DFT: Basic idea and Practical calculations

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How the electronic structure calculation works

- **Part I: DFT**
  - Understanding the basic ideas
  - Limitations
- **Part II: Practical methods**
  - Computational method
  - Calculation technique
Part I outline

- Calculation of Materials
- Hartree-Fock method
- Density Functional Theory
- Exchange-Correlation
- Solving Kohn-Sham equation
- Force calculation
- Limitation of DFT
Calculation of materials

- Basic problem – many electrons in the presence of the nuclei
- Fundamental Hamiltonian:

\[
\hat{H} = \frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|}
\]

- Born-Oppenheimer approximation
  - Nuclei are fixed – neglect the kinetic term of nuclei
  - The last term is a constant added to the electronic part
Many-body interacting electron problem

- Schrödinger equation for many electron system
  \[ \hat{H}\Psi(r_1, r_2, ..., r_N) = E\Psi(r_1, r_2, ..., r_N) \]

- If we could solve the Schrödinger equation, we could predict the behavior of any electronic system

- Many electron wave functions \( \Psi(r_1, r_2, ..., r_N) \) is a function of \( 3N \) variables, where \( N \) is the number of electron

- Too many degree of freedom \( \Rightarrow \) Can’t be solved
Approaching to many-body problem

- Hartree-Fock
  - Independent electron approximation

- Density Functional Theory
  - Consider electron density instead of the wavefunction

- Quantum Monte Carlo
  - Statistical method
Hartree approximation

- Neglecting the correlation – assumes the electrons are uncorrelated
- Total wave function is written as the product of single electron wave functions
  \[ \Psi(r_1, r_2, \ldots, r_N) = \psi_1(r_1), \psi_2(r_2) \ldots \psi_N(r_N) \]

- Variational principle leads to Hartree equation
  \[ \left[ -\frac{1}{2} \nabla_i^2 + V_{\text{ion}} + V_H(r_i) \right] \psi_i(r_i) = \varepsilon_i \psi_i(r_i) \]

  \[ V_H(r_i) = 2 \sum_{j \neq i} \int \frac{\left| \psi_j(r_j) \right|^2}{|r_i - r_j|} \, dr_j \quad \text{Hartree potential, average Coulomb potential from other electrons} \]
Hartree-Fock (HF)

- Electrons are fermions; obey the Pauli exclusion principle and Fermi statistics
  - Wave function changes sign when the coordinates of two electrons are interchanged
  - Wave function is zero if two electrons are in the same state
  - Wave function is written to be an antisymmmtrized product (Slater Determinant)

\[
\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(r_1) & \psi_1(r_2) & \cdots & \psi_1(r_N) \\
\psi_2(r_1) & \psi_2(r_2) & \cdots & \psi_2(r_N) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_N(r_1) & \psi_N(r_2) & \cdots & \psi_N(r_N)
\end{vmatrix}
\]
Exchange interaction

- Minimize the energy with respect to Slater determinant leads to the Hartree-Fock equations

\[
\left[-\frac{1}{2} \nabla_i^2 + V_{\text{ion}} + V_H(r_i) + V_X(r_i)\right] \psi_i(r_i) = \varepsilon_i \psi_i(r_i)
\]

\[
V_X(r_i) = -\frac{1}{2} \left[ \sum_j \int \frac{\psi_j^*(r_j) \psi_i(r_i)}{|r_i - r_j|} dr_j \right] \frac{\psi_j(r_i)}{\psi_i(r_i)}
\]

- Adding Fermionic nature of electrons to the Hartree method give rise to an effective potential called exchange interaction

- still neglect the correlation effect, so large deviation from the experiment results
Density Functional Theory (DFT)

- Hohenberg-Kohn-Sham proposed a new approach to the many-body interacting electron problem
- All ground state properties are determined by the ground state density
- Hohenberg-Kohn theorems (1964)
  - Two statements constitute the basis of DFT
  - Do not offer a way of computing in practice
- Kohn-Sham ansatz (1965)
  - Turn DFT into practical method
Hohenberg-Kohn theorem

