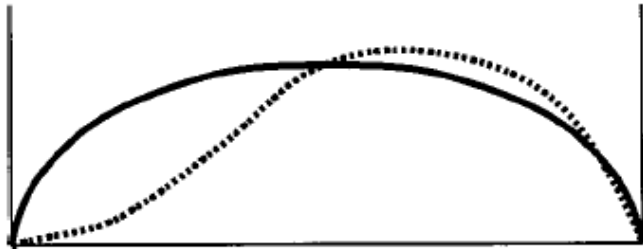
DMC

□ “path integral”



DMC

□ Fixed-node approximation



Hartree-Fock (HF) Self-Consistency Field (SCF)

- ❑ Efficiently calculate ground-state electronic structures
- ❑ Based on two simplifications:
 - *Born-Oppenheimer* approximation: solve the Schrödinger equation for the electrons in the field of static nuclei
 - Replace the many-electron Hamiltonian with an effective one-electron Hamiltonian which acts on one-electron wave functions called *orbitals*

Slate Determinant

- HF approximation (Fock 1930; Slater 1930) is the simplest theory that incorporates the *antisymmetry* of the wave function

$$\Psi(\dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots) = -\Psi(\dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots)$$

where $\mathbf{x}_i = \{\mathbf{r}_i, \sigma_i\}$ represents the coordinates and spin of electron i .

- The antisymmetry ensures that no two electrons can have the same set of quantum numbers and the Pauli exclusion principle is satisfied.

$$\Psi(\dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots) = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \cdots & \psi_1(\mathbf{x}_N) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & \cdots & \psi_2(\mathbf{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{x}_1) & \psi_N(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

where $\psi_i(\mathbf{x}_j) = \phi_i(\mathbf{r}_j) \delta_{\sigma_i, \sigma_j}$ with $\delta_{\sigma_i, \sigma_j} = \begin{cases} 1 & (\sigma_i = \sigma_j) \\ 0 & \text{otherwise} \end{cases}$

HF-SCF

- ❑ The exact ground-state wave function, as our target of calculation, cannot be represented as a single Slater determinant.
- ❑ Yet we use a Slater determinant as a variational trial function and minimize the expected value of Hamiltonian w.r.t. the orbitals $\psi_i(\mathbf{r}_j)$'s.
- ❑ *Born-Oppenheimer* approximation

$$\mathcal{H}^{BO} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{I,i} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

HF-SCF

□ *Hartree-Fock* approximated Hamiltonian

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} g(i, j)$$

$$\text{where } h(i) = -\frac{1}{2} \nabla_i^2 - \sum_n \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} \quad \text{and} \quad g(i, j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

□ applied to the Slater determinant

$$\langle \Psi | \sum_i h(i) | \Psi \rangle = N \frac{(N-1)!}{N!} \sum_k \langle \psi_k | h | \psi_k \rangle = \sum_k \langle \psi_k | h | \psi_k \rangle = \sum_k \int dx \psi_k^*(x) h(\mathbf{r}) \psi_k(\mathbf{x}).$$

$$\langle \Psi | \sum_{ij} g(i, j) | \Psi \rangle = \sum_{kl} \langle \psi_k \psi_l | g | \psi_k \psi_l \rangle - \sum_{kl} \langle \psi_k \psi_l | g | \psi_l \psi_k \rangle$$

$$\text{where } \langle \psi_k \psi_l | g | \psi_m \psi_n \rangle = \int \int dx_1 dx_2 \psi_k^*(x_1) \psi_l^*(x_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_m(x_1) \psi_n(x_2)$$

HF-SCF

- Define operators J_k and K_k as

$$J_k \psi(x) = \int dx' \psi_k^*(x') \frac{1}{r_{12}} \psi_k(x') \psi(x) \quad K_k \psi(x) = \int dx' \psi_k^*(x') \frac{1}{r_{12}} \psi(x') \psi_k(x)$$

- Define **Coulomb** operator J and **exchange** operator K

$$J = \sum_k J_k; \quad K = \sum_k K_k;$$

- The energy becomes

$$E = \sum_k \langle \psi_k | h + \frac{1}{2}(J - K) | \psi_k \rangle.$$

under *orthonormality* constraint $\langle \psi_k | \psi_l \rangle = \delta_{kl}$

