Kohn-Sham equation

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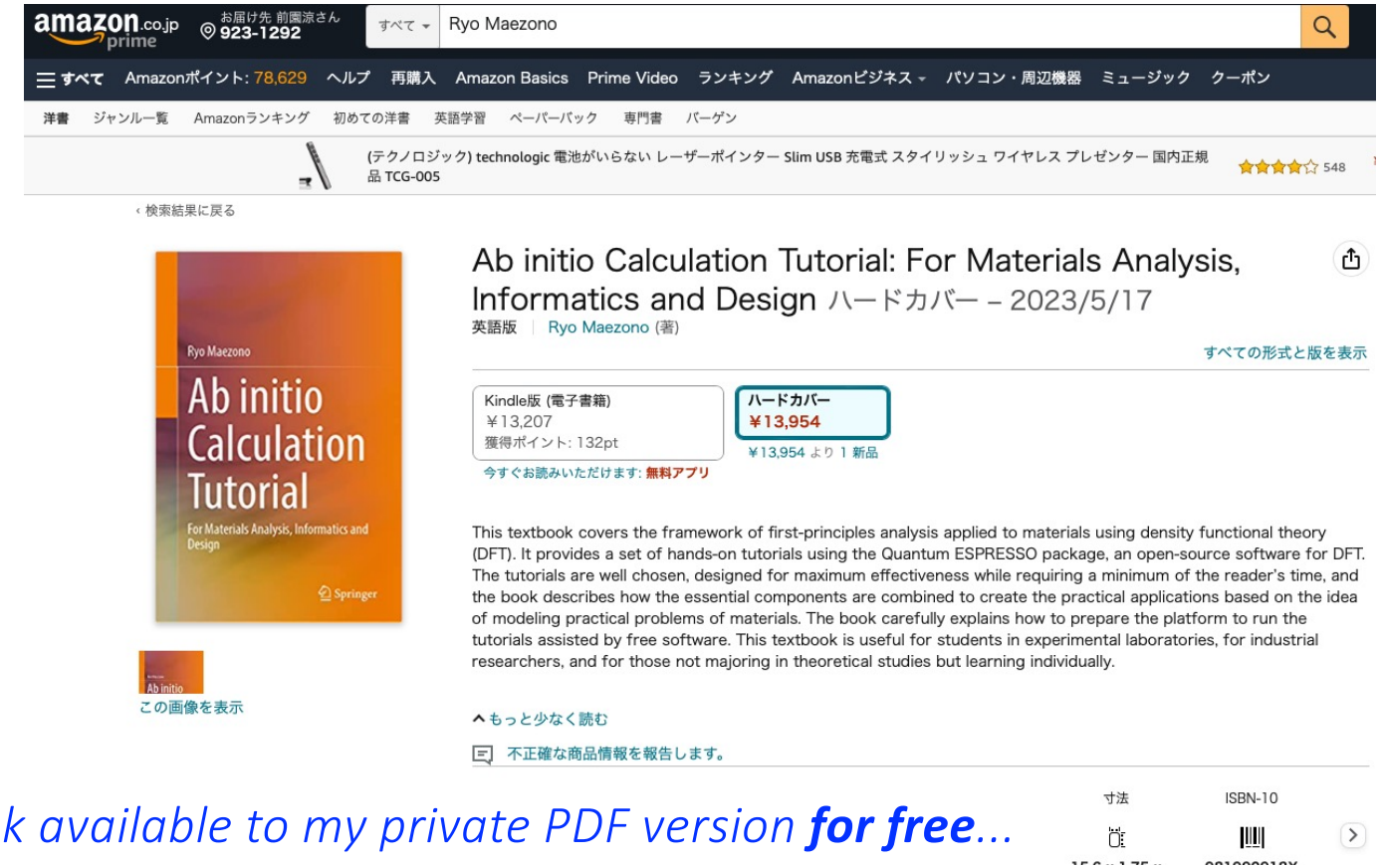
Book composed

*for **experimentalists/industrial** researchers*



*Link available to my private PDF version **for free**...*

— *https://www.dropbox.com/s/o0o93j25obb8jtj/book.pdf?dl=0*

In its Acknowledgement...

The content of this book is based on a Japanese book (ISBN-13: 978-4627170315) published by Morikita Publishing in 2020. The concept of this book was based on the tutorial training program funded by JST-Sakura Science plan, which accepted intern students from Asian countries, the tutorial training program 'ASESMA' (African School on Electronic Structure Methods and Applications) funded by ICTP (International Centre for Theoretical Physics), the workshop at Department of Metallurgical and Materials Engineering of IITM (Indian Institute of Technology, Madras), at Department of Materials Science of Chulalongkorn University (Thailand), *etc.* In particular, I would like to express my respectful acknowledgement to Prof. Richard Martin for his guidance in these activities.

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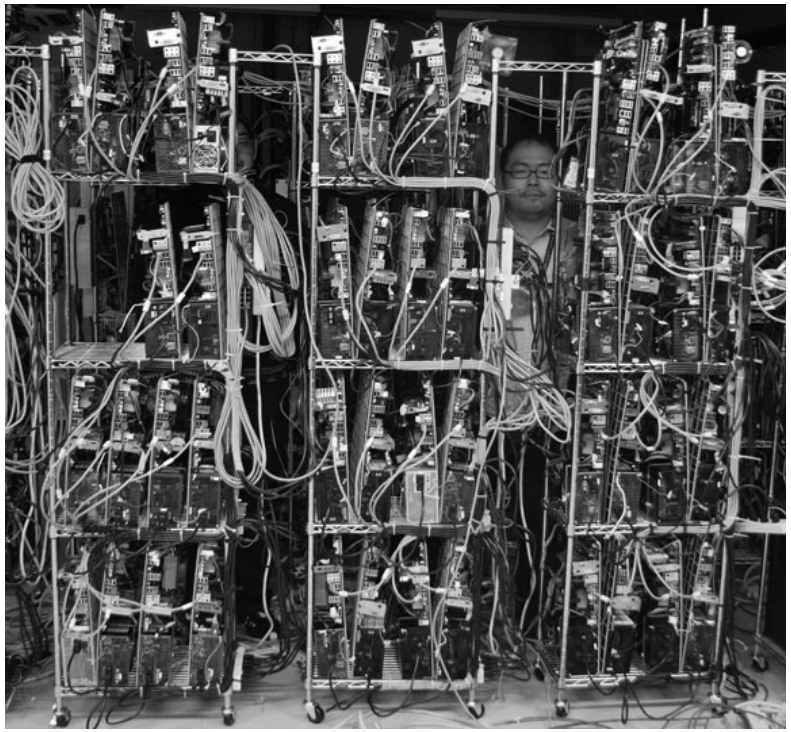
Book composed

PC cluster building and administration for experimentalists/industrial researchers

※ *Note, authors major is not about this, but numerical many-body physics!*

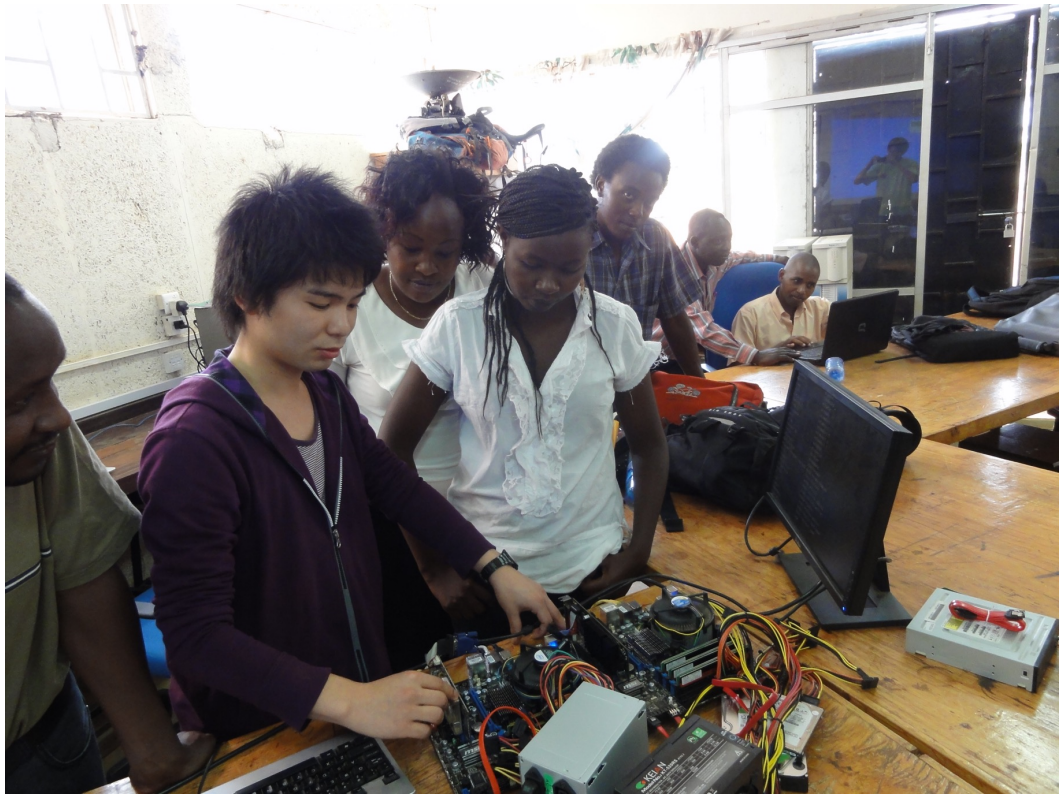
Computational resource within a group...

