Teori Kuantum untuk Material Bagian #06

- First-principles methods
- Density functional theory

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Pusat Riset Fisika Kuantum, Badan Riset & Inovasi Nasional

Reminder: Sains Prediktif u/ Material

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. Introduction.

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Already before the arrival of quantum mechanics there existed a theory of atomic structure, based on Bohr's ideas of quantised orbits, which was fairly successful in a wide field. To get agreement with experiment it was found necessary to introduce the spin of the electron, giving a doubling in the number of orbits of an electron in an atom. With the help of this spin and Pauli's exclusion principle, a satisfactory theory of multiplet terms was obtained when one made the additional assumption that the electrons in an atom all set themselves with their spins parallel.

It seemed to show that there were large forces coupling the spin vectors of the electrons in an atom, much larger forces than could be accounted for as due to the interaction of the magnetic moments of the electrons. The position was thus that there was empirical evidence in favour of these large forces, but that their theoretical nature was quite unknown.

> Hukum-hukum dasar yang diperlukan untuk melakukan prosedur matematis dari sebagian besar ilmu fisika dan seluruh ilmu kimia telah diketahui sepenuhnya. Kesulitannya hanya terletak pada kenyataan bahwa penerapan hukum-hukum ini sering memberikan persamaan yang terlalu rumit untuk dipecahkan.

P. A. M. Dirac, Proc. R. Soc. Lond. A, 123 (792), 714-733 (1929)

Energi total dan dinamika molekuler

Aproksimasi Born-Oppenheimer (BO):

- Ion dianggap sebagai partikel klasik tetap dalam ruang

- Peran ion sebagai penyedia potensial eksternal yang memengaruhi gerak elektron

$$H_{BO}(\{r_i\};\{R_i\}) = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i<j}^{n} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i}^{n}\sum_{j}^{N} \frac{e^2 Z_i}{|\vec{r}_i - \vec{R}_j|} + \sum_{i<j}^{N} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

$$H_{BO}(\{r_i\};\{R_i\})\psi(\{r_i\};\{R_i\}) = E(\{R_i\})\psi(\{r_i\};\{R_i\})$$

Pemecahan persamaan Schrödinger memberikan:

- Fungsi gelombang elektron (bergantung parametris pada posisi ion)

- Nilai eigen (energi) merupakan fungsi posisi ion, yang menyertakan energi kinetik elektron dan interaksi lainnya terkait elektron, tetapi tidak menyertakan energi kinetik ion

Energi total dan dinamika molekuler

Persamaan Schrödinger dengan Hamiltonian Born-Oppenheimer:

$$H_{BO}(\{r_i\}; \{R_i\})\psi(\{r_i\}; \{R_i\}) = E(\{R_i\})\psi(\{r_i\}; \{R_i\})$$

Ion bergerak pada bentangan $E(\{R_i\})$, yang dinamikanya dapat didekati oleh mekanika klasik

$$H_{ion}(\{R_i\}; \{P_i\}) = \sum_{i=1}^{3N} \frac{P_i^2}{2M_i} + E(\{R_i\})$$

$$\begin{cases} \dot{R}_i = \dfrac{\partial H_{ion}}{\partial P_i} \\ \dot{P}_i = -\dfrac{\partial H_{ion}}{\partial R_i} \end{cases}$$

Tantangan yang ada

Fungsi gelombang elektron berada pada ruang berdimensi 3*n*

$$\psi(\{r_i\}; \{R_i\})$$

Tinjau contoh kasus *unit* cell untuk kristal silikon (2 atom, 28 elektron)

Misalkan kita mau menghitung integral terkait derajat kebebasan elektron dan kita diskretisasi setiap dimensi dengan 10 titik. Apa yang terjadi?

- Operasi perhitungan integral yang perlu dilakukan adalah $10^{(3\times28)} = 10^{84}$
- Superkomputer canggih *exascale* bisa melakukan 10^{18} operasi per detik
- Berarti kita butuh 10^{66} detik! (padahal usia alam semesta: 10^{17} s)

Permulaan Solusi
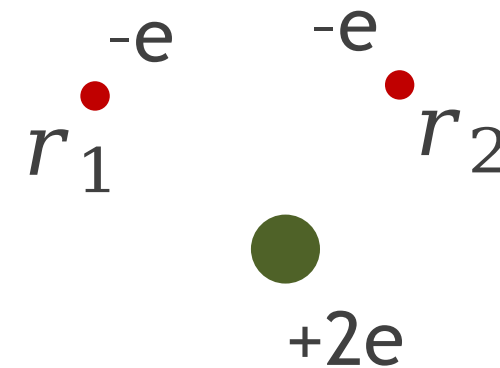
Pecahkan: $$H_{BO}\psi = E\psi$$

$$H_{BO}(\{r_i\}; \{R_i\})\psi(\{r_i\}; \{R_i\}) = E(\{R_i\})\psi(\{r_i\}; \{R_i\})$$

Fungsi gelombang benda banyak adalah perkalian dari fungsi-fungsi gelombang elektron tunggal (tetapi tanpa korelasi)

$$\psi(\{r_i\}) = \phi_1(r_1)\phi_2(r_2)...\phi_n(r_n)$$

Contoh kasus Helium

$$H = -\frac{\hbar^2}{2m}(\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|r_1 - r_2|}$$

Fungsi gelombang ansatz: $\psi(r_1, r_2) = \phi(r_1)\phi(r_2)$

$$\left[-\frac{\hbar^2}{2m}(\nabla_{r_1}^2 + \nabla_{r_2}^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|r_1 - r_2|}\right]\phi(r_1)\phi(r_2) = E\phi(r_1)\phi(r_2)$$

