MSE6701H Multiscale Materials Modeling and Simulation
First Principles Calculations
A brief Introduction & Density Functional Theory

Ling-Ti Kong

EMail: konglt@sjtu.edu.cn

School of Materials Science and Engineering, Shanghai Jiao Tong University

Sep 29, 2021

Outline for today

All is about energy

Properties/processes of materials depend on the total energy (change):

- Equilibrium lattice constant (density)
- Elastic moduli and elastic constants
- Phonon frequencies
- Magnetism
- Thermodynamic stability (phase diagram)
- Phase transitions
- Vacancy formation
- Diffusion
- Chemical reaction
- Interatomic forces
- ...

Fundamentals of Quantum Mechanics

> ## Schrödinger Equations
>
> $$i\hbar\frac{\partial}{\partial t}\Psi = \hat{\mathbf{H}}\Psi$$

Ψ: the wave function;

the **probability amplitude** for different configurations of the system at different times;

$i\hbar\frac{\partial}{\partial t}$: energy operator;

$\hat{\mathbf{H}}$: Hamiltonian operator;

Quantum Mechanics

Time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{\mathbf{H}} \Psi$$

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}$$

$$\hat{\mathbf{T}} = \hat{\mathbf{T}}_e + \hat{\mathbf{T}}_n, \quad \hat{\mathbf{V}} = \hat{\mathbf{V}}_{e-e} + \hat{\mathbf{V}}_{e-n} + \hat{\mathbf{V}}_{n-n} + \hat{\mathbf{V}}_{\text{ext}}$$

Time independent or stationary Schrödinger equation

$$\hat{\mathbf{H}} \Psi = E \Psi$$

$$
\begin{aligned}
\hat{\mathbf{H}} &= -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} \\
&\quad - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{8\pi\epsilon_0} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_J - \mathbf{R}_I|} \\
\Psi &= \Psi(r_1, r_2, \cdots, r_i, \cdots, R_1, R_2, \cdots, R_I, \cdots)
\end{aligned}
$$

Solvable Quantum Systems: two examples

Free particle

The Schrödinger equation

$$-\frac{\hbar^2}{2m}\,\bigtriangledown^2\,\psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)$$

Solution for a particular momentum

$$\psi(\mathbf{r},t) = e^{i(\mathbf{k}\mathbf{r}-\omega t)}$$

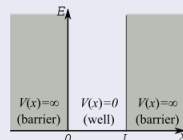with the constraint

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega.$$

$\langle\mathbf{p}\rangle = \langle\psi|-i\hbar\bigtriangledown|\psi\rangle = \hbar\mathbf{k}$

$\langle E\rangle = \langle\psi|i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hbar\omega$

1D infinite potential well

Potential:

E, $V(x)=\infty$ (barrier), $V(x)=0$ (well), $V(x)=\infty$ (barrier), 0, L, x

Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t),$$

Solution:

$$\psi_n(x,t) = \begin{cases} A\sin(k_n x)e^{-i\omega_n t}, & 0 < x < L, \\ 0, & \text{otherwise,} \end{cases}$$

Constraint:

$$k_n = \frac{n\pi}{L}, \quad \text{where} \quad n = \{1,2,3,4,\ldots\},$$

Energy levels: $E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 h^2}{8mL^2}$

Born-Oppenheimer/Adiabatic Approximation

Wave function for general system:

$$\Psi_{\text{total}} = \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_i, \cdots, \mathbf{R}_1, \cdots, \mathbf{R}_I, \cdots)$$

BO Approximation:

$$\Psi_{\text{total}} = \psi(\mathbf{r}; \mathbf{R}) \cdot \phi(\mathbf{R})$$

First step of BO Approximation:

$$\hat{\mathbf{H}}_e \psi(\mathbf{r}, \mathbf{R}) = E_e \psi(\mathbf{r}, \mathbf{R})$$

where $\hat{\mathbf{H}}_e = \hat{\mathbf{T}}_e + \hat{\mathbf{V}}_{e-e} + \hat{\mathbf{V}}_{e-n}$

Second step of BO Approximation:

$$[\hat{\mathbf{T}}_n + E_e(R) + \hat{\mathbf{V}}_{n-n}]\phi(\mathbf{R}) = E\phi(\mathbf{R})$$

M Born and J R Oppenheimer, Ann. Physik 84, 457 (1927)
http://en.wikipedia.org/wiki/Born%E2%80%93Oppenheimer_approximation

Born-Oppenheimer/Adiabatic Approximation

Neglect quantum effect in ionic system $\rightarrow$ replacing Schrödinger Eq. by Newton Eq.

$$M_I \frac{\partial^2 \vec{R}_I(t)}{\partial t^2} = -\bigtriangledown_I E_0(\vec{R})$$

$$E_0(\vec{R}) = E_e(\vec{R}) + V_{nn}(\vec{R})$$

Force $-\bigtriangledown_I E_0(\vec{R})$ contains contributions from the direct ion-ion interaction and a term from the gradient of the electronic total energy.