- The *minimization* with the Lagrange multipliers Λ_{kl}

requires $\delta E - \sum \Lambda_{kl} [\langle \delta \psi_k | \psi_l \rangle - \langle \psi_k | \delta \psi_l \rangle] = 0$

with $\delta E = \sum_k \langle \delta \psi_k | \mathcal{F} | \psi_k \rangle + \langle \psi_k | \mathcal{F} | \delta \psi_k \rangle$, *Fock* operator $\mathcal{F} = h + J - K$

- That is,

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

- The solution is $\mathcal{F} \psi_k = \varepsilon_k \psi_k$ with *orbital energies* ε_k 's.

HF-SCF

- $\mathcal{F}\psi_k = \varepsilon_k\psi_k$ is solved by a *self-consistency* procedure
- the many electron problem is approximated by a sequential calculation of the motion of one electron in the average potential field generated by the rest of the electrons and nuclei.

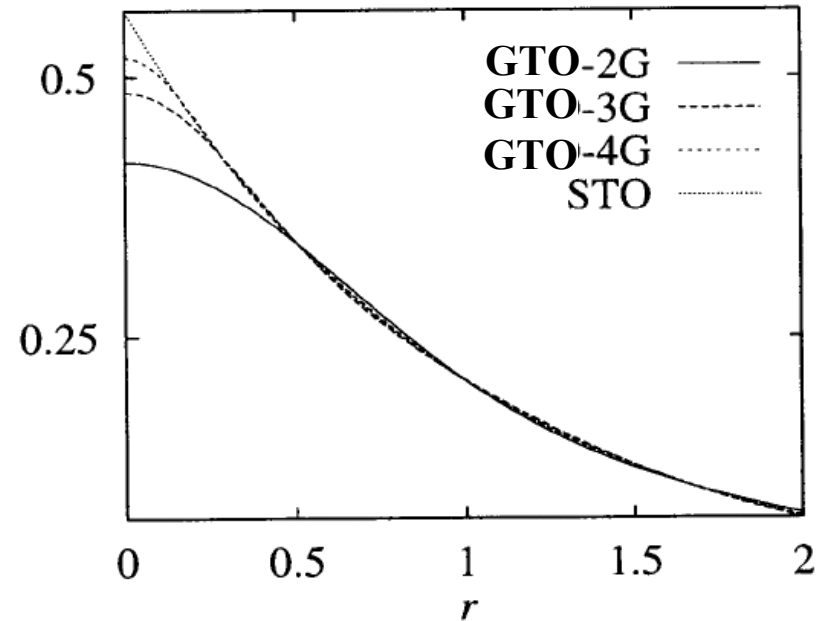
HF-SCF

□ Basis functions

$$\psi_k(\mathbf{x}) = \sum_{p=1}^M C_{pk} \chi_q(\mathbf{x})$$

- Plane waves $\sim e^{i\mathbf{k}\cdot\mathbf{r}}$
- Slate orbitals $\sim e^{-\beta|\mathbf{r}|}$
- Gaussian orbitals $\sim e^{-\beta|\mathbf{r}|^2}$
- Approximation of STO by GTO-NG

$$\sum_{i=1}^N D_i e^{-\beta_i|\mathbf{r}|^2}$$



HF-SCF

□ Generalized Eigenvalue Problem

- Plug $\psi = \sum_q C_p \chi_q(\mathbf{x})$ into $H\psi = E\psi$, we have

$$H \sum_q C_p \chi_q(\mathbf{x}) = E \sum_q C_p \chi_q(\mathbf{x})$$

- With left inner product for each pair of p and q

$$H_{pq} = \langle \chi_p | H | \chi_q \rangle \quad S_{pq} = \langle \chi_p | \chi_q \rangle$$

- We have $\mathbf{HC} = \mathbf{ESC}$

where $\mathbf{H} = [H_{pq}]$ is the Hamilton matrix, $\mathbf{S} = [S_{pq}]$ is the *overlap* matrix, $\mathbf{C} = [C_{pq}]$ is the *density* matrix with

$$C_{pq} = 2 \sum_{k=1}^{\text{occupied}} C_{pk} C_{qk}^*$$

- In unit form $\mathbf{H}'\mathbf{C}' = \mathbf{EC}'$

where $\mathbf{C}' = \mathbf{V}^{-1}\mathbf{C}$, $\mathbf{H}' = \mathbf{V}^{-1}\mathbf{H}\mathbf{V}$, and matrix \mathbf{V} transforms \mathbf{S} to the unit matrix as $\mathbf{V}^{-1}\mathbf{S}\mathbf{V} = \mathbf{I}$.