Kalikan dengan $\phi^*(r_2)$ dari kiri dan integralkan terhadap r_2:

$$[\int \phi^*(r_2)\phi(r_2)dr_2\left(-\frac{\hbar^2}{2m}\right)\nabla_{r_1}^2 - \frac{\hbar^2}{2m}\int\phi^*(r_2)\nabla_{r_2}^2\phi(r_2)dr_2 + \int\phi^*(r_2)\phi(r_2)dr_2\left(-\frac{2e^2}{r_1}\right)$$

$$-\int\phi^*(r_2)\frac{2e^2}{|r_2|}\phi(r_2)dr_2 + \int\phi^*(r_2)\frac{e^2}{|r_1 - r_2|}\phi(r_2)dr_2]\ \phi(r_1) = E\int\phi^*(r_2)\phi(r_2)dr_2\phi(r_1)$$

Helium: aproksimasi medan rata-rata

$$\left[\left(-\frac{\hbar^2}{2m}\right)\int|\phi(r_2)|^2 dr_2 \nabla^2_{r_1} - \frac{\hbar^2}{2m}\int \phi^*(r_2)\nabla^2_{r_2}\phi(r_2)dr_2 - \left(\frac{2e^2}{r_1}\right)\int|\phi(r_2)|^2 dr_2\right.$$

$$\left.-2e^2\int\frac{|\phi(r_2)|^2}{|r_2|}dr_2 + e^2\int\frac{|\phi(r_2)|^2}{|r_1-r_2|}dr_2\right]\phi(r_1) = E\phi(r_1)$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2_1 - \frac{2e^2}{r_1} + e^2\int\frac{|\phi(r_2)|^2}{|r_1-r_2|}dr_2\right]\phi(r_1) = E'\phi(r_1)$$

EK   el-ion   el-el

Persamaan Schrödinger efektif seperti kasus 1 partikel
- Elektron melihat satu sama lain secara rata-rata
- Hamiltonian partikel tunggal bergantung pada orbital yang ingin kita temukan

Pendekatan Hartree

Masukkan: $\psi(\{r_i\}) = \phi_1(r_1)\phi_2(r_2)...\phi_n(r_n)$

ke Persamaan Schrödinger:

$$\left(-\sum_{i=1}^{n}\frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i<j}^{n}\frac{e^2}{|r_i - r_j|} - \sum_{i}^{n}\sum_{j}^{N}\frac{Z_ie^2}{|r_i - R_j|}\right)\psi(\{r_i\}) = E\psi(\{r_i\})$$

Persamaan Hartree (1927):

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \sum_{i}^{N}\frac{Z_ie^2}{|R_i - r|} + \sum_{i\neq j}^{n}e^2\int\frac{|\phi_i(r')|^2}{|r - r'|}d^3r'\right]\phi_j(r) = E'\phi_j(r_1)$$

Alih-alih fungsi berdimensi 3n, kita punya n fungsi 3D (lumayan!)

Kuis #13

- Manakah dari suku energi berikut ini yang tidak tercakup dalam pemecahan persamaan Schrödinger dalam aproksimasi Born-Oppenheimer?

(A) Energi kinetik elektron
(B) Interaksi elektron dan ion
(C) Interaksi elektron-elektron
(D) Energi kinetik ion

Permasalahan teori Hartree

$$\psi(\{r_i\}) = \phi_1(r_1)\phi_2(r_2)...\phi_n(r_n)$$

- Tidak ada korelasi
- Elektron dapat dibedakan (pertukaran dua elektron mengubah fungsi gelombang)
  $\rightarrow$ melanggar prinsip dasar statistika elektron

Simetri fungsi gelombang

$$\psi(r_1, r_2, ..., r_i, ..., r_j, ..., r_n) = c\psi(r_1, r_2, ..., r_j, ..., r_i, ..., r_n)$$

$$c = 1 \text{ untuk boson dan } c = -1 \text{ untuk fermion}$$

Determinan Slater

$$\psi(r_1, r_2, ..., r_i, ..., r_j, ..., r_n) = -\psi(r_1, r_2, ..., r_j, ..., r_i, ..., r_n)$$

Kalau kita gunakan $\psi(r_1, r_2) = \phi_1(r_1)\phi_2(r_2)$

Maka $\psi(r_1, r_2) \neq -\psi(r_2, r_1)$ Masalah besar!

Solusi masalah: $\psi(r_1, r_2) = \dfrac{1}{\sqrt{2}}[\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2)]$

Secara umum : $\psi(r_1, ..., r_N) = \dfrac{1}{\sqrt{N}}\begin{vmatrix} \phi_1(r_1) & ... & \phi_N(r_1) \\ \vdots & \ddots & \vdots \\ \phi_1(r_N) & ... & \phi_N(N) \end{vmatrix}$

Hartree-Fock

Penggunaaan orbital spin ortonormal, *x = r, s*

$$\int d^3 r ds\, \phi_i^*(x)\phi_j(x) = \delta_{ij}$$

$$\Psi(x_1,\ldots,x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \ldots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \ldots & \phi_N(x_2) \\ \vdots & \vdots & & \\ \phi_1(x_N) & \phi_2(x_N) & \ldots & \phi_N(x_N) \end{vmatrix}$$

Masukkan ke pers. Schrodinger:

$$\left(\sum_{i=1}^{n} -\frac{\left|\vec{\nabla}_{r_i}\right|^2}{2m_e} - \sum_{i,j}^{n,N} \frac{Z_i e^2}{\left|r_i - R_j\right|} + \sum_{i<j}^{n} \frac{e^2}{\left|r_i - r_j\right|} \right) \psi(\{r_i\}) = E\,\psi(\{r_i\})$$