Handmade Parallel Cluster



AMD-EPYC/64cores with 100Gbps interconnect...

2011, Kenya/Eldoret



International Tutorials

QMC tutorial workshop

Organized @JAIST, 10-days.

25 International Participants

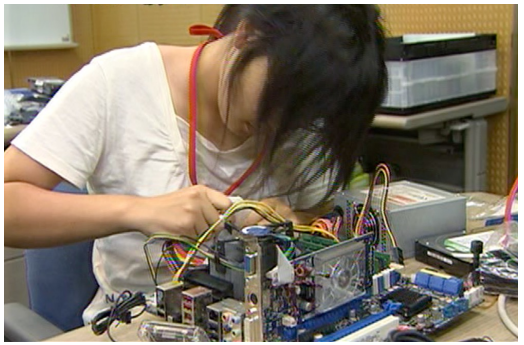
Lectures from (Japan/Taiwan/UK)
Participants(Iran、Zimbabue、Kenya、Korea、India、Russia、
Ethiopia、Nigeria、China、Cameroon、
Taiwan、Thai、Indonesia)

Tutorial Activities

How to build hand-made parallel simulations

For Japanese high-school teachers/high school students (funded by government)
For Asian Under-Grad. internship (funded by government)

Organized as well in abroad! [Kenya2011/Thai2017 (Phuket)]



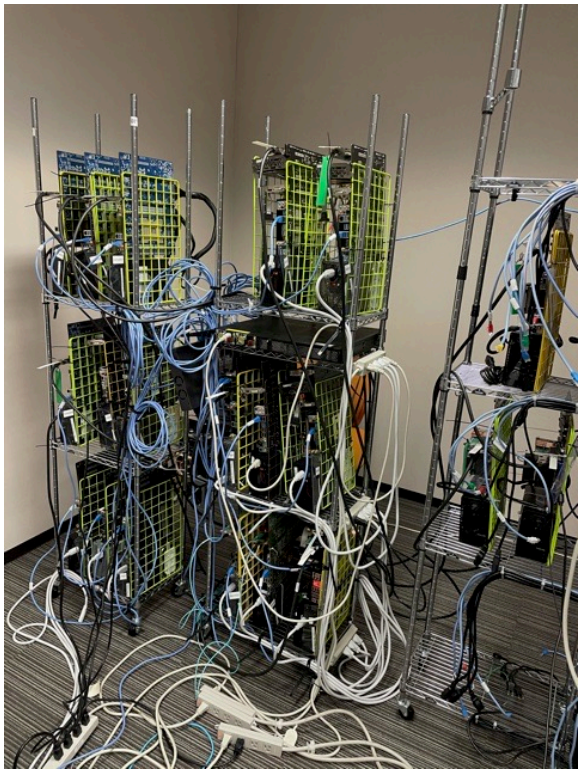
MPI-parallel simulation for materials science.

Interdisciplinary among Materials Sci. and Computer Sci.

[an40]

100GB/OmniPath

Inter-connect becomes '*Not bottle-neck*'! DDR4 memory becomes bottle-neck...



Real hand-made supercomputer!

AMD-EPYC/64cores

Network: SuperMicro 100G Omni-Path switch

around 10 nodes in operation

- Much cheaper than the one purchased from Vendors...

- Very nice materials for training up students
for server-administration!

Outline of the talk...

- Overview of approaches for many-body Schrodinger equation

Several comparable methods including DFT.

- Molecular orbital method (traditional introduction to one-body form)

Good starting-point to understand DFT concept under the contrast...

Starting from practical usage/how to handle...

- Concept of DFT (density functional method) (mapping to one-body form)

- Idea to get Kohn-Sham equation (overview)

- Exchange-correlation functionals (**eventual goal**!)

- Formulation to derive Kohn-Sham equation

Not starting from fundamentals...

... Getting audience bored by long stories without a goal in mind...

- Handling of Kohn-Sham equation

SCF procedure/Convergence/Smearing

- Notes on Kohn-Sham equation

Contrast with molecular orbitals/Quantum many-body interactions

Overview of approaches for many-body Schrodinger equation

Kohn-Sham framework is one of the approaches

Many-body Schrodinger Equation

(after Non-relativistic, Adiabatic approx.)

To be solved...

Set of electrons at $(\vec{r}_1,\cdots,\vec{r}_N)$

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

Positions of nuclei

(Eigenvalue Equation)

Equation to dominate electrons in materials

Equation to find...

- *Function* $\Psi(\vec{r}_1,\cdots,\vec{r}_N)$
- *Value* ***E***

... satisfying the above '='

Once it is found, then ***E*** *represents the energy for your electronic system*

How to treat fundamental equation

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

Sorted into…

- *mainly in Phys.* $\frac{\delta E[n(\vec{r})]}{\delta n} = 0$ *… Variational w.r.t. Density*
  - **Density Functional Theory**
- *mainly in Chem.* $\frac{\delta E[\Psi(\vec{r}_1,\cdots,\vec{r}_N)]}{\delta \Psi} = 0$ *… Variational with respect to Wave Function*
  - **Molecular Orbital method** $\Phi(\vec{r}_1,\cdots,\vec{r}_N) = \Phi[\{\varphi_j(\vec{r}_j)\}]$
    … 3-dim. orbital to decouple 3N-dim. problem.
  - **Quantum Monte Carlo** *(electronic structure calc.)*

$$\langle\hat{O}\rangle = \frac{\int d\vec{R}\cdot\Psi^*(\vec{R})\cdot\hat{O}\Psi(\vec{R})}{\int d\vec{R}\cdot\Psi^*(\vec{R})\Psi(\vec{R})} = \frac{\int d\vec{R}\cdot|\Psi|^2\cdot[\Psi^{-1}(\vec{R})\cdot\hat{O}\Psi(\vec{R})]}{\int d\vec{R}\cdot|\Psi|^2} = \langle\Psi^{-1}(\vec{R})\cdot\hat{O}\Psi(\vec{R})\rangle$$

…Monte Carlo Sampling for this type of Integrals

Major Engines for single point calculation

1) ***MO (Molecular Orbital method)***

   Traditionally precise methods.

   *Only applicable to **smaller** systems (atom and molecules)*

2) ***DFT (Density Functional method)***

   Computationa cost performance is good (feasible for larger systems)

   *Reliability is quite "**unknown**" for some systems (to what extent it can be reliable?)*

3) ***QMC (Quantum Monte Carlo method)***

   Believed as most accurate method, but costly!

   Massive Parallel Computation is quite good at it.

Variety of Solvers

Drastic Assumptions → **Less Assumptions as possible**

Tractable/Practical → *Reliable*

Low-cost ← *Expensive*

Introduction of

One-body picture

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N)=\Psi[\psi_1(\vec{r}_1),\psi_2(\vec{r}_2),\cdots,\psi_N(\vec{r}_N),\psi_2(\vec{r}_1),\cdots]$$

Effective one-body potentials $\psi_j(\vec{r})\leftrightarrow v_{eff}(\vec{r})$

Drastic approximation applied here

Molecular Orbital

MO method *(Gaussian03)*

DFT method *(QuantumEspresso)*

Density Functional Theory

Retain **many-body picture**

$\Psi(\vec{r}_1,\cdots,\vec{r}_N)$ *and* $U(\vec{r}_1,\cdots,\vec{r}_N)$

Quantum Monte Carlo

(CASINO, QMCPack, TurboRVB)

How "original many-body form" is handled by one-body form?

How the one-body form introduced?

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Contrast with molecular orbitals/Quantum many-body interactions

Molecular orbital method

traditional introduction to one-body form

Good material to understand DFT concept by the contrast...

Variable Separation

... conventional strategy in Math. ...