HF-SCF

□ Hartree-Fock-Roothaan equations

$$\mathbf{F}\mathbf{C}_k = \varepsilon_k \mathbf{S}\mathbf{C}_k$$

where elements of Fock matrix $\mathbf{F} = [F_{pq}]$ is

$$F_{pq} = h_{pq} + \sum_k \sum_{rs} C_{rk}^* C_{sk} (2\langle pr | g | qs \rangle - \langle pr | g | sq \rangle)$$

and $h_{pq} = \langle p | h | q \rangle = \int d^3r \chi_p^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|\mathbf{R}_n - \mathbf{r}|} \right] \chi_q(\mathbf{r})$

$$\langle pr | g | qs \rangle = \int \int d^3r_1 d^3r_2 \chi_p^*(\mathbf{r}_1) \chi_r^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_q(\mathbf{r}_1) \chi_s(\mathbf{r}_2)$$

- density matrix $\mathbf{P} = [P_{pq}]$

$$P_{pq} = 2 \sum_k C_{pk} C_{qk}^* = 2 \sum_k^{\text{occupied}} C_{pk} C_{qk}^*$$

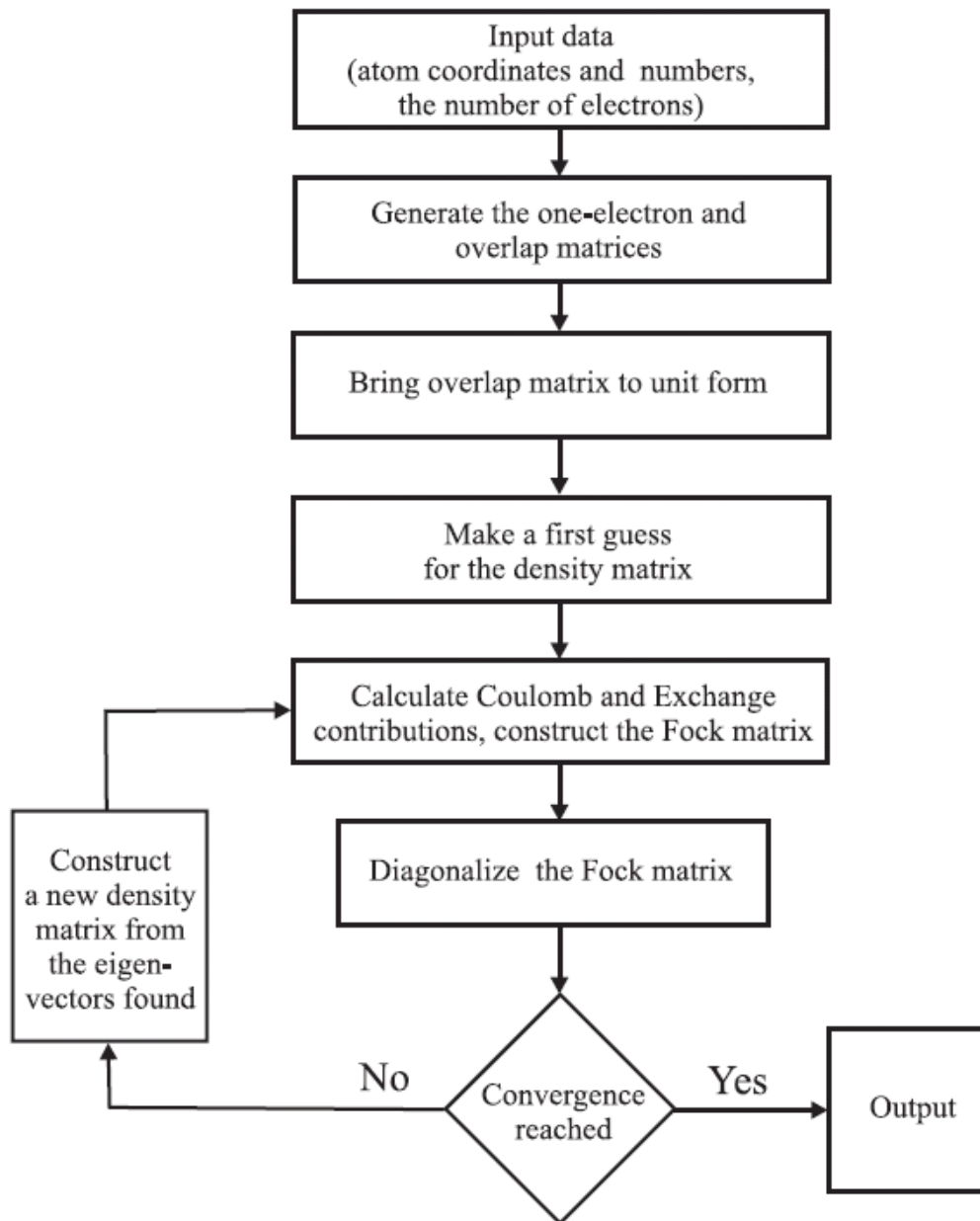
- Fock matrix

$$F_{pq} = h_{pq} + \frac{1}{2} \sum_{rs} P_{rs} (2\langle pq | g | qs \rangle - \langle pr | g | sq \rangle)$$

- Energy

$$E = \sum_{pq} P_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} P_{pq} P_{rs} \left[\langle pr | g | qs \rangle - \frac{1}{2} \langle pr | g | sq \rangle \right]$$

HF-SCF Algorithm



Density Functional Theory (DFT)

- ❑ Very efficiently calculate ground-state electronic structures
- ❑ Based on three simplifications:
 - *Born-Oppenheimer* approximation: solve the Schrödinger equation for the electrons in the field of static nuclei
 - Electrons interacts with a *density* field $\rho(\mathbf{r})$, which is approximated by wave functions