Hellmann-Feynman theorem

$$\bigtriangledown_I E_e(\vec{R}) = \langle \psi(\vec{R})| \bigtriangledown_I \hat{H}_e(\vec{R})|\psi(\vec{R})\rangle$$

Couples the electronic Schrödinger Eq. with the ionic Newtonian Eq..

Car-Parrinello

http://en.wikipedia.org/wiki/Hellmann%E2%80%93Feynman_theorem

Schrödinger for electrons

$$\hat{\mathbf{H}}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$
\begin{aligned}
\hat{\mathbf{H}} &= \hat{T}_e + \hat{V}_{e-e} + v(r) \\
&= -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} - \frac{1}{4\pi\epsilon_0} \sum_{i,l} \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|}
\end{aligned}
$$

Usual procedure to solve SE:

$v(\mathbf{r}) \;\; \underset{\longrightarrow}{\text{SE}} \;\; \psi(\mathbf{r}) \;\; \langle\psi|\cdots|\psi\rangle \;\;\; \text{observables.}$

- Define the system by choosing $v(\mathbf{r})$;
- Plug into SE and solves ψ;
- Get observables by operations over ψ.

Chemical approaches: Hartree approximation

Postulation

ψ can be written as a simple product of one-electron wave functions

$$\psi(\mathbf{r}) = \prod_i \phi_i(\mathbf{r}_i)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}^{(i)}(\mathbf{R}, \mathbf{r}) \right] \phi_i(\mathbf{r}_i) = \epsilon_i \phi_i(\mathbf{r}_i)$$

$$V_{\text{eff}}^{(i)}(\mathbf{R}, \mathbf{r}) = \int \frac{\sum_{j \neq i} \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' + V(\mathbf{R}, \mathbf{r})$$

$$\rho_j(r) = |\phi_j(r)|^2$$

Problem

Electrons are Fermions and indistinguishable, follow Pauli exclusion principles.

Chemical approaches: Hartree-Fock approximation (SCF)

Introduce Pauli exclusion principle

$$\psi(\mathbf{r}) = \mathrm{SD}\{\phi_i(r_i, \sigma_i)\}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \int \frac{\sum_{j \neq i} \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' + V(\mathbf{R}, \mathbf{r}) \right] \phi_i$$

$$- \sum_j \left[\sum_{\sigma'} \int \frac{\phi_j^* \phi_i}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' \right] \phi_j \;\; = \;\; \sum_j \lambda_{ij} \phi_j$$

Problem

The implied mean field approximation neglects electron correlation for the electrons of opposite spin.

Density Functional Theory: Preliminaries

Function

Function is a relation that uniquely associates members of one set with members of another set. $f : x \longrightarrow f(x)$

Functional

Functional is a real-valued function on a vector space V, usually of functions. $V = \{f : [0,1] \longrightarrow \Re : f \text{ is contineous}\}$

A functional is a function of functions. It maps a function to a number.

Extremum

x_0 minimizes/maximizes $f(x)$ if $\frac{df(x)}{dx}|_{x=x_0} = 0$.
$f_0(x)$ minimizes/maximizes $F[f(x)]$ if $\frac{\delta F[f(x)]}{\delta f(x)}|_{f=f_0} = 0$.