- **Theorem I**: density as a basic variable
- The total energy of a many-body system is a unique functional of electron density
- The total energy functional can be written as

\[
E[n] = F[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}
\]

interaction with nuclei and any other field

- Universal functional \( F[n] \) is independent of external potential — but unknown!

\[
F[n] = T[n] + U[n]
\]
Hohenberg-Kohn theorem

- Theorem II: variational for the energy in term of density
- The functional $E[n(r)]$ has its minimum when electron density is at the equilibrium electron density $n_0(r)$
- The minimum of the energy $E_0$ is exactly equivalent to the true ground-state energy

$$E_0 = \min E[n(r)] = E[n_0(r)]$$
The Kohn-Sham ansatz

- Replace original many-body problem with an independent electron problem that can be solved
- The unknown functional $F[n]$ is cast in the form
  \[
  F[n] = T_s[n] + \frac{n(r)n(r')}{|r - r'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n]
  \]
- $T_s[n] -$ non-interacting kinetic energy
  \[
  T_s[n] = \frac{\hbar^2}{2m} \sum_i \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r}
  \]
- Put the rest unknown into $E_{xc}[n]
- Exact theory but unknown functional $E_{xc}[n]
Exchange-correlation functional

- **Exchange**
  - Keep electrons of same spin away from each other (Pauli exclusion)

- **Correlation**
  - Keep electrons away from each other due to Coulombic forces

- **Finding** $E_{xc}$ functional is the great challenge, but approximate functionals work:
  - LDA
  - GGA
  - Hybrid functional
  - EXX
Local (Spin) Density Approximation L(S)DA

- The simplest but surprisingly good approximation
- Assume that the charge density varies slowly; each small volume looks like a uniform electron gas
- $E_{xc}[n]$ can be obtained by integrating uniform e⁻ gas results

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

- $\varepsilon_{xc}(n)$ is the exchange-correlation energy per electron in homogenous electron gas at density $n$, which can be calculated

- More generally, formulation for spin density

$$E_{xc}^{LSDA}[n^\uparrow, n^\downarrow] = \int n(\mathbf{r})\varepsilon_{xc}(n^\uparrow, n^\downarrow)d\mathbf{r}$$
Generalized-Gradient Approximation (GGA)

- Density gradient expansion
- Take the value of the density at each point as well as the magnitude of the gradient of the density

\[ E_{xc}^{GGA}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n, \nabla n) d\mathbf{r} \]

- Make improvement over LDA for many cases
  - E.g. improve predicted binding and dissociation energies
Hybrid functional

- Combination of orbital-dependent HF and an explicit density functional (LDA/GGA)
- The most accurate functionals available (as far as energetic is concerned)
- The method of choice in chemistry
- Example:

\[
E_{xc}^{\text{half}} = \frac{1}{2} (E_{x}^{\text{HF}} + E_{xc}^{\text{DF}})
\]

\[
E_{xc}^{\text{B3LYP}} = (1 - a)E_{xc}^{\text{LDA}} + aE_{x}^{\text{HF}} + bE_{x}^{\text{Becke}} + cE_{c}^{\text{LYP}} + (1 - c)E_{c}^{\text{VWN}}
\]
Orbital functionals - OEP

- Functional explicitly dependence on orbitals
- **Optimized effective potential method (OEP)** allows orbital dependent functionals to be used in DFT
- The most common approach is to evaluate the HF exchange energy within KS orbitals, **exact exchange (EXX)**, and solve using OEP
- Typically, OEP-EXX methods have **much better band gaps**
- But the computational cost of solving the OEP is a major drawback
Kohn-Sham equations

- Kohn-Sham energy functional:

\[
E[n] = T_s[n] + \int \frac{n(r)n(r')}{|r - r'|} \, drdr' + E_{xc}[n] + \int v_{ext}(r)n(r) \, dr
\]

- Minimizing the energy functional leads to the Kohn-Sham equations (Schrödinger equations of single electron in effective potential)

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r)
\]

\[
V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{\text{H}}(r) + V_{\text{xc}}(r)
\]

\[
n(r) = \sum_i |\psi_i(r)|^2
\]
Solving Kohn-Sham equation

- Because the effective potential $V_{\text{eff}}$ depends upon $n(r)$, and hence $\psi(r)$, which is the solution of the equation

- The Kohn-Sham equations must be solved by an iterative technique; self-consistent field method
Self-consistent calculation procedure

1. **Guess density** \( n(\mathbf{r}) \)

2. **Construct effective potential**
   \[
   V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n] + V_{\text{xc}}[n]
   \]

3. **Solve KS equation**
   \[
   \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})
   \]

4. **Calculate new density and Compare**
   \[
   n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2
   \]

5. **Self-consistent?**

6. **Obtain output:** Total energy, Force, Eigenvalues, ...