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V\left(\vec{r}_1,\cdots,\vec{r}_N\right)\right]\cdot\Psi\left(\vec{r}_1,\cdots,\vec{r}_N\right) = E\cdot\Psi\left(\vec{r}_1,\cdots,\vec{r}_N\right)$$

$\Psi\left(\vec{r}_1,\cdots,\vec{r}_N\right)$; *many-variable function... Difficult to be imagined...*

(many-body Wavefunction)

Usual practice...

$$\Psi\left(\vec{r}_1,\cdots,\vec{r}_N\right) = \psi_1\left(\vec{r}_1\right)\psi_2\left(\vec{r}_2\right)\psi_3\left(\vec{r}_3\right)\cdots\psi_N\left(\vec{r}_N\right) \qquad \textbf{[Assumption]}$$

... always as represented in this form or not??

1-fold 'many-body equation'

➔ *N-fold 'one-body equation' with respect to* $\left\{\psi_j\left(\vec{r}\right)\right\}_{j=1}^{N}$

(one-body Orbital function)

Much easier to be solved...

Updated ver. of variable separation

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

$\Psi(\vec{r}_1,\cdots,\vec{r}_N) = \psi_1(\vec{r}_1)\cdot\psi_2(\vec{r}_2)\cdot\psi_3(\vec{r}_3)\cdots\psi_N(\vec{r}_N)$; *Simple variable separation*

But for electronic systems, exact solution should satisfy... *[**Hartree** approximation]*

$\Psi(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) = (-)\cdot\Psi(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots)$; ***anti-symmetric constraint***

e.g.) 3-body system ; Ψ(2,1,3) = (-) Ψ(1,2,3) should be satisfied, but...

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \psi_1(\vec{r}_1)\cdot\psi_2(\vec{r}_2)\cdot\psi_3(\vec{r}_3) \Rightarrow \Psi(\vec{r}_2,\vec{r}_1,\vec{r}_3) = \psi_1(\vec{r}_2)\cdot\psi_2(\vec{r}_1)\cdot\psi_3(\vec{r}_3) \neq -\psi_1(\vec{r}_1)\cdot\psi_2(\vec{r}_2)\cdot\psi_3(\vec{r}_3)$$

***... cannot** satisfy anti-symmetric constraint...*

Revising Hartree approx. by composing linear combination,

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \begin{pmatrix} \psi_1(\vec{r}_1)\cdot\psi_2(\vec{r}_2)\cdot\psi_3(\vec{r}_3) + \psi_2(\vec{r}_1)\cdot\psi_3(\vec{r}_2)\cdot\psi_1(\vec{r}_3) + \psi_3(\vec{r}_1)\cdot\psi_1(\vec{r}_2)\cdot\psi_2(\vec{r}_3) \\ -\psi_1(\vec{r}_1)\cdot\psi_3(\vec{r}_2)\cdot\psi_2(\vec{r}_3) - \psi_3(\vec{r}_1)\cdot\psi_2(\vec{r}_2)\cdot\psi_1(\vec{r}_3) - \psi_2(\vec{r}_1)\cdot\psi_1(\vec{r}_2)\cdot\psi_3(\vec{r}_3) \end{pmatrix}$$; *Ψ(2,1,3) = (-) Ψ(1,2,3) now satisfied!*

$= \sum_P (-)^P \psi_{P_1}(\vec{r}_1)\cdot\psi_{P_2}(\vec{r}_2)\cdot\psi_{P_3}(\vec{r}_3)$; *anti-symmetrized products* *[**Hartree-Fock** approximation]*

Updated ver. of variable separation

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

1) $\Psi(\vec{r}_1,\cdots,\vec{r}_N) = \psi_1(\vec{r}_1)\cdot\psi_2(\vec{r}_2)\cdot\psi_3(\vec{r}_3)\cdots\psi_N(\vec{r}_N)$; *simple variable separation*

cannot satisfy...

$\Psi(\cdots,\vec{r}_i,\cdots,\vec{r}_j,\cdots) = (-)\cdot\Psi(\cdots,\vec{r}_j,\cdots,\vec{r}_i,\cdots)$; ***anti-symmetric constraint***

[for solution describing electrons (fermion)]

2) ***Hartree-Fock approximation***

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N) = \sum_P (-)^P \psi_{P_1}(\vec{r}_1)\cdot\psi_{P_2}(\vec{r}_2)\cdot\cdots\psi_{P_N}(\vec{r}_N) = \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \ddots & & \vdots \\ \vdots & & & \\ \psi_N(\vec{r}_1) & \cdots & & \psi_N(\vec{r}_N) \end{vmatrix}$$

anti-symmetrized *variable separation*

Slater Determinant

*[c.f., definition of determinant as **anti-symmetrized sum of products**]*

One-body form with molecular orbitals

(c.f., contrast to Kohn-Sham orbital)

Original many-body form

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

1-fold 'many-body equation'

anti-symmetrized variable separation

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N) = \sum_P (-)^P \psi_{P_1}(\vec{r}_1)\cdot\psi_{P_2}(\vec{r}_2)\cdot\cdots\psi_{P_N}(\vec{r}_N)$$ *[Assumption/Approx.]*

... substituting this assumption into many-body equation leads to...

One-body form

N-fold 'one-body equation' w.r.t. $\{\psi_j(\vec{r})\}_{j=1}^N$

The term already appeared in Hartree approx. *The term only appeared when anti-symmetry considered.*

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \sum_{j\neq i}\int d\vec{r}'\cdot\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\cdot\psi_i(\vec{r}) - \sum_{j\neq i}\left[\int d\vec{r}'\cdot\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\cdot\psi_j(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$ ***[Hartree-Fock equation]***

Classical Coulomb (***Hartree term***)

*Statistical Effect by Quantum Mech. (**Pauli exclusion**)* (***Exchange term***)

[The most basic concept of Molecular Orbital Method...]

Computational Implementation for this has well been developed over decades...

*N.B./**Interaction** evaluated by the **non-interacting WF**. (Variable-separation justified when non-interacting)*

Hartree-Fock approximation

'Reference zero' for further improvements...

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$ *; many-body Schrodinger equation*

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N) = \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \ddots & & \\ \vdots & & & \\ \psi_N(\vec{r}_1) & & & \psi_N(\vec{r}_N) \end{vmatrix}$$ *is assumed form of wavefunction*

*[**Interactions** are evaluated by this **non-interacting solution**]*

$$\rightarrow \left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \sum_{j\neq i}\int d\vec{r}'\cdot\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\cdot\psi_i(\vec{r}) - \sum_{j\neq i}\left[\int d\vec{r}'\cdot\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\cdot\psi_j(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$ ***[Hartree-Fock equation]***

Classical Coulomb (***Hartree term***)

Statistical Effect by Quantum Mech. (***Exchange term***)

Reality *: interactions should be evaluated by '**deformed** wavefunction by the **interaction**)*

$$\rightarrow \left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \sum_{j\neq i}\int d\vec{r}'\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\psi_i(\vec{r}) - \sum_{j\neq i}\left[\sum_{j\neq i}\int d\vec{r}'\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\psi_j(\vec{r}) + \hat{V}_C\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$

effect due to deformation of WF

(***Hartree term***) (***Exchange term***) (***Correlation term***)

... just as a conceptual explanation... (note caret on V_c as general operator)

What is explained in this lecture...

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N)=\begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \ddots & & \\ \vdots & & & \\ \psi_N(\vec{r}_1) & & & \psi_N(\vec{r}_N) \end{vmatrix}$$

is assumed form of wavefunction

Interactions are evaluated by this approximated wavefunction...

$$\left[-\frac{1}{2}\nabla^2+v_{ext}(\vec{r})+\sum_{j\neq i}\int d\vec{r}'\cdot\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\cdot\psi_i(\vec{r})-\sum_{j\neq i}\left[\int d\vec{r}'\cdot\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\cdot\psi_j(\vec{r})=\varepsilon_i\cdot\psi_i(\vec{r})$$ ***[Hartree-Fock equation]***

Classical Coulomb (***Hartree term***)

Statistical Effect by Quantum Mech. (***Exchange term***)

Reality *: interactions should be evaluated by '**deformed** wavefunction by the **interaction**)*

effect due to deformation of WF

$$\left[-\frac{1}{2}\nabla^2+v_{ext}(\vec{r})+\sum_{j\neq i}\int d\vec{r}'\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\psi_i(\vec{r})-\sum_{j\neq i}\left[\sum_{j\neq i}\int d\vec{r}'\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\psi_j(\vec{r})+\hat{V}_C\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r})$$ ***[Kohn-Sham equation]***

(***Hartree term***) (***Exchange term***) (***Correlation term***)

Derived by what & how ?? On what way of concept ??

(Never via approximation using variable separation!)

Concept of DFT

Though both takes similar one-body form…

Molecular Orbital theory

MO/ *original Many-body* ➔ *Set of One-body form.*

(***Approximation***/*Variable separation)*

Density Functional Theory

DFT/ ***equivalent*** *one-body form EXACTLY reproducing original many-body form possible?*

(***Mapping*** *onto the equivalent prob.)*

Concept of DFT

equivalent *one-body form EXACTLY reproducing original many-body form possible?*

*(**Mapping** onto the equivalent prob.)*

How is it justified??