Hartree-Fock

Ceritanya penurunannya panjang. Jadi, kita langsung bandingkan saja Hartree vs. Hartree-Fock

Hartree

$$\langle H \rangle = \sum_{i=1}^{n} \int d^3 r \phi_1^*(r) \left[\frac{\vec{\nabla}}{2m_e} - \sum_{j}^{N} \frac{Z_i e^2}{|r - R_j|} \right] \phi_i(r) + \sum_{i<j}^{n} \int d^3 r_i d^3 r_j \frac{e^2 |\phi_i(r_i)|^2 |\phi_j(r_j)|^2}{|r_i - r_j|}$$

Kinetic energy

Electron-electron interactions

Electron ion-interactions

Hartree-Fock

$$\langle H \rangle = \sum_{i=1}^{n} \int d^3 r \phi_1^*(r) \left[\frac{\vec{\nabla}}{2m_e} - \sum_{j}^{N} \frac{Z_i e^2}{|r - R_j|} \right] \phi_i(r) + \sum_{i<j}^{n} \int d^3 r d^3 r' \frac{e^2 |\phi_i(r)|^2 |\phi_j(r')|^2}{|r - r'|}$$

$$- \sum_{i<j}^{n} \int d^3 r d^3 r' \frac{e^2 \phi_i^*(r) \phi_j^*(r') \phi_i(r') \phi_j(r)}{|r - r'|}$$

Exchange energy (no classical counterpart)

Kuis #14

- Manakah dari pilihan berikut yang merupakan fungsi gelombang yang benar untuk sistem dua elektron?

(A) $\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[\phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2)]$

(B) $\psi(r_1, r_2) = \phi_1(r_1)\phi_2(r_2)$

(C) $\psi(r_1, r_2) = \phi_2(r_1)\phi_1(r_2)$

(D) $\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[\phi_1(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_1(r_2)]$

Teori Kuantum untuk Material Bagian #06-2

Teori Fungsional Kerapatan

- Kerapatan elektron
- Teorema Hohenberg-Kohn
- Persamaan Kohn-Sham
- Fungsional Pertukaran dan Korelasi

Outline

Formalism

— Density Functional Theory

- Exchange-Correlation Potentials
- Pseudopotentials and Related Approaches

Practical Issues

— Implementation

- Periodic boundary conditions
- k-Points
- Plane-wave basis sets

— Parameters controlling numerical precision

Density Functional Theory

Hohenberg and Kohn (1964), Kohn and Sham (1965)

- For each external potential there is a unique ground-state electron density

- Energy can be obtained by *minimizing a density functional with respect to density of electrons n(r)*

$$E_{groundstate} = min\{E_{tot}[n(r)]\}$$

$$E_{tot}[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{int}[n(\mathbf{r})] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + \dots$$

Kinetic Energy   Electron-Electron Interactions   Electron-Ion Interactions   Other terms

Kohn-Sham Approach

$$n(r) = -e \sum_{i=1}^{n} \left| \varphi_i(r) \right|^2$$

$$E[\{\varphi_i\}] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \int \varphi_i^* \nabla_i^2 \varphi_i \, d^3r + \int V_{ext}(r) n(r) d^3r$$

$$+ \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} d^3r \, d^3r' + E_{xc}[n(r)]$$

Many-body electron-electron and other interactions are all put into $E_{xc}[n(r)]$

"Exchange-Correlation Energy"

Kohn-Sham Equations

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V_{ext}(r) + \int \frac{n(r')}{|r-r'|}d^3r' + V_{xc}(r) \right]\phi_i(r) = \varepsilon_i\phi_i(r)$$

$$V_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$$

Most of the research on improvement of DFT were dedicated to establish good exchange-correlation "functionals"

Local Density Approximation

(e.g., J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981))

$$E_{xc}[n(r)] = \int \varepsilon_{xc}^{\text{hom}}(n(r))n(r)d^3r$$

$$\varepsilon_{xc}^{\text{hom}}(n(r)) \rightarrow \text{Exchange} - \text{Correlation Energy of Homogeneous}$$

$$\text{Electron Gas of Density } n(\text{r})$$

Generalized Gradient Approximation

J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77 (1996)

$$E_{xc}^{GGA}[n(r)] = \int \varepsilon_{xc}^{\text{hom}}(n(r))n(r)F_{xc}(r_s,\zeta,s)d^3r$$

A Note on Accuracy and Ongoing Research

- LDA leads to "overbinding"
  - Lattice constants commonly 1-3% too small, elastic constants 10-15% too stiff, cohesive energies 5-20% too large

  but, errors are largely systematic
  - Energy differences tend to be more accurate

- GGA corrects for overbinding
  - Sometimes "overcorrects"

- "Beyond DFT" Approaches
  - For "highly correlated" systems LDA & GGA perform much worse and corrections required (DFT+U, Hybrid Hartree-Fock/DFT, …)
  - Non-bonded interactions, e.g., van der Waals interactions in graphite, require additional terms or functionals (e.g., vdW-DF)

External electron-ion interaction

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V_{ext}(r) + \int\frac{n(r')}{|r-r'|}d^3r' + V_{xc}(r) \right]\phi_i(r) = \varepsilon_i\phi_i(r)$$

- Potential due to ions is singular at ion core
- Eigenfunctions oscillate rapidly near singularity
- Eigenfunction in bonding region is smooth

Difficult to solve KS equation!