If yes, the process is complete. If no, iterate back to the guess density step.
Output from KS equations

- We have solved the Kohn-Sham equations and found the eigen-energies and eigen-functions, what next?
- We can obtained
  - Ground state total energy
  - Forces acting on atom
  - Charge density
  - Band structure and density of states
  - Vibrational properties
Kohn-Sham eigenvalues and orbitals

- Kohn-Sham eigenvalues and orbitals have no physical meaning
- Only the ground state density and total energy can be trusted
- Except only highest occupied KS eigenvalues has a meaning as the first ionization energy (but only for exact functional)
- There is no straightforward relationship between KS eigen-energies and the excitation energy of quasiparticles
- But many band-structure calculations in solid state physics is from KS eigenvalues
Hellmann-Feynman theorem: forces and stress

- Forces acting on ions can be evaluated analytically

\[ F_I = -\langle \psi | \frac{\partial H}{\partial R_I} | \psi \rangle \]

- This formula correct for position independent basis and complete basis set

- Forces are very sensitive to errors in total energy; the ground state must be determined very accurately

- This theorem can also be applied for stress on unit cells

\[ \sigma_{\alpha\beta} = -\langle \psi | \frac{\partial H}{\partial t_{\alpha\beta}} | \psi \rangle \]

derivative energy with respect to strain tensor
The accuracy of DFT

- **Molecular structures**
  - bond lengths are accurate to within 1-2%

- **Vibrational frequencies**
  - within 5-10% accuracy

- **Atomization energies**
  - LDA < GGA < hybrid
  - desired accuracy for hybrid functionals

- **Ionization and affinity energies**
  - Average error around 0.2 eV for hybrid functionals
Limitations of DFT

- Band-gap problem
  - HKS theorem is not valid for excited states
  - Band gap in semiconductors and insulators are always underestimated
  - EXX and hybrid functionals lead to better gaps

- Overbinding
  - LSDA calculations usually give too large cohesive energies, too high bulk moduli
  - GGA largely correct overbinding
  - The use of the GGA is mandatory for calculating adsorption energies
Limitations of DFT

- **Difficulty in strong correlations**
  - No one knows a feasible approximation valid for all problems – especially for cases with strong electron-electron correlation

- **Neglect of van-der-Waals interactions**
  - Not included in any DFT functional
  - Possible solution – approximate expression of dipole-dipole vdW forces on the basis of local polarizabilities derived from DFT
Summary

- Calculation of electronic structure of materials by solving many-electron problem need approximations
- HF – neglect electron correlation lead to large deviations from the experiment results
- DFT – no attempt to compute many-body wave function, instead energy is written in term of the electron density
- KS – treat the kinetic energy properly, bring back the wave function
- $E_{xc}$ – approximation forms have proved to be very successful, but there are failures
- Requires care and understanding of limitation of the functionals
Part II outline

- Periodic solid and Bloch’s theorem
- Basis set
- Plane wave method
- Pseudopotential
- Brillouin zone integration
- Some practical aspect
Finite vs. Extended systems

- **Finite system**
  - Atom, molecules, clusters
  - Boundary is open
  - Discrete energy level

- **Extended system**
  - Crystal, surface, ...
  - Boundary condition is normally periodic
  - Lead to continuous band
Periodic solids

- **Crystal structures** = Infinite repeated unit cell
- **Real (direct) space**
  - Bravais lattice: \( \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \)
- **Reciprocal space**
  - Reciprocal lattice: \( \mathbf{G} = g_1 \mathbf{b}_1 + g_2 \mathbf{b}_2 + g_3 \mathbf{b}_3 \)
  - where real space and reciprocal space are related by
    \[ e^{i \mathbf{G} \cdot \mathbf{R}} = 1 \implies \mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3 \]
- **1st Brillouin zone (BZ)**
  - primitive cell of reciprocal lattice
Bloch’s theorem