Hohenberg-Kohn Theorem *(in 1960's)*

Normal Way...

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

Primary...

Energy as Eigenvalue E_G *[primary to be identified first]*

$\Psi(\vec{r}_1,\cdots,\vec{r}_N)$ *as Eigenfunction*

Secondary...

Then, Charge Density

$$n(\vec{r}) = \frac{\int\left|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)\right|^2\cdot\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\cdot d\vec{r}_1\cdots d\vec{r}_N}{\int\left|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)\right|^2\cdot d\vec{r}_1\cdots d\vec{r}_N} = \left\langle\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\right\rangle$$

$$n(\vec{r}) = n\left[\Psi(\vec{r}_1,\cdots,\vec{r}_N)\right]$$

Hohenberg-Kohn theorem...

$E_{GS} = E_{GS}\left[n(\vec{r})\right]$ *Formally proved (proof by contradiction)*

completely specified from charge density

Then we can skip to solve $\Psi(\vec{r}_1,\cdots,\vec{r}_N)$

Applying Hohenberg-Kohn Theorem...

Original Many-body form

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

$$n(\vec{r}) = \frac{\int\left|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)\right|^2\cdot\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\cdot d\vec{r}_1\cdots d\vec{r}_N}{\int\left|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)\right|^2\cdot d\vec{r}_1\cdots d\vec{r}_N} = \left\langle\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\right\rangle$$

$E_{GS} = E_{GS}[n(\vec{r})]$ *identical charge density*

Equivalent One-body form

$$n(\vec{r}) = \sum_{\alpha=1}^{N}\left|\psi_\alpha(\vec{r})\right|^2$$

$$\left\{\left[-\frac{1}{2}\nabla^2 + v_{one-body}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})\right\}_{i=1}^{N} \quad (\textbf{reference system})$$

If there exists such a one-body form... that gives the exact n(r), then...

The same exact Ground state energy estimated!

Any proof assuring the existence? --> YES! *Hohenberg/Kohn/Levy etc. in 60's [**Density Functional Theory**]*

Kohn-Sham framework

Original Many-body form

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

$$n(\vec{r}) = \frac{\int|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)|^2\cdot\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\cdot d\vec{r}_1\cdots d\vec{r}_N}{\int|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)|^2\cdot d\vec{r}_1\cdots d\vec{r}_N} = \left\langle\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\right\rangle$$

$E_{GS} = E_{GS}[n(\vec{r})]$ *identical charge density*

Equivalent One-body form

$n(\vec{r}) = \sum_{\alpha=1}^{N}|\psi_\alpha(\vec{r})|^2$; ***Kohn-Sham Orbital*** *(orbitals just represent charge density)*

$$\left\{\left[-\frac{1}{2}\nabla^2 + v_{one-body}^{(eff)}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})\right\}_{i=1}^{N}$$ *(**reference system/Kohn-Sham equation**)*

Instead of working on original complicated interacting form,

Solve the equivalent reference system! *Well-established numerical framework available...*

Effective one-body potential *so that it can give the same n(r)*

of exact interacting many-body system

How? in Kohn-Sham framework...

$$E_{GS} = E_{GS}\left[n(\vec{r})\right]$$

Equivalent One-body form

$$n(\vec{r}) = \sum_{\alpha=1}^{N} \left|\psi_\alpha(\vec{r})\right|^2$$; **Kohn-Sham Orbital** *(orbitals just reproduce exact charge density)*

$$\left\{\left[-\frac{1}{2}\nabla^2 + v_{one-body}^{(eff)}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})\right\}_{i=1}^{N}$$ (**reference system/Kohn-Sham equation**)

Effective one-body potential so that it can reproduce exact n(r).

How to get such an Effective Problem giving the exact n(r) ?

Another theorem $\frac{\delta E_{GS}[n]}{\delta n(\vec{r})} = 0$ *restricts the form of one-body equation.*

... leading to derive Kohn-Sham eq. (explained later)

exact solution satisfies this.

... though we don't know what is exact n(r),

but we know exact n(r) should satisfy what...

Density Functional Theory only ***ensures*** *...*

Existence of such a problem/potential

but ***not how to construct it***.

XC potential practical

effective one-body potential *so that it can reproduce exact n(r).*

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\left[n(\vec{r})\right]\right]\cdot\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$

Density Functional Theory just ensures ... ***Existence of such a problem/potential***

but not how to construct it...

Variety of XC potentials practically used...

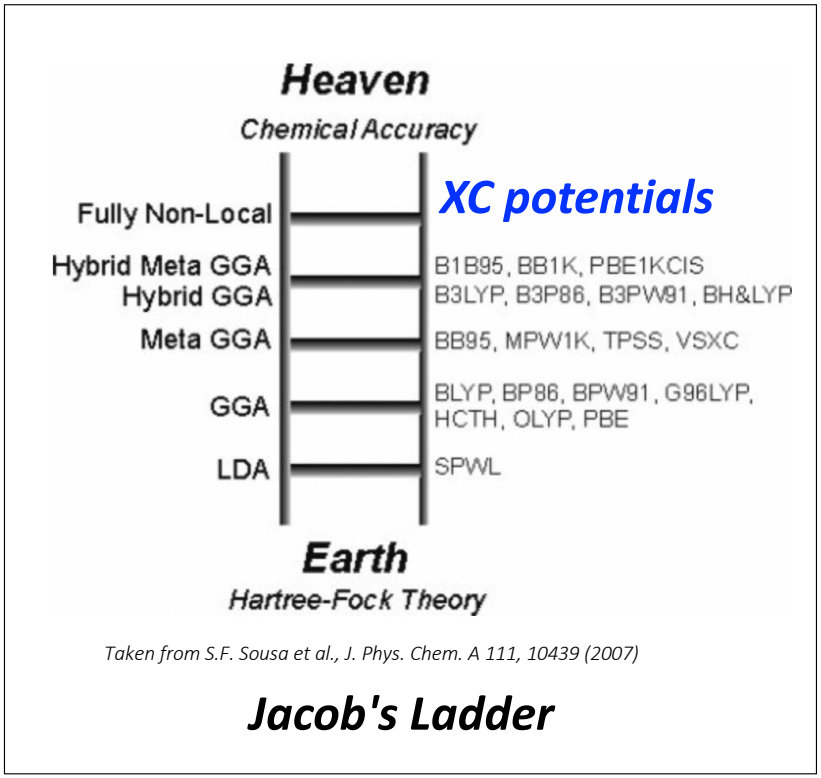
- *Those constructed based on* ***'Homogeneous Electron Gas****' estimations.*
- *Those constructed based on* ***'Benchmark molecules****'.*
- *Those constructed so that required* ***conservation rules*** *are satisfied.*

DFT framework itself ***rigorous****, but* ***approximations*** *introduced*

at the level when practical implementation of XC potentials made...

Random walk is capable to climb up

Ladder



Taken from S.F. Sousa et al., J. Phys. Chem. A 111, 10439 (2007)

Jacob's Ladder

DFT

Japanese drinker's Ladder

('Ladder drinker' in Japanese Language)

QMC

Outline of the talk...

- Overview of approaches for many-body Schrodinger equation

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Starting from practical usage/how to handle...

- Concept of DFT (density functional method) (mapping to one-body form)

- Idea to get Kohn-Sham equation (overview)

- Exchange-correlation functionals (**eventual goal**!)

- Formulation to derive Kohn-Sham equation

Not starting from fundamentals...

... Getting audience bored by long stories without a goal in mind...

- Handling of Kohn-Sham equation

SCF procedure/Convergence/Smearing

- Notes on Kohn-Sham equation

Contrast with molecular orbitals/Quantum many-body interactions

How Kohn-Sham equation derived...

How Kohn-Sham equation derived (1)

To perform $\frac{\delta E[n(\vec{r})]}{\delta n} = 0$

setting a form for $E_{GS} = E_{GS}[n(\vec{r})]$

as $E[n] \equiv \int v_{\text{ext}}(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} + F[n]$.

internal *factors of interacting particles*

...separating out the interaction with ***external*** *factors*

[Interaction with Nuclei array (geometry)]

'Universal *functional'*

... taking universal form with respect to n for a kind of interaction.

(Coulomb interaction/Nucleus interaction/etc.)

How Kohn-Sham equation derived (2)

To perform $\frac{\delta E[n(\vec{r})]}{\delta n} = 0$

internal *factors of interacting particles*

setting $E[n] \equiv \int v_{\text{ext}}(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r} + F[n].$

Classical Coulomb *Other excess*

and setting, $F[n] = T_s[n] + \frac{1}{2} \iint \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r} d\boldsymbol{r}' + E_{\text{xc}}[n]$

Kinetic energy of ***reference system***

namely,

$$T_s[n] = \sum_i \varepsilon_i - \int v_{\text{eff}}(\boldsymbol{r}) n(\boldsymbol{r})$$

$$\left[-\frac{\nabla^2}{2} + v_{\text{eff}}(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r})$$

$$\left(n(\boldsymbol{r}) = \sum_i |\psi_i(\boldsymbol{r})|^2 \right)$$

[N.B.; every formulation is motivated just on 'without losing generality'...]