Ref: http://mathworld.wolfram.com

K. Kang, C. Weinberger, and W. Cai, *A Short Essay on Variational Calculus*, Stanford University, 2006.

Density Functional Theory (DFT)

$$n(r) = N \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \psi^*(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)\psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)$$

DFT procedure to solve SE:

$$n(\mathbf{r}) \implies \psi(\mathbf{r}) \implies v(\mathbf{r}).$$

$$V_{ext}(r) \overset{HK}{\Longleftarrow} n(r)$$
$$\Downarrow \qquad \Uparrow$$
$$\Psi_i(\{r\}) \implies \Psi_0(\{r\})$$

Pierre C. Hohenberg

(1934.10-2017.12)

Walter Kohn

(1923.3-2016.4)

Lujeu Sham

(1938.4-)

P. Hohenberg and W. Kohn, Phys. Rev. **136**:B864, 1964.   W. Kohn and L. J. Sham, Phys. Rev. **140**:A1133, 1965.

Hohenberg-Kohn theorem

First (existence) theorem

For any system of interacting particles in $v_{\text{ext}}(\mathbf{r})$, $n_0(\mathbf{r})$ is uniquely determined, i.e., there is a one-to-one correspondence between $v_{\text{ext}}(\mathbf{r})$ and $n_0(\mathbf{r})$.

Second (variational) theorem

An energy functional $E[n]$ can be defined. The exact ground state is the global minimum value of this functional, i.e, $E_v[n_0] \leq E_v[n]$.

Interpretation

- Unique mapping of $v(\mathbf{r}) \Leftrightarrow n_0$;
- All properties are given by $n_0(\mathbf{r})$;
- Each property is a functional of $n_0(\mathbf{r})$, $f[n_0]$;
- A functional $f[n_0]$ maps a function to a result: $n_0(\mathbf{r}) \rightarrow f$.

Advantages

- reduces problem *dim.* from $3N$ to 3;
- $n(\mathbf{r})$ is an *experimental* observable;
- Easy to visualize.

Hohenberg-Kohn theorem

Hamiltonian of electrons

$$\hat{\mathbf{H}} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} - \frac{1}{4\pi\epsilon_0}\sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

Specially for energy

- ψ_0 produces n_0, minimizes $E \Rightarrow n_0$ reproduces ψ_0, minimizes E;
- Total energy functional:

$$E[n] = F[n] + V[n] = T[n] + U[n] + V[n].$$

$T[n]$ and $U[n]$: universal (system independent);
$V[n]$: system dependent, but once $v(\mathbf{r})$ is known, $V[n] = \int n(\mathbf{r})v(\mathbf{r})d^3r$.

For a given system ($v(\mathbf{r})$), all one has to do is to minimize $E[n]$ with respect to n.

Hohenberg-Kohn theorem

pros

simple; exact.

cons

$T[n]$ and $U[n]$ are unknown.

Borrow ideas from Thomas-Fermi approximation ?

$$U[n] \approx U_H[n] = \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

$$T[n] \approx T_{\text{single particle}}^{\text{LDA}}[n] = \int t_s^{hom}(n(\mathbf{r})) d^3 r.$$

$$t_s^{hom}(n) = \frac{3\hbar^2 (3\pi)^{2/3} n^{5/3}}{10m}$$

Unfortunately: unstable molecules.
Reasons: 1) neglect of correlations; 2) LDA in $T[n]$.

Kohn-Sham equations

Decompose $T[n]$ and $U[n]$:

$$T[n] = T_s[n] + T_c[n]$$

$$U[n] = U_H[n] + U_x[n]$$

Rewrite the exact energy functional:

$$E[n] = T_s[n] + U_H[n] + E_{xc}[n] + V[n]$$

Energy minimization:

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V[n]}{\delta n(\mathbf{r})} + \frac{\delta U_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$= \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

$$= 0.$$

Kohn-Sham equations

Noninteracting particles moving in the potential field of $v_s(\mathbf{r})$:

$$0 = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V_s[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r})$$

Effective external field:

$$v_s(\mathbf{r}) \equiv v_{eff}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

Auxiliary Schrödinger Equation:

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) \equiv n_s(\mathbf{r}) = \sum_i^N f_i \cdot |\phi_i(\mathbf{r})|^2.$$

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d^3 r, \qquad T_s[n] + V_s[n] = \sum_i f_i \cdot \epsilon_i.$$