- Bloch’s theorem: The density is periodic so the wave function is

\[ \psi_k^n(r) = u_k^n(r) \exp(ik \cdot r) \]

  - The function \( u(r) \) has the periodicity of the unit cell
  - Wave function is repeat with a change of phase

- Imply that it suffices to calculate \( \psi_k^n \) in \textbf{just one unit cell}

- All possible states are specified by wave vector \( \mathbf{k} \) within the BZ and \textbf{band index} \( n \)

- The eigenvalues \( \varepsilon(n, \mathbf{k}) \) become continuous bands
The whole electronic structure of periodic crystal are represented by the band structure.

The band structure plot shows $\epsilon(n,k)$ only along the high symmetry directions in the BZ.
Modeling non-periodic system

- Molecule, cluster, defect, surface, ...
- As almost all plane wave codes impose periodic boundary conditions, the calculation of non-periodic system must be performed using 'supercell approach'
- The interaction between repeated images must be handled by a sufficiently large vacuum region
- For surface calculation, the thickness of the slab must be large enough
Basis function

- Expand wave function on the basis function
  \[ \psi(r) = \sum_i c_i \phi_i(r) \]
  - We want to find the coefficients \( c_i \)
  - Diagonalize H matrix to find the eigenvalues and eigenfunctions

- There are three basic approaches to the calculation of independent-particle electronic states in materials
  - Plane waves
  - Localized atomic orbitals
  - Augmented methods

- Each method has its advantages and pitfalls
Plane wave

- Wave functions are written as sum of plane waves

\[ \Psi_i(\mathbf{r}) = c_1 e^{i\mathbf{G}_1 \cdot \mathbf{r}} + c_2 e^{i\mathbf{G}_2 \cdot \mathbf{r}} + c_3 e^{i\mathbf{G}_3 \cdot \mathbf{r}} + \ldots \]

- Historical reason: related to free electron picture for metal
- Perfect for crystals (periodic systems)
- Simple to implement
- Calculation is simplicity and efficiency using FFT’s
Pros and Cons of the plane wave basis set

• **Pros**
  - Plane wave basis set is complete and unbiased
  - There is single convergence criterion
  - Plane waves are mathematical simple, and their derivatives are product in k-space
  - Plane waves do not depend on the atomic positions (force do not depend on the basis set; no Pulay forces)

• **Cons**
  - The number of plane waves needed is quite large
  - Empty space is included in the calculation
Localized atomic orbital

- Wave function are written as sum of atomic-like orbitals (s, p, d, f)
  \[ \psi_i(r) = c_1 |1s\rangle + c_2 |2s\rangle + c_3 |2p\rangle + \ldots \]

- Advantage
  - The intuitive appeal of atomic-like states
  - Gaussian basis widely used in chemistry
  - Simplest interpretation in tight-bind form
  - Small basis sets are required

- Disadvantage
  - Non orthogonal
  - Depend on atomic position
  - Basis set super position errors (BSSE)
Augmented Plane Wave (APW)

- Partition space into space around each atom and interstitial region
  - Wave function outside sphere represent with plane wave
  - Wave function inside sphere represent with spherical harmonic functions

- Best of both region
- Require matching inside and outside functions
Pseudopotential approximation

- For the plane wave basis set, the number of plane waves would be very large ($>10^6$)
  - Valence-electron wave function is far from free-electron like near atomic cores
  - The valence-electron wave functions vary rapidly because the requirement for orthogonal to core-electron wave functions
  - Core-electron wave functions are localized
- To make plane wave basis set feasible; pseudopotential instead of exact pseudopotential must be applied
- Why pseudopotential approximation work:
  - Only valence electrons participate in chemical bonding and core electrons are almost unaffected
  - The detail of valence wave functions near the atomic nuclei is unimportant
Pseudopotential concept