How Kohn-Sham equation derived (3)

Then, $E_{\mathrm{GS}}[n(\vec{r})] = T_{\mathrm{S}} + \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r} - \vec{r}'|} + E_{\mathrm{XC}}[n(\vec{r})] + \int d\vec{r} \cdot v_{\mathrm{ext}}(\vec{r}) \cdot n(\vec{r})$

$$T_s[n] = \sum_i \varepsilon_i - \int v_{\mathrm{eff}}(\boldsymbol{r}) n(\boldsymbol{r})$$

Performing $\frac{\delta E[n(\vec{r})]}{\delta n} = 0$

consequence of the variational requirement

we get a relation... $v_{\mathrm{eff}}(\vec{r}) = v_{\mathrm{ext}}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\mathrm{XC}}[n(\vec{r})]}{\delta n(\vec{r})}$

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{eff}}(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r})$$

reference system to give true density $n(\boldsymbol{r}) = \sum_i |\psi_i(\boldsymbol{r})|^2$

[density identical to that of an interacting system]

How Kohn-Sham equation derived (4)

Kohn-Sham equation

Classical Coulomb *Quantum effects (exchange & correlation)*

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{\text{XC}}[n(\vec{r})]}{\delta n(\vec{r})}\right] \cdot \psi_i(\vec{r}) = \varepsilon_i \cdot \psi_i(\vec{r})$$

Exchange-correlation *functional ;* $V_{\text{XC}}[n(\vec{r})] = \frac{\delta E_{\text{XC}}[n(\vec{r})]}{\delta n(\vec{r})}$

reference system to give true density $n(\boldsymbol{r}) = \sum_i |\ \psi_i(\boldsymbol{r})|^2$

[density identical to that of an interacting system]

Ground state energy ; $E_{GS} = E_{GS}\left[n(\vec{r})\right]$

Though the form is similar...

Conceptual extension of Hartree-Fock equation...

Reality : interactions should be evaluated by '**deformed** wavefunction by the **interaction**)

effect due to deformation of WF

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \sum_{j\neq i}\int d\vec{r}' \frac{\left|\psi_j(\vec{r}')\right|^2}{\left|\vec{r}-\vec{r}'\right|}\right]\psi_i(\vec{r}) - \sum_{j\neq i}\left[\sum_{j\neq i}\int d\vec{r}'\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{\left|\vec{r}-\vec{r}'\right|}\psi_i(\vec{r}')\right]\psi_j(\vec{r}) + \hat{V}_C\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

(**Hartree term**) (**Exchange term**) (**Correlation term**)

Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\vec{r}) + \int d\vec{r}'\frac{n(\vec{r}')}{\left|\vec{r}-\vec{r}'\right|} + \frac{\delta E_{\text{XC}}[n(\vec{r})]}{\delta n(\vec{r})}\right]\cdot\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$

(**Hartree term**)

How Kohn-Sham equation derived (5)

Since, $T_s[n] = \sum_i \varepsilon_i - \int v_{\text{eff}}(\boldsymbol{r}) n(\boldsymbol{r})$

$$T_{\text{S}} = \sum_i \varepsilon_i - \int d\vec{r} \cdot \left[v_{\text{ext}}(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{\text{XC}}[n(\vec{r})]}{\delta n(\vec{r})} \right] \cdot n(\vec{r})$$

$$= \sum_i \varepsilon_i - \int d\vec{r} \cdot v_{\text{ext}}(\vec{r}) \cdot n(\vec{r}) - \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r} - \vec{r}'|} - E_{\text{XC}}[n(\vec{r})]$$

Ground state energy gets, ...

$$E_{\text{GS}}[n(\vec{r})] = T_{\text{S}} + \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r} - \vec{r}'|} + E_{\text{XC}}[n(\vec{r})] + \int d\vec{r} \cdot v_{\text{ext}}(\vec{r}) \cdot n(\vec{r})$$

$$= \left(\sum_i \varepsilon_i - \int d\vec{r} \cdot v_{\text{ext}}(\vec{r}) \cdot n(\vec{r}) - \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r} - \vec{r}'|} - E_{\text{XC}}[n(\vec{r})] \right)$$

$$+ \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}')\, n(\vec{r})}{|\vec{r} - \vec{r}'|} + E_{\text{XC}}[n(\vec{r})] + \int d\vec{r} \cdot v_{\text{ext}}(\vec{r}) \cdot n(\vec{r})$$

$$= \sum_i \varepsilon_i$$

...sum of Kohn-Sham levels...

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- Notes on Kohn-Sham equation

Contrast with molecular orbitals/Quantum many-body interactions

Procedure on Kohn-Sham equation

self-consistent field *Kohn-Sham*

SCF procedure to solve KS equation

Kohn-Sham equation ;

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\right\}\cdot\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$$

$$v(\vec{r}) = v_{ext}(\vec{r}) + e^2\int d^3r'\cdot\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc}\left[n(\vec{r})\right]$$

To setup concrete form of equation, its solution required...

Iteration to converge

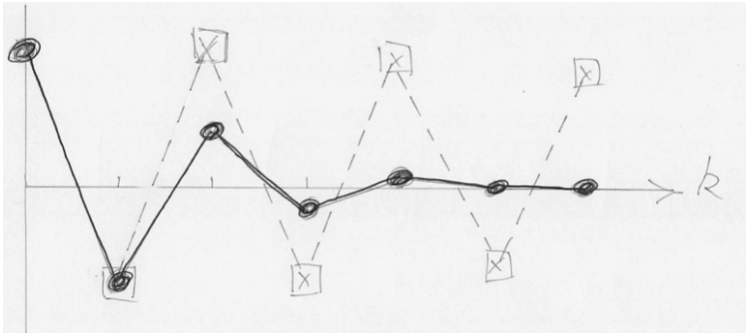
$n_0(r)$ --> $n_1(r)$ --> $n_2(r)$ --> $n_3(r)$ --> ...

***Initial guess**, $n_0(r)$, provided at beginning*

Package provides automatically as default

Convergence of calculation

$\delta_k = n_k(r) - n_{k-1}(r)$

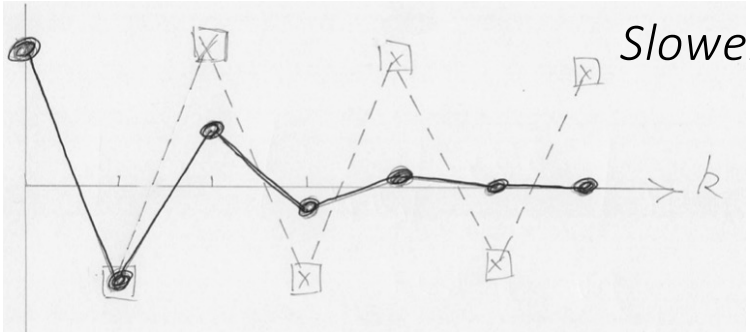


Getting eventual convergence,

$$n(\vec{r}) = \sum_{j=1}^{N}\left|\psi_j(\vec{r})\right|^2 \qquad E_{GS}' = \sum_{j=1}^{N}\varepsilon_j$$

Tough convergence and resume

$\delta_k = n_k(r)-n_{k-1}(r)$



Slower convergence...

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\right\}\cdot\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$$

$$v(\vec{r}) = v_{ext}(\vec{r}) + e^2\int d^3r'\cdot\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc}\left[n(\vec{r})\right]$$

Repeated cycles taking over the densities

'From scratch' → $n_0(r)$ → $N_{iteration}$=500 → $n_{500}(r)$ → **'resume'** → $N_{iteration}$=500 → $n_{2*500}(r)$ → **'resume'** → $N_{iteration}$=500 → $n_{3*500}(r)$

'From scratch' → $n_0(r)$ → $N_{iteration}$=500 →

'From scratch' → $n_0(r)$ → $N_{iteration}$=500 →

'From scratch' → $n_0(r)$ → $N_{iteration}$=500 →

How to improve the convergence??

Silly mistake found frequently for beginners...

- *Modifying initial guess (closer to final solution)*

  effectively works [as expert's skill!]

- *Smearing technique (explained later...)*

Further notes for Kohn-Sham equation

Though the form is similar...