Kohn-Sham equations

Total energy:

$$
\begin{aligned}
E_0 \\
= \quad & T_s[n] + U_H[n] + E_{xc}[n] + V[n] \\
= \quad & T_s[n] + U_H[n] + E_{xc}[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\
= \quad & T_s[n] + U_H[n] + E_{xc}[n] + \int [v_s(\mathbf{r}) - v_H(\mathbf{r}) - v_{xc}(\mathbf{r})]n(\mathbf{r})d\mathbf{r} \\
= \quad & T_s[n] + U_H[n] + E_{xc}[n] + V_s[n] - \int v_H(\mathbf{r})n(\mathbf{r})d\mathbf{r} - \int v_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\
= \quad & T_s[n] + V_s[n] + U_H[n] - \int v_H(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}[n] - \int v_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\
= \quad & \sum_i f_i \epsilon_i - \frac{e^2}{8\pi\epsilon_0} \int \int \frac{n_0(\mathbf{r})n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n] - \int \frac{\delta E_{xc}[n]}{\delta n} n(\mathbf{r})d\mathbf{r}
\end{aligned}
$$

Kohn-Sham equations
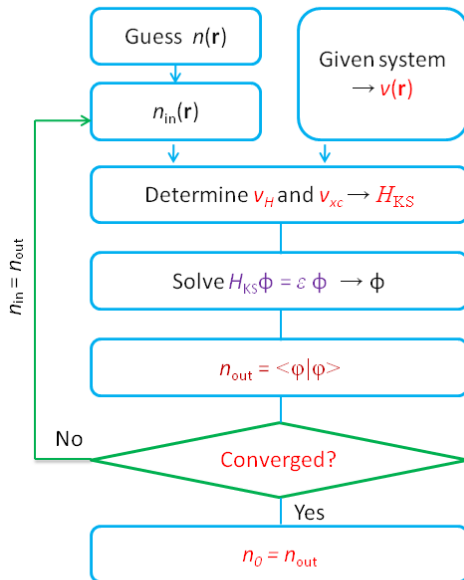
Kohn-Sham equations

non relativistic: Schrödinger

scalar relativistic

relativistic: Dirac

L(S)DA
GGA
hybrids
MGGA

Lagrange multipliers
band structure

$$\left[-\frac{\nabla^2}{2m} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \phi_n(\mathbf{r}) = \varepsilon_n \phi_n(\mathbf{r})$$

Poisson eq.
integral

nuclei
pseudopotential

mesh/basis
GTO/STO/...
LMTO/LAPW/PW/...

DFT in practice: approximations

Local Density Approximation (LDA)

$$E_x^{\mathrm{LDA}} = -\frac{3e^2}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\mathbf{r})^{4/3} d^3 r$$

$$E_{xc}[n] \simeq E_{xc}^{\mathrm{LDA}}[n] = \int e_{xc}^{\mathrm{hom}}(n) d^3 r|_{n\to n(\mathrm{r})} = \int e_{xc}^{\mathrm{hom}}[n(\mathbf{r})] d^3 r.$$

Generalized Gradient Approximation (GGA)

$$E_{xc}^{\mathrm{GGA}}[n] = \int f(n(\mathbf{r}), \bigtriangledown n(\mathbf{r})) d^3 r.$$

Chemistry: BLYP   Physics: PBE

Spin-polarized

$$E_{xc}^{\mathrm{LSDA}}[n_\alpha, n_\beta] = \int f(n_\alpha, n_\beta) n(\mathbf{r}) d^3 r.$$

$n = n_\alpha + n_\beta$.

Homework

1. Go through all the slides and deduce all equations by yourself.
2. Read through: Bloch theorem.
3. **Think:** If you evaluate the kinetic energy of a Kohn-Sham system, does it equal to the physical kinetic energy? why?
4. **Hand in:** Solve the free particle and 1-D infinite potential well problems illustrated in page 6.
5. **Hand in:** Derive the Kohn-Sham equations (page 17) by yourself.
6. **Hand in:** When we say $F[n]$ is a *universal* functional, what do we mean exactly? Since $v_{ext}(r)$ itself is a functional of $n(r)$, is the total energy functional universal?

Due: **Oct 13th, 2021.** Submit electronic/scanned version on canvas or written version in class. You can refer to any kind of literature, but specify your references **explicitly**.

References and further readings

1. K. Capelle, A Bird's-Eye View of DFT,
   http://arxiv.org/abs/cond-mat/0211443.

2. Fabio Finocchi, Density Functional Theory for Beginners: Basic
   Principles and Practical Approaches.

3. R. O. Jones and O. Gunnarsson, Review of Modern Physics
   61(3):689, 1989.

4. J. Hafner, *Atomic-scale computational materials science*, Acta
   Materialia 48:71-92, 2000.

5. R.M. Dreizler and E.K.U. Gross, *Density Functional Theory*,
   Springer-Verlag (1990), ISBN 3-540-51993-9.