- Replace nucleus and core electrons by a fixed effective potential
- Only valence electrons are taken into account in the calculation
- Remove core state from the spectrum

occupation, eigenvalues

\begin{align*}
3p & \quad 1 \quad -2.7 \text{ eV} \\
3s & \quad 2 \quad -7.8 \text{ eV}
\end{align*}

valence states

\begin{align*}
2p & \quad 6 \quad -69.8 \text{ eV} \\
2s & \quad 2 \quad -108 \text{ eV}
\end{align*}

core states

\begin{align*}
1s & \quad 2 \quad -1512 \text{ eV}
\end{align*}

pseudo atom

\( Z = 3 \)

\[ (-\frac{1}{2}\nabla^2 + V_{\text{eff}})\psi_i = \varepsilon_i \psi_i \]

\[ (-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\text{ps})\psi_{\text{eff}}(\text{ps}) = \varepsilon_i^{(\text{ps})} \psi_i^{(\text{ps})} \]
Pseudopotential generation

\[ \psi_{l}^{AE} \Rightarrow \psi_{l}^{PS} \Rightarrow V_{l}^{PS} \]

1. Calculate exact all electron wave functions for a reference atom
2. Replace the exact wave function by a node less pseudo-wave function
3. Invert Schrödinger equation to obtain the pseudopotential

- Pseudopotentials must \textit{conserve exactly the scattering properties} of the original atom in the atomic configuration
- Pseudopotentials must be generated with the \textit{same functional} that will be later used in calculations.
- Choice of pseudopotential is not unique; lot of freedom to construct
Transferability and softness

- **Transferability**: a pseudopotential such that can be used in whatever environment (molecule, cluster, solid, surface, insulator, metal, ...) is called **transferable**.

- **Softness**: a pseudopotential is called **soft** when a few plane waves are needed.
  - Ultrasoft means very small amount of plane waves needed.

- The art of creating good pseudopotential is to find one that are both (ultra)soft and transferable.
Norm-conserving pseudopotential

- The pseudo-wave functions, generally, do not have the same norm as the all electron wave functions inside the spheres.
- Obviously, one would like to get integrating the charge in the core region the same as the all-electron one:

\[
\int_0^{R_c} |\psi^{PS}(\mathbf{r})|^2 d\mathbf{r} = \int_0^{R_c} |\psi^{AE}(\mathbf{r})|^2 d\mathbf{r}
\]

- Key step to improve the accuracy, transferable of pseudopotentials.
- But not so soft as we desired (especially, first row elements and transition metals).
Ultrasolft pseudopotential

- Relaxing the norm-conservation constraint for the valence wave function and put more complexity in the core
- Define an (smooth) auxiliary wave function add to plane wave around each atom
- Can make as soft as desired because norm-conservation is not required
  - Basis sets are roughly a factor 2-3 smaller
  - Accuracy can be better than norm-conserving pseudopotential
- Closely relate (approximation) to projector augmented wave method (PAW), which is as accurate as an all electron method
Projector augmented wave (PAW)

- Combination of the pseudopotential approach and the augmented wave method

\[ \psi = \tilde{\psi} + \sum_m (\phi_m - \tilde{\phi}_m) \langle \tilde{p}_m | \tilde{\psi} \rangle \]

- Better method than pseudopotential
  - Total density of the system is computed; no transferability problem
  - Plane wave cutoff is equivalent to ultrasoft
  - PAW method is as accurate as all an electron method
Pseudopotential conclusion

- Use PAW or ultrasoft whenever possible
  - but it is not available in every code
- Use provided pseudopotentials
  - almost plane wave codes come with well tested pseudopotential databases
  - create one by yourself is not a good idea, but you may have to
- Always test your pseudopotentials
Plane wave cutoff

- Wave functions are written as sum of plane waves
  \[ \psi_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \]
  - \( \mathbf{G} \) is reciprocal lattice vectors
- In principle, infinite number of plane waves are required
- In practice, the number of plane waves is determined by the cutoff kinetic energy \( E_{\text{cut}} \)
  - Only reciprocal lattice vectors satisfied following condition are included in expansion
  \[ |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}} \]
- The quality of the plane wave basis set depend on this cutoff
Plane wave cutoff

The radius of the sphere is proportional to the square root of the cutoff energy.