V(r)

valence electrons

ion core
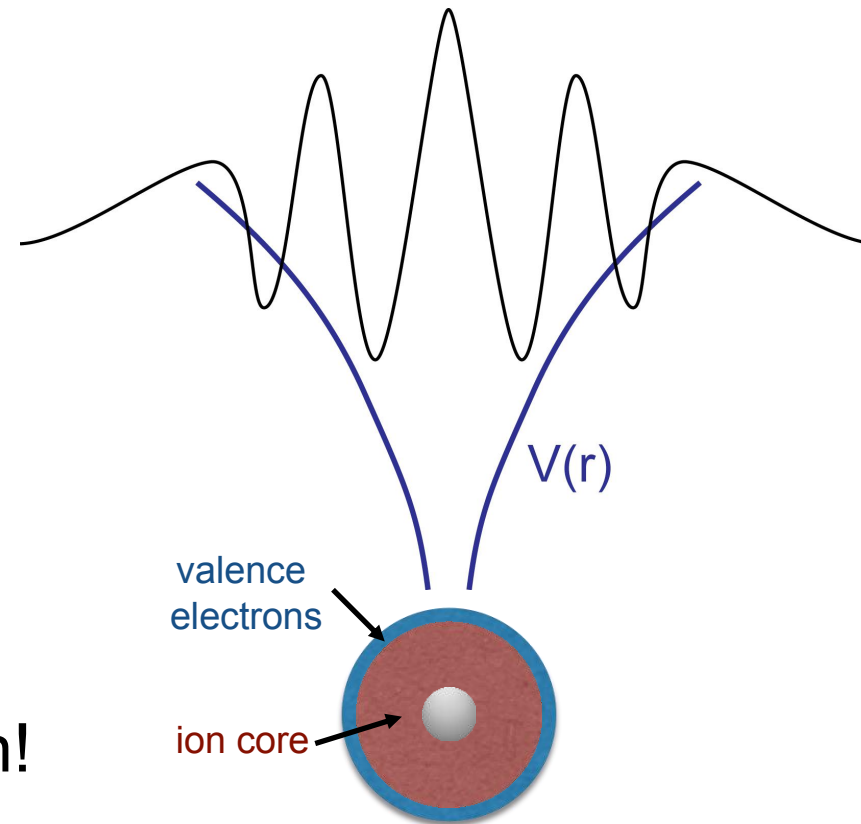
Pseudopotentials

- For plane-wave basis sets, rapid oscillations require large number of basis functions
  - expensive
  - unnecessary
    - these oscillations don't alter bonding properties

$V(r)$

- Replace potential with nonsingular potential
  - preserve bonding tails of eigenfunction
  - preserve distribution of charge between core and tail regions
  - reduces number of plane waves required for accurate expansion of wavefunction

"Pseudopotential"

pseudo

$V_{pseudo}(r)$
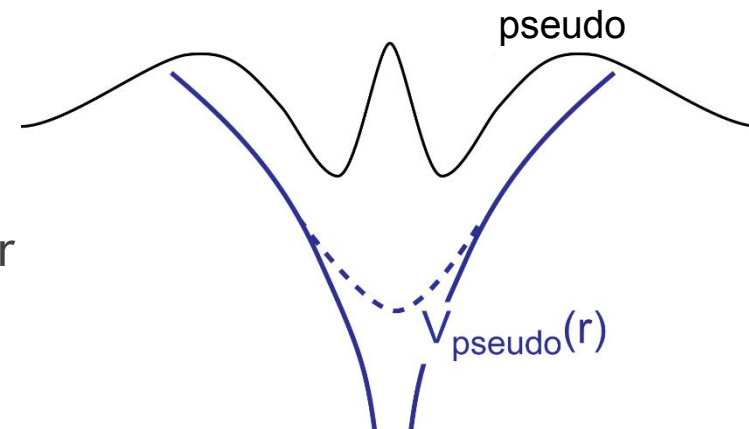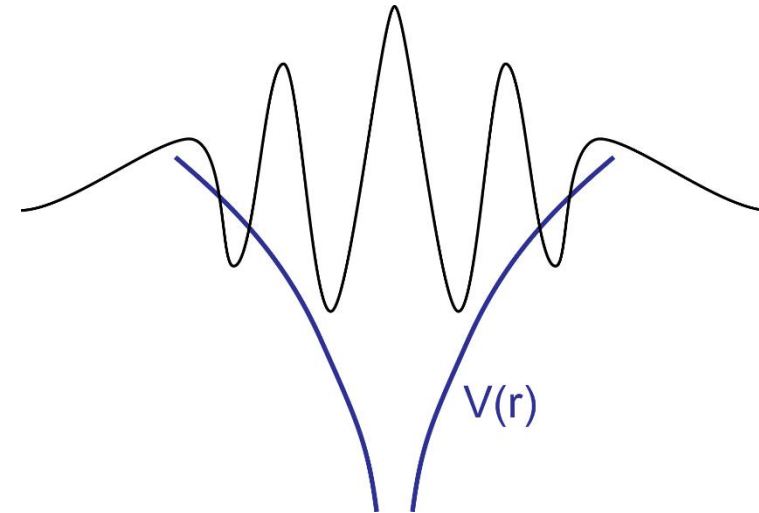
Summary of Kohn-Sham DFT

KS equation

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V_{ext}(r) + \int \frac{n(r')}{|r-r'|}d^3r' + V_{xc}(r) \right]\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