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$; many-body Schrodinger equation

$$\Psi(\vec{r}_1,\cdots,\vec{r}_N) = \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & \cdots & \psi_1(\vec{r}_N) \\ \psi_2(\vec{r}_1) & \ddots & & \\ \vdots & & & \\ \psi_N(\vec{r}_1) & & & \psi_N(\vec{r}_N) \end{vmatrix}$$

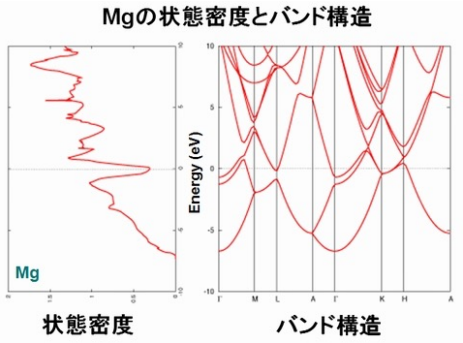
'many-body' decomposed into *'product of one=body'*

(Hartree term) (Exchange term)

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \sum_{j\neq i}\int d\vec{r}'\cdot\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\cdot\psi_i(\vec{r}) - \sum_{j\neq i}\left[\int d\vec{r}'\cdot\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\cdot\psi_j(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$

Classical Coulomb — Statistical Effect by Quantum Mech.

[*Hartree-Fock orbital*]



アドバンスソフトのweb頁から転記

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\vec{r}) + \int d\vec{r}'\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{\text{XC}}[n(\vec{r})]}{\delta n(\vec{r})}\right]\cdot\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$$ **[*Kohn-Sham ortibal*]**

(Hartree term) (Exchange-Correlation term)

Original Many-body form

$$\left[-\frac{1}{2}\sum_j \nabla_j^2 + V(\vec{r}_1,\cdots,\vec{r}_N)\right]\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N) = E\cdot\Psi(\vec{r}_1,\cdots,\vec{r}_N)$$

$$n(\vec{r}) = \frac{\int|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)|^2\cdot\sum_{j=1}^N\delta(\vec{r}-\vec{r}_j)\cdot d\vec{r}_1\cdots d\vec{r}_N}{\int|\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)|^2\cdot d\vec{r}_1\cdots d\vec{r}_N} = \left\langle\sum_{j=1}^N\delta(\vec{r}-\vec{r}_j)\right\rangle$$

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

Equivalent One-body form

$n(\vec{r}) = \sum_{\alpha=1}^N|\psi_\alpha(\vec{r})|^2$; **Kohn-Sham Orbital** (orbitals just represent charge density)

$$\left\{\left[-\frac{1}{2}\nabla^2 + v_{one-body}^{(eff)}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})\right\}_{i=1}^N$$ (reference system)

Orbital is introduced along ***completely different context****!*

Meaning of $\{\varepsilon_i\}, \psi_i(\vec{r})$ *??* ***No physical meaning*** *in the original context...*

It's just introduced to describe the density as $n(\boldsymbol{r}) = \sum_i |\psi_i(\boldsymbol{r})|^2$

Though $\{\varepsilon_i\}$ *are practically used as if with physical meaning...*

Quantum many-body interaction

Classical Coulomb (***Hartree term***) *Statistical Effect (Pauli exclusion)* (***Exchange term***) *Deformation of WF by interaction* (***Correlation term***)

$$\left[-\frac{1}{2}\nabla^2+v_{ext}(\vec{r})+\sum_{j\neq i}\int d\vec{r}'\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\psi_i(\vec{r})-\sum_{j\neq i}\left[\sum_{j\neq i}\int d\vec{r}'\psi_j^*(\vec{r}')\frac{\delta_{\sigma_i\sigma_j}}{|\vec{r}-\vec{r}'|}\psi_i(\vec{r}')\right]\psi_j(\vec{r})+\hat{V}_C\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r})$$

$$=\left[-\frac{1}{2}\nabla^2+v_{ext}(\vec{r})+\sum_{j\neq i}\int d\vec{r}'\frac{|\psi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right]\psi_i(\vec{r})+\hat{V}_X\psi_i(\vec{r})+\hat{V}_C\psi_i(\vec{r})$$

$$=\left[-\frac{1}{2}\nabla^2+V_{classical}(\vec{r})\right]\psi_i(\vec{r})+\left(\hat{V}_X+\hat{V}_C\right)\psi_i(\vec{r})$$

(***exchange-correlation***)

[Quantum many-body interaction] = [Classical meanfield] + [Quantum statistical] + [Electronic correlation]

= [Classical meanfield] + [Exchange & Correlation]

= [Classical meanfield] + [Quantum statistical] + [Electronic correlation]

= [quantum meanfield] + [fluctuation]

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Metals and smearing techniques

Ryo Maezono

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School of Information Science,

*Japan Advanced Institute of Science and Technolegy, (**JAIST**),*

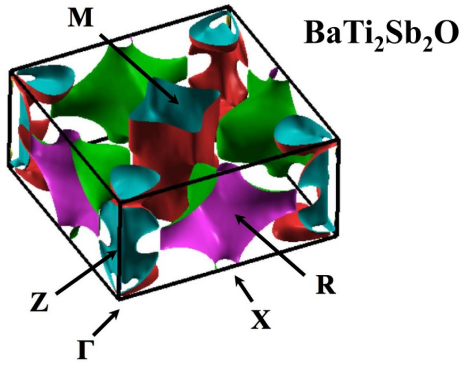
Nomi, Ishikawa, Japan.

Which is difficult, metal or insulator??

Complex shape of Fermi surface...

Numerical integral by mesh... gets difficult... *[Reciprocal space picture]*

"Computational-costly"



K. Nakano, K. Hongo, and R. Maezono, Sci. Rep. 6, 29661 (2016).

More fundamental viewpoint...

- Huge degeneracy on the choice of Slater det.

[c.f, 'Huge electronic correlation' /Geometrical correlation/Static correlation]

... Convergence gets difficult... (explained later...)

"Sloshing" and "Smearing technique"... (explained later...)

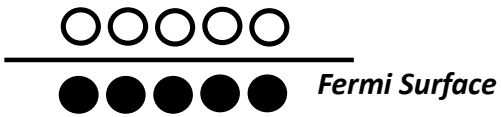
- Difference in coherent length.... *[Real space picture]*

"Twisting average" (explained later...)

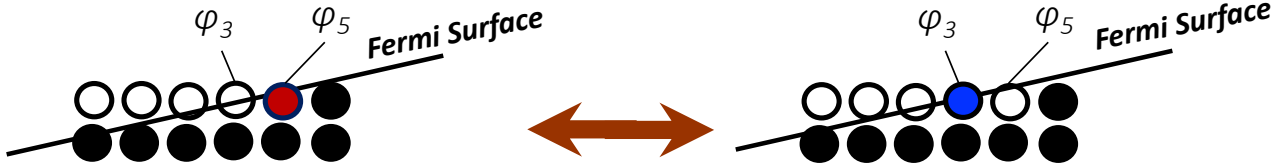
Multi-determinant nature of metal...

Simulation with Integer number of electrons... (e.g., 8)

Insulator



Metal



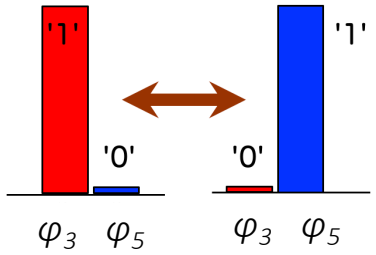
|**-***| ... φ_3 vacant, φ_5 occupied |****-*| ... φ_3 occupied, φ_5 vacant

*Describing the reality requires **multi-determinants**...*

$$D_{true} = c_1|****oo| + c_2|***o*o| + ...$$

*But in practical computation, we artificially select **a single configuration**...*

$$D_{simulation} = |****oo|$$

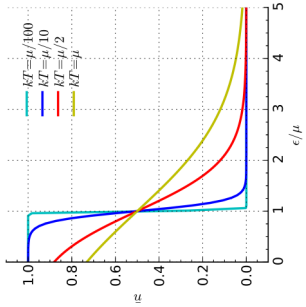


More fundamental viewpoint...