 - Approximations of the unknown exchange-correlation energy functional, which accounts for complicated correlated motion of electrons (e.g. local-density approximation (LDA), generalized gradient approximation (GGA)).

DFT

Energy

$$E[\rho] = \underbrace{\sum_m^{\text{occup}} \int \psi_m^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \psi_m(\mathbf{r}) d\mathbf{r}}_{\text{Kinetics of non-interacting electrons}} + \underbrace{\int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}}_{\text{External}} + \underbrace{\frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2}_{\text{Coulombic interaction}} + E_{xc}[\rho(\mathbf{r})]$$

Kinetics of
non-interacting
electrons

External

Coulombic
interaction

Unknown
exchange and
correlation

Kohn-Sham equations

$$\left[-\frac{1}{2} \nabla^2 + \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}) \right] \psi_m(\mathbf{r}) = \varepsilon_m \psi_m(\mathbf{r})$$

kinetic

External
potential

Hartree
potential

Exchange-Correlation
potential

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$

$$\rho(\mathbf{r}) = \sum_{m=1}^{\text{cccup}} |\psi_m(\mathbf{r})|^2$$

DFT

□ Exchange-correlation potential

- depends on density and its variations

$$V_{xc}[\rho](\mathbf{r}) = V_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla(\nabla\rho(\mathbf{r})), \dots]$$

- Local density approximation (LDA): only \mathbf{r} (not gradients)