Total energy

$$E[\{\phi_i\}] = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\int \phi_i^* \nabla_i^2 \phi_i d^3r + \int V_{ext}(r)n(r)d^3r$$

$$+\frac{1}{2}\int \frac{n(r)n(r')}{|r-r'|}d^3rd^3r' + E_{xc}[n(r)]$$
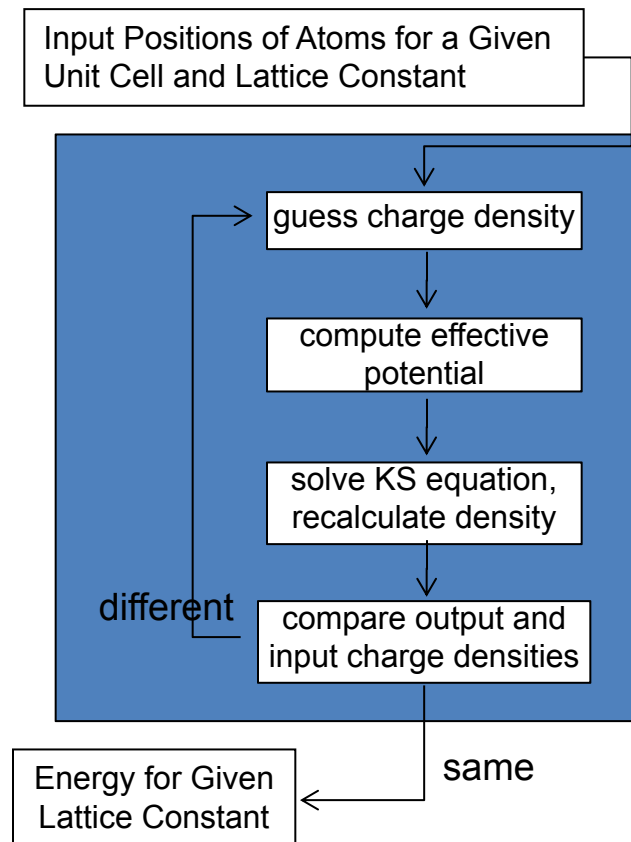
Electron Density $\qquad n(r) = -e\sum_{i=1}^{n}\left|\varphi_i(r)\right|^2$

Electron Wavefunctions $\qquad \varphi_i(r)$

Potential Electrons Feel from Nuclei $\qquad V_{ext}(r)$

Exchange-Correlation Energy $\qquad E_{xc}[n(r)] \qquad\qquad V_{xc}(r) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)}$

Form depends on whether we use LDA or GGA

Self-Consistent Solution to DFT Equations

Input Positions of Atoms for a Given Unit Cell and Lattice Constant

guess charge density

compute effective potential

solve KS equation, recalculate density

different

compare output and input charge densities

same

Energy for Given Lattice Constant

1. Set up atom positions

2. Make initial guess of "input" charge density (often overlapping atomic charge densities)

3. Solve Kohn-Sham equations with this input charge density

4. Compute "output" charge density from resulting wavefunctions

5. If energy from input and output densities differ by amount greater than a chosen threshold, mix output and input density and go to step 2

6. Quit when energy from input and output densities agree to within prescribed tolerance (e.g., 10^{-5} eV)
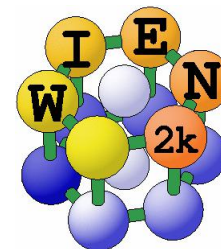
Some of Widely Used DFT Codes

Free

- Quantum Espresso / PWSCF (http://www.quantum-espresso.org/)
- ABINIT (http://www.abinit.org/)
- CASTEP (http://ccpforge.cse.rl.ac.uk/gf/project/castep/)

Commercial:

- VASP (http://cms.mpi.univie.ac.at/vasp/)
- WIEN2K (http://www.wien2k.at/)

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- k-Points
- Plane-wave basis sets

— Parameters controlling numerical precision

Implementation of DFT for a Single Crystal

Crystal Structure Defined by Unit Cell Vectors and Positions of Basis Atoms

Example: Diamond Cubic Structure of Si
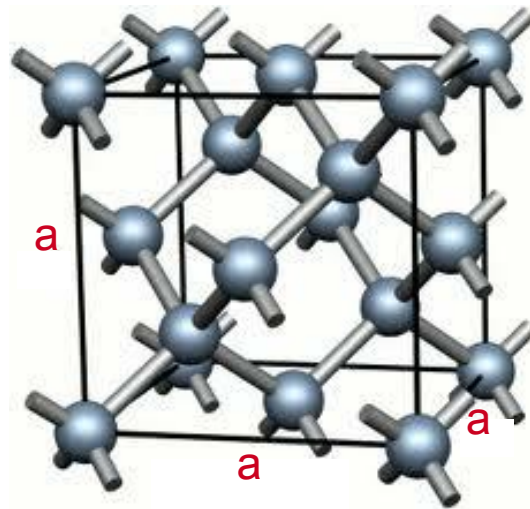
Unit Cell Vectors
$\mathbf{a}_1$ = a (-1/2, 1/2 , 0)
$\mathbf{a}_2$ = a (-1/2, 0, 1/2)
$\mathbf{a}_3$ = a (0, 1/2, 1/2)

Basis Atom Positions
0 0 0
¼ ¼ ¼

All atoms in the crystal can be obtained by adding integer multiples of unit cell vectors to basis atom positions