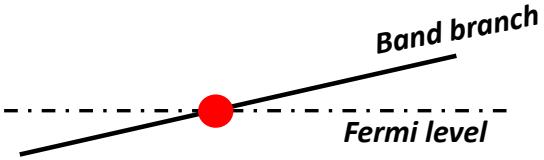
- *Huge degeneracy on the choice of Slater det.*

  [c.f, 'Huge electronic correlation' /Geometrical correlation/Static correlation]

Smearing



Simulation with Integer number of electrons... (e.g., 8)

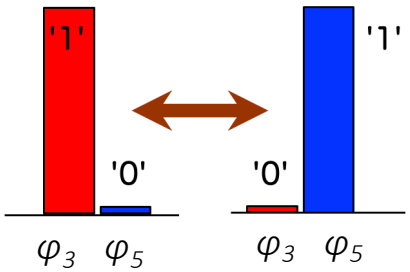


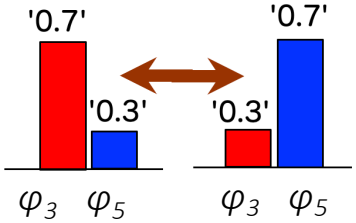
|**-***| ... φ_3 vacant, φ_5 occupied

*Describing the reality requires **multi-determinants**...*

$D_{true} = c_1|****oo|\ + c_2|***o*o| + ...$

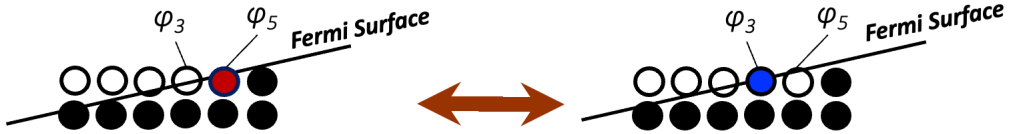
***Viscosity** to suppress the amplitude...*





Then 'sloshing' occurs...

Metal



|**-***| ... φ_3 vacant, φ_5 occupied |****-*| ... φ_3 occupied, φ_5 vacant

$D_{true} = c_1|****oo| + c_2|***o*o| + \ldots$

In self-consistent loop...

Kohn-Sham equation ; $\left\{-\frac{\hbar^2}{2m}\nabla^2 + v(\vec{r})\right\}\cdot\psi_i(\vec{r}) = \varepsilon_i\cdot\psi_i(\vec{r})$

$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$

$v(\vec{r}) = v_{ext}(\vec{r}) + e^2\int d^3r'\cdot\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc}[n(\vec{r})]$

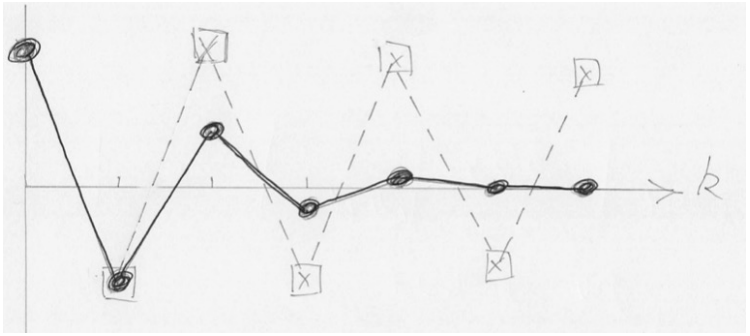
To setup concrete form of equation, its solution required...

Iteration to converge

$n_0(r)$ --> $n_1(r)$ --> $n_2(r)$ --> $n_3(r)$ --> ...

Initial guess, $n_0(r)$, *provided at beginning*

$\delta_k = n_k(r) - n_{k-1}(r)$



From Wikipedia

1) $n_0(r)$ *composed using ...* $D_5 = |****oo|$ *i.e., '*φ_3 ***less*** *stable than* φ_5 *'* ***assumed****...*

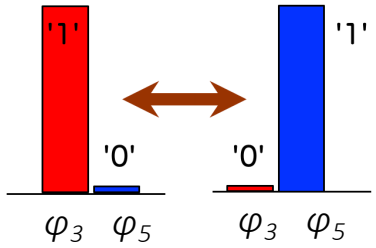
2) *Then, '*φ_3 ***more*** *stable than* φ_5*'* ***predicted****...*

3) *Then,* $n_1(r)$ *should be composed using ...* $D_3 = |***o*o|$ *i.e., '*φ_3 ***more*** *stable than* φ_5 *'* ***assumed****...*

4) *Then, '*φ_3 ***less*** *stable than* φ_5*'* ***predicted****...*

5) *Then,* $n_2(r)$ *should be composed using ...* $D_5 = |****oo|$ *i.e., '*φ_3 ***less*** *stable than* φ_5 *'* ***assumed****...*

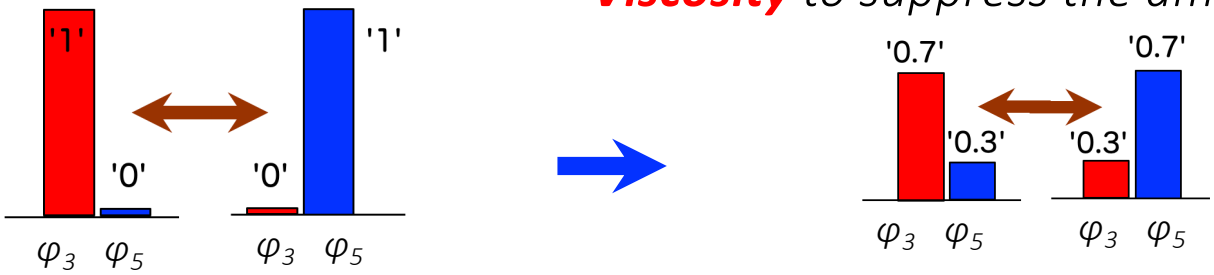
...



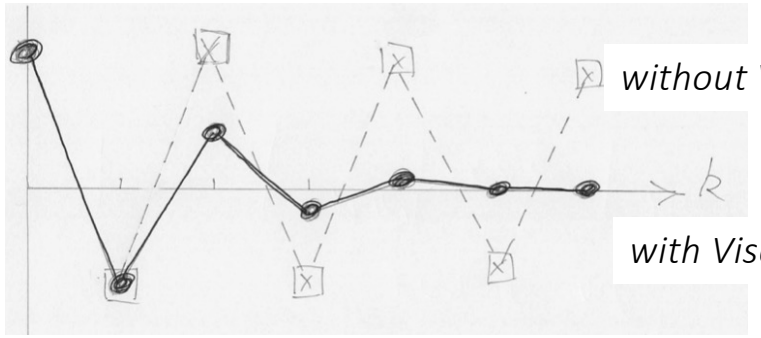
'Smearing' for improving convergence

Drastic change of occupations leads to oscillation behavior...

***Viscosity** to suppress the amplitude...*



$\delta_k = n_k(\boldsymbol{r})-n_{k-1}(\boldsymbol{r})$



without Viscosity

with Viscosity

[c.f, Another remedy ; Mixing adjustment in SCF]

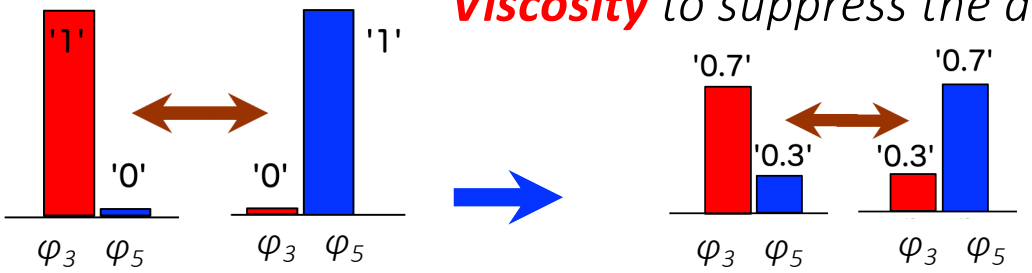
Too sensitive update in SCF leading to sloshing.

$$n_{next}[k] = (1-x)*n[k] + x*n[k-1]$$

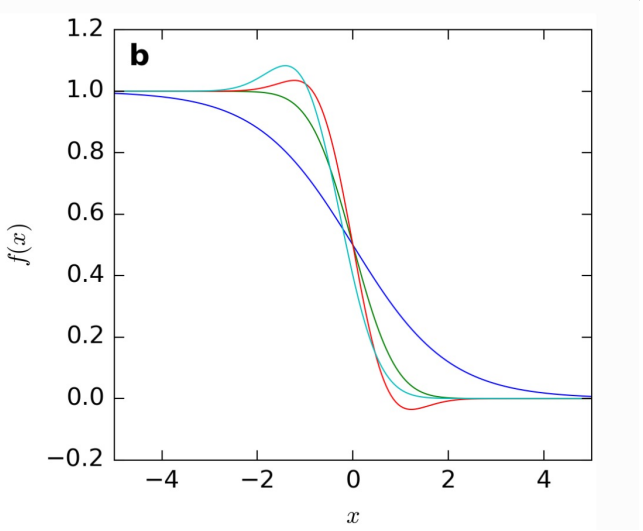
...moderate update of charge density
so that no drastic sloshing occurs...

'Smearing' scheme

Schemes to generate fractional-wise occupations...