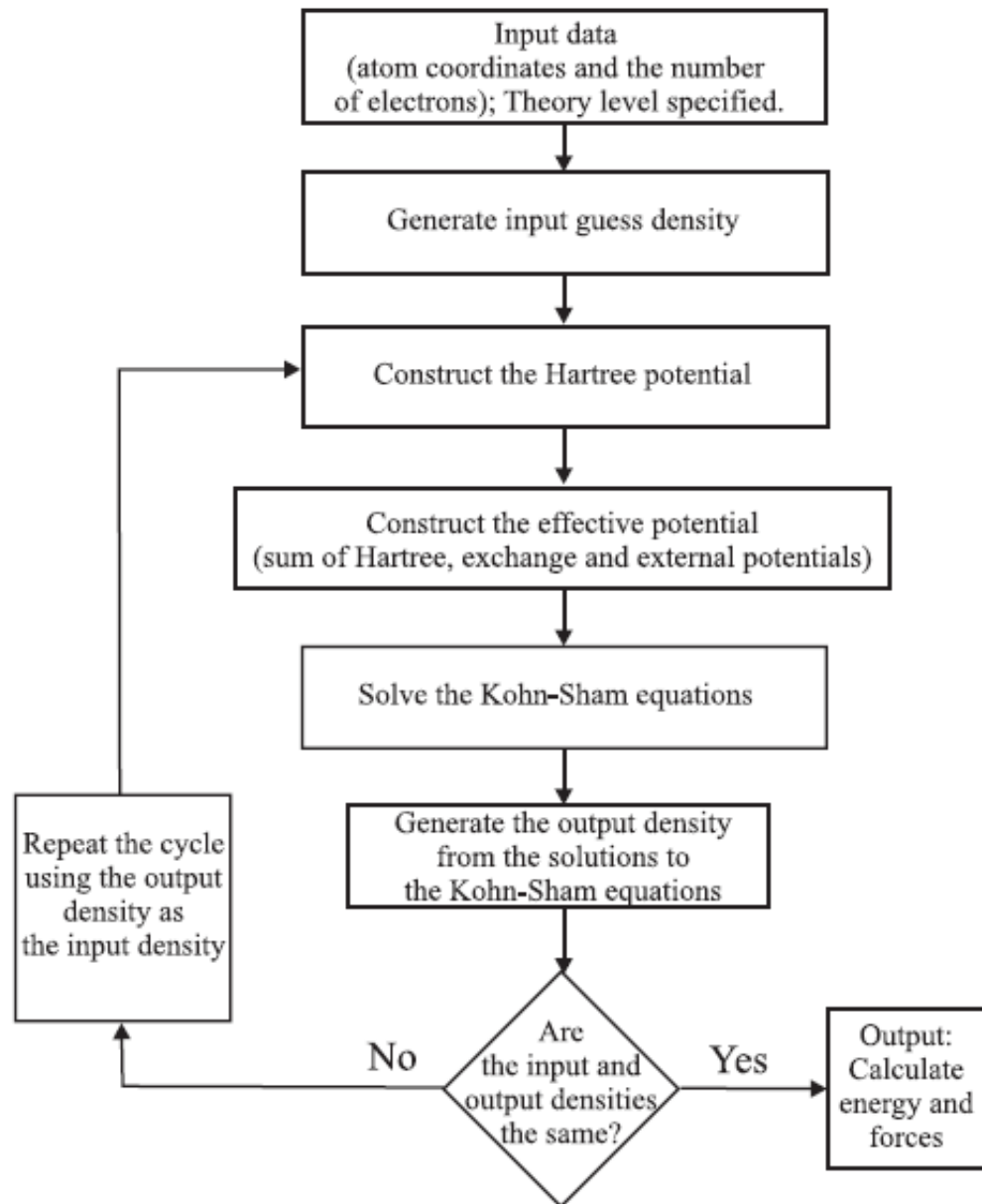
$$E_{xc}^{LDA}(\mathbf{r}) = \int \rho(\mathbf{r}) \varepsilon_{ec}[\rho(\mathbf{r})] d\mathbf{r}$$

where $\varepsilon_{ec}[\rho(\mathbf{r})] = C \times \rho^{1/3}(\mathbf{r})$ and $C = -3 / 4 \times (3 / \pi)^{1/3}$

- Generalized gradient approximation (GGA): with gradient

$$E_{xc}^{GGA}(\mathbf{r}) = \int F[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})] d\mathbf{r}$$

DFT Algorithm



Summary

- ❑ Quantum Monte Carlo
- ❑ Hartree-Fock Self-Consistency Field
- ❑ Density Functional Theory

wave functions
approximation

Further Readings

Quantum Monte Carlo

- ❑ Foulkes W.M.C., Mitas L., Needs R.J. and Rajagopal G. (2001) Quantum Monte Carlo simulations of solids. *Reviews of Modern Physics*, **73**(1):33-83

Density Functional Theory

- ❑ Koch W. and Holthausen M.C. (2001) *A Chemist's Guide to Density Functional Theory* (Weinheim: Wiley-VCH) ISBNs:3-527-30372-3, 3-527-60004-3