Electron Density in Crystal Lattice
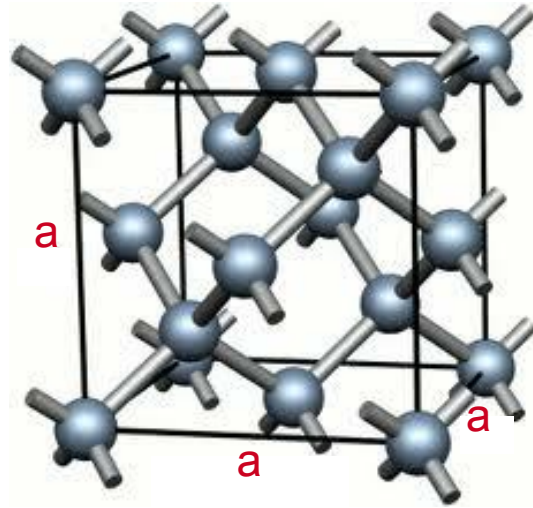
Unit-Cell Vectors

$\mathbf{a}_1 = a\ (-1/2,\ 1/2\ ,\ 0)$

$\mathbf{a}_2 = a\ (-1/2,\ 0,\ 1/2)$

$\mathbf{a}_3 = a\ (0,\ 1/2,\ 1/2)$

Electron density is periodic with periodicity given by $\mathbf{R}_{uvw}$

$$n(\mathbf{r}) = n(\mathbf{r} + \mathbf{R}_{uvw})$$

Translation Vectors: $\mathbf{R}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$

Electron Density is Periodic

because wavefunctions in a crystal obey Bloch's Theorem

For a given band β

$$\varphi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$$

where $u_{\mathbf{k}}^{\beta}(\mathbf{r})$ is periodic in real space: $u_{\mathbf{k}}^{\beta}(\mathbf{r}) = u_{\mathbf{k}}^{\beta}(\mathbf{r} + \mathbf{R}_{uvw})$

Translation Vectors: $\mathbf{R}_{uvw} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$

Representation of Electron Density

$$\varphi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$$

$$n(\mathbf{r}) = -e \sum_{i=1}^{N_e} \left| \varphi_i(\mathbf{r}) \right|^2 \longrightarrow n(\mathbf{r}) = -e \sum_{\beta} \int_{\Omega_{BZ}} \left| \varphi_{\mathbf{k}}^{\beta}(\mathbf{r}) \right|^2 f(\varepsilon_k^{\beta} - \varepsilon_F) \frac{d^3 k}{\Omega_{BZ}}$$

Integral over k-points in first Brillouin zone
f(ε − ε$_F$) is Fermi-Dirac distribution function with Fermi energy ε$_F$

In practice the integral over the Brillouin zone is replaced
with a sum over a finite number of k-points (N_{kpt})

$$n(\mathbf{r}) \approx -e \sum_{\beta} \sum_{j=1}^{N_{kpt}} w_j \left| \varphi_{\mathbf{k}_j}^{\beta}(\mathbf{r}) \right|^2 f(\varepsilon_{\mathbf{k}_j}^{\beta} - \varepsilon_F)$$

One parameter that needs to be checked for numerical convergence is
number of k-points

Representation of Wavefunctions
Fourier-Expansion as Series of Plane Waves

For a given band: $\varphi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}^{\beta}(\mathbf{r})$

Recall that $u_{\mathbf{k}}^{\beta}(\mathbf{r})$ is periodic in real space: $u_{\mathbf{k}}^{\beta}(\mathbf{r}) = u_{\mathbf{k}}^{\beta}(\mathbf{r}+\mathbf{R}_{uvw})$

$u_{\mathbf{k}}^{\beta}(\mathbf{r})$ can be written as a Fourier Series: $u_{\mathbf{k}}^{\beta}(\mathbf{r}) = \sum_{lmn} u_{\mathbf{k}}^{\beta}(\mathbf{G}_{lmn})\exp(i\mathbf{G}_{lmn}\cdot\mathbf{r})$

$$\mathbf{G}_{lmn} = l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3$$

where the $\mathbf{b}_i$ are primitive *reciprocal lattice vectors* $\quad \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$