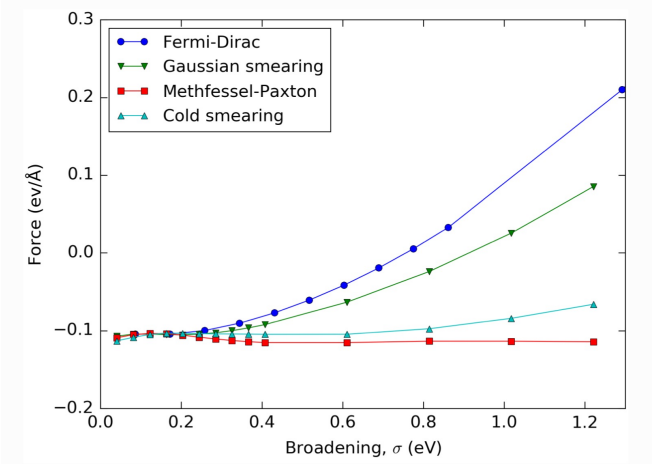
Viscosity *to suppress the amplitude...*



Fermi-distribution function

Viscosity ***against relaxation*** *to true ground state configuration...*

... leading to ***bias*** *in energy evaluation.*

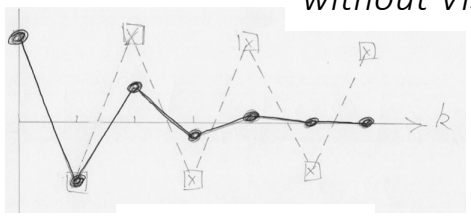


Beyond the naive Fermi-dist. function,

several schemes *are developed...*

$\delta_k = n_k(\boldsymbol{r}) - n_{k-1}(\boldsymbol{r})$

without Viscosity



with Viscosity

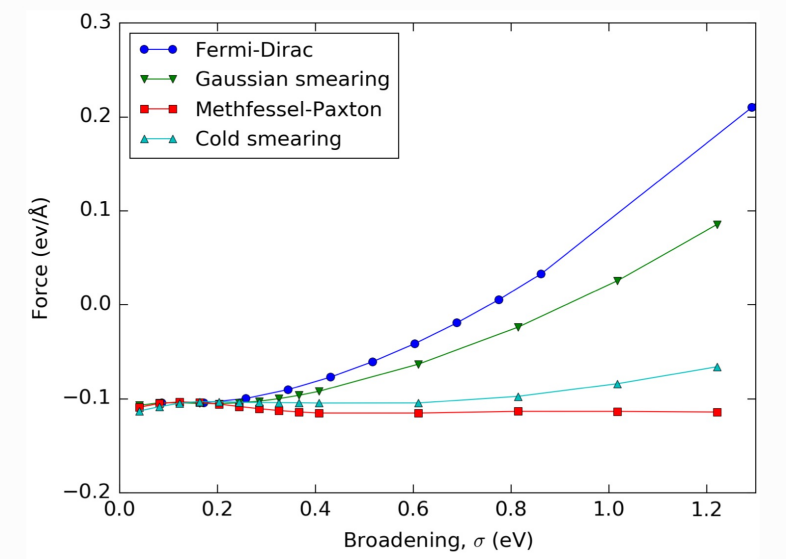
to further improve the convergence.

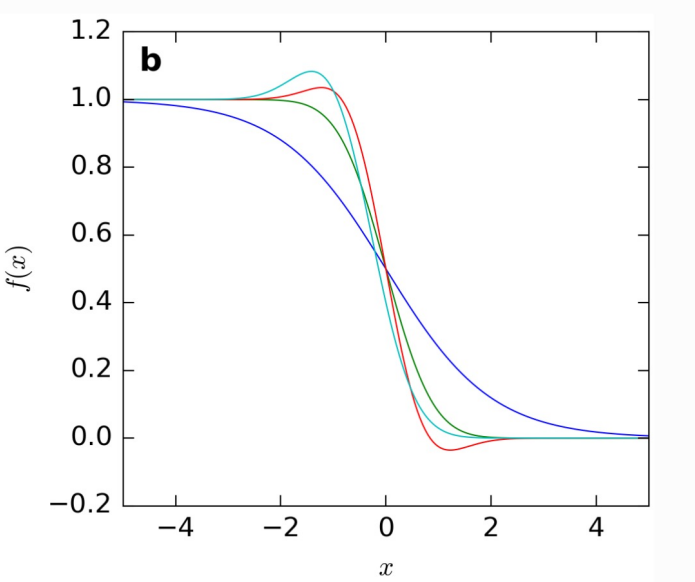
- *'Gaussian',*
- *'Methfessel-Paxton(MP)',*

...

https://docs.quantumatk.com/manual/technicalnotes/occupation_methods/occupation_methods.html

'Smearing' scheme

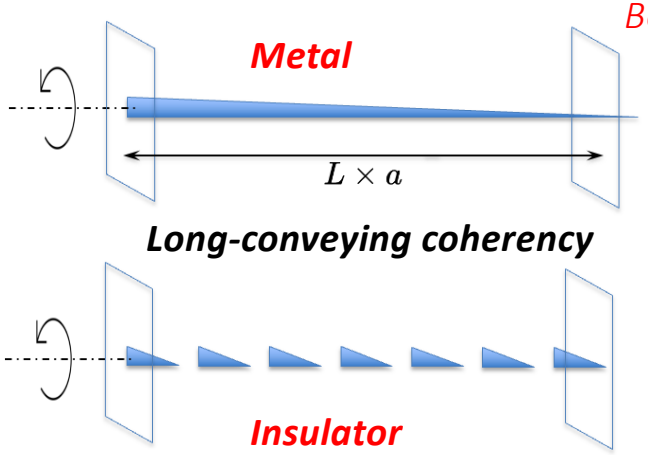




https://docs.quantumatk.com/manual/technicalnotes/occupation_methods/occupation_methods.html

Twisted boundary condition

Real space image of metal/insulator...



Boundary ... ***artificially introduced*** *for computational convenience..*

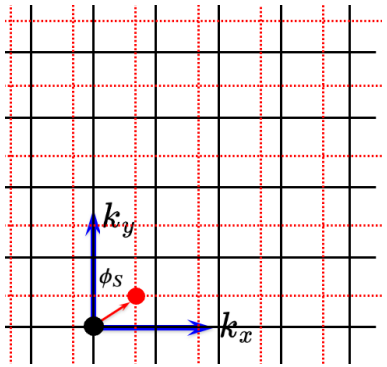
$$n(r + La) = n(r) \qquad \textit{i.e.,}\ |\psi(r + La)| = |\psi(r)|$$

$$\longrightarrow \quad \psi(r + La) = \exp[i\phi_s] \cdot \psi(r)$$

Note, $\phi_s = 0$ (***Born-von Karman boundary condition***)

is just one of the choice for convenience...

$\phi_s \neq 0$ (***Twisting boundary condition***) *is also possible for your calculation.*



Easily understood that...

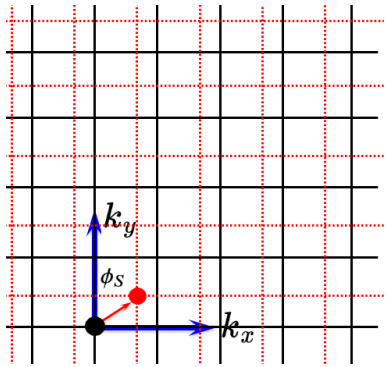
(*Born-von Karman boundary condition*)... *Non-shifted mesh calculation*

(*Twisting boundary condition*)... ***Shifted mesh*** *calculation*

$$k(L \times a) = \phi_s + 2\pi N \longrightarrow k = \frac{\phi_s}{La} + \frac{2\pi}{La} \cdot N$$

Twisted averaging scheme

You can perform the simulation with twisted boundary condition using shifted mesh calculation



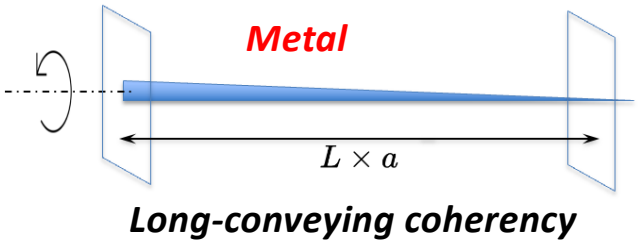
Practically, you'll observe ...

Results depending on the choice of ϕ_S *This is an* ***artifact****!*

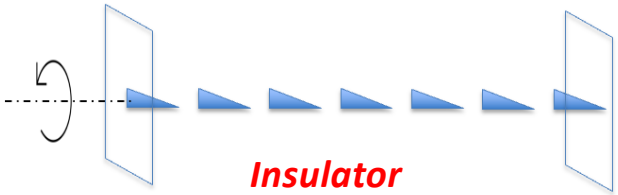
It's meaning ...

Your simulation happens to feel the artificial wall at boundary...

(Such wall is completely artificial thing, isn't it?)



Long-conveying coherency



The dependence on. ϕ_S *...*

Bias due to the ***finite-size error***

To correct the bias...

Averaging *over the results*

with several choices of non-zero ϕ_S

Boundary ... artificially introduced for computational convenience..

Thank you