Representation of Wavefunctions

Plane-Wave Basis Set

For a given band

$$\varphi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}^{\beta}(\mathbf{r})$$
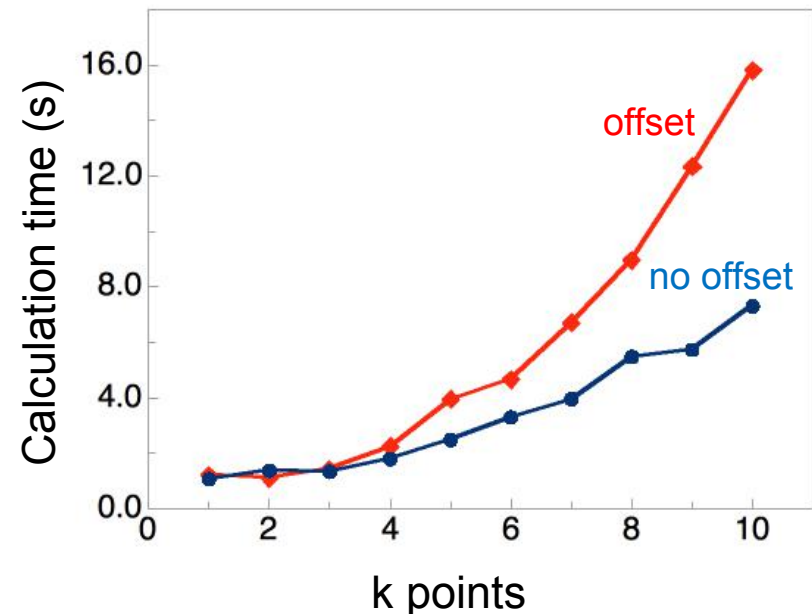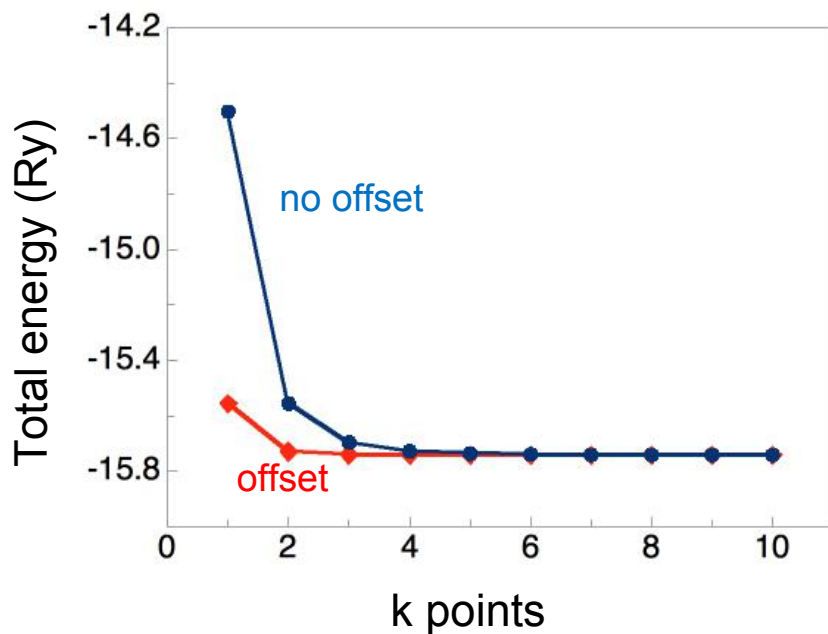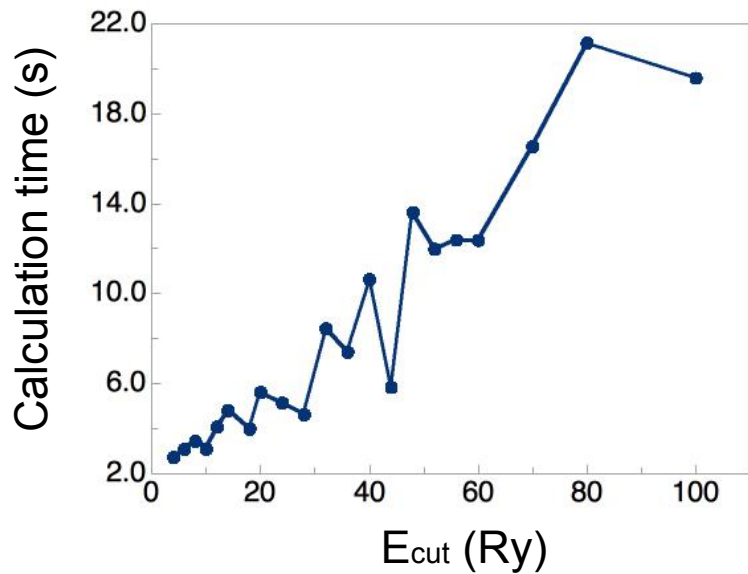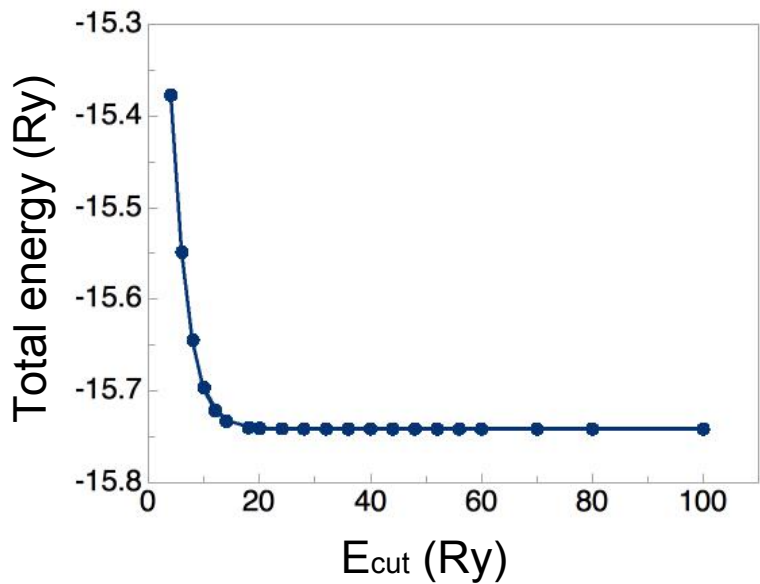
Use Fourier Expansion

$$\varphi_{\mathbf{k}}^{\beta}(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{k}}^{\beta}(\mathbf{G}) \exp\left[i(\mathbf{G} + \mathbf{k}) \cdot \mathbf{r}\right]$$

In practice the Fourier series is truncated to include all **G** for which:

$$\frac{\hbar^2}{2m}(\mathbf{G} + \mathbf{k})^2 < E_{\text{cut}}$$

Another parameter that needs to be checked for convergence is the "plane-wave cut-off energy" E_{cut}

Examples of Convergence Checks

Example calculation inputs

```
&CONTROL
 calculation='scf',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../work/',
 /
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 /
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
 /
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

```
&CONTROL
 calculation='bands',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../work/',
 /
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 nbnd=8,
 /
&ELECTRONS
 conv_thr=1d-8,
 /
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25

K_POINTS {crystal_b}
5
   0.0000000000     0.0000000000     -0.5000000000     20
   0.0000000000     0.0000000000      0.0000000000     30
  -0.5000000000     0.0000000000     -0.5000000000     10
  -0.3750000000     0.0000000000     -0.6250000000     30
   0.0000000000     0.0000000000      0.0000000000     20
```

By only 2 input files, we can "easily" calculate electronic band structure!

Example calculation inputs

```
&CONTROL
 calculation='scf',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../work/',
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
/
&ELECTRONS
 mixing_beta=0.7,
 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25
K_POINTS automatic
4 4 4 1 1 1
```

```
&CONTROL
 calculation='bands',
 restart_mode='from_scratch',
 prefix='si',
 pseudo_dir='../pseudo/',
 outdir='../work/',
/
&SYSTEM
 ibrav=2,
 celldm(1)=10.2625,
 nat=2,
 ntyp=1,
 ecutwfc=60.0,
 nbnd=8,
/
&ELECTRONS
 conv_thr=1d-8,
/
ATOMIC_SPECIES
 Si 28.0855 Si.pbe-rrkj.UPF
ATOMIC_POSITIONS (alat)
Si  0.00  0.00  0.00
Si  0.25  0.25  0.25

K_POINTS {crystal_b}
5
  0.0000000000    0.0000000000    -0.5000000000    20
  0.0000000000    0.0000000000     0.0000000000    30
 -0.5000000000    0.0000000000    -0.5000000000    10
 -0.3750000000    0.0000000000    -0.6250000000    30
  0.0000000000    0.0000000000     0.0000000000    20
```
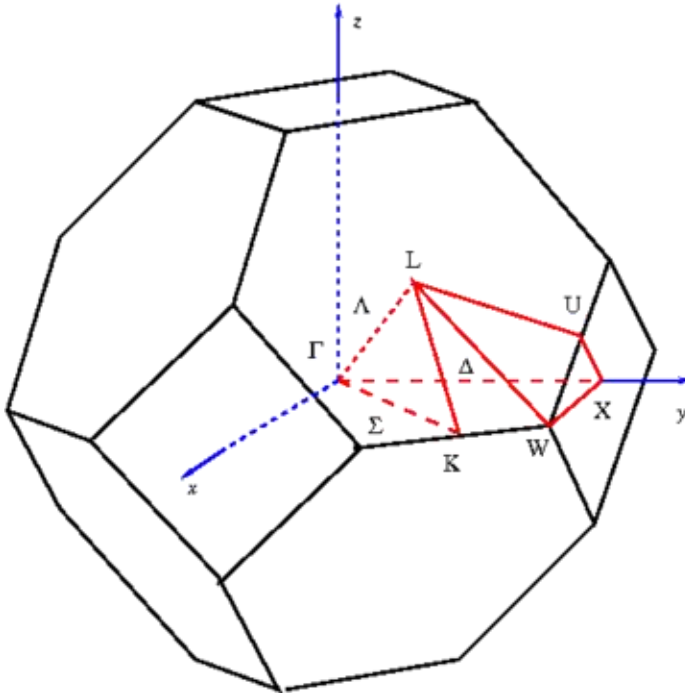
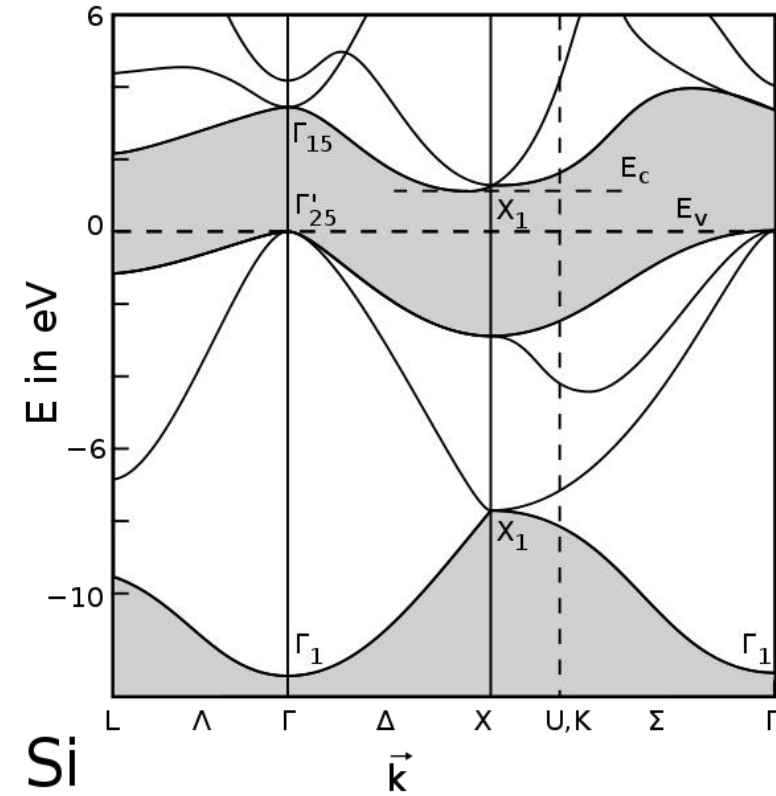By only 2 input files, we may be able to publish some papers!

Electronic Bandstructure
Example for Si

Brillouin Zone

Energy dispersion

Si

Kuis #15

- Manakah pernyataan berikut ini yang benar

    (A) Pendekatan LDA untuk interaksi pertukaran-korelasi kerap memberikan *band gap* lebih besar dari seharusnya
    (B) Pendekatan GGA untuk interaksi pertukaran-korelasi kerap memberikan *band gap* lebih kecil dari seharusnya
    (C) Pseudopotential diciptakan sebagai pengganti potensial singular yang merepresentasikan interaksi elektron-ion yang sulit dipecahkan secara numerik
    (D) Semua di atas benar