- Only reciprocal lattices inside the sphere are used in expansion.
- Basis set size is dependent on cutoff and volume of box only.

Twice cutoff radius is needed for density expansion.
Convergence test

- $E_{\text{cut}}$ control the completeness of the basis set
- Truncation of basis set will lead to an error
- Reduce the error by increasing the value of cutoff energy
- Always check the convergence of physical properties against $E_{\text{cut}}$
Fast Fourier Transform (FFT)

- FFT is essential for efficiency:
  - Transforming the wave functions and density between real and reciprocal space
  - e.g., $V(r)\psi(r)$: convolution in G-space scale as $N\log(N)$ instead of $N^2$ for a direct computation

$$V(r)\psi(r) = \text{FFT}^{-1}(V(G)\psi(G))$$

Real space grid

<table>
<thead>
<tr>
<th>$\psi(r)$</th>
<th>$V(r)$</th>
<th>$\rho(r)$</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

G–space grid

<table>
<thead>
<tr>
<th>$\psi(G)$</th>
<th>$V(G)$</th>
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</tr>
</thead>
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</table>

Fourier grid must contain all wave vectors up to $G_{c2}$
Brillouin zone integration

- Many quantities require integration over Brillouin zone, e.g. charge density, total energy, ...
  \[ n(r) = \sum_n^{occ} \int_{\Omega_{BZ}} \left| \psi_n(k, r) \right|^2 \frac{d^3k}{\Omega_{BZ}} \]

- To evaluate computationally – the integrals transform to weighted sum over special k-points
  \[ n(r) \approx \sum_n^{occ} \sum_j w_j \left| \psi_n(k_j, r) \right|^2 \]

- **Sampling of k-point** within the Brillouin zone is crucial to the accuracy of the integration
Reducing the number of k-points

- **Point group symmetry**
  - Hamiltonian is invariant under any symmetry operator
  - Irreducible Brillouin zone (IBZ), which is the smallest fraction of the BZ that is sufficient to determine all the information on the states in the crystal
  - Only k-points within IBZ should be taken into account; the states at all other k points outside the IBZ are related by the symmetry operations

- **Shift of k-point**
  - It is possible to add a constant shift to all of the points in the set before symmetrization
Monkhorst-Pack scheme

- One of the most popular schemes for generating k-points.
- A uniform grid of k-points in BZ
- Example:
  - quadratic 2-dimensional lattice
  - $q_1 = q_2 = 4 \Rightarrow 16$ k-points
  - only 3 inequivalent k-points ($\Rightarrow$ IBZ)
    - $4 \times k_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$
    - $4 \times k_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$
    - $8 \times k_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$
  - construction-rule:
    $$k_{pr} = u_1 b_1 + u_r b_2 + u_3 b_3$$
    $$u_r = \frac{2r - q_r - 1}{2q_r}, \quad r = 1, 2, \ldots, q_r$$
Smearing method

- Problem with metallic system
  - Discontinuities in occupation numbers (partially filled band)
  - High Fourier components are required
  - Large number of k point is necessary

- In order to improve convergence with number of k-points, replace step function by a smoother function (smearing)

- Various schemes of smearing
  - Fermi-Dirac smearing
  - Gaussian smearing
Linear tetrahedron method

- Another popular method for integrating over BZ
- Main idea:
  - Dividing up BZ into tetrahedra
  - Linear interpolation of the function to be integrated $X$ within these tetrahedra
  - Integration of the interpolated function

- Good for
  - DOS calculation
  - Very accurate total energy
Running a calculation

- **Pseudopotential**: Choose appropriate pseudopotential that models the science you want hard, soft, semicore

- **Basis set**: Test convergence of physical property you are interested in against the basis speed vs. accuracy

- **k-points**: Test convergence of physical property you are interested in against k-points metals!

- **Production run**: The whole setup must be the same for comparison between calculations to be meaningful

If your results are unphysical, then you may have to start again.
Ionic relaxation

- **Conditions for equilibrium**
  - Forces on all atoms = 0
  - Stress = externally applied stress

- **Method**
  - minimization algorithm (CG, BFGS)
  - by hand – minimum of total energy curve

- **Warning**
  - Symmetry could change during geometry optimization (may or may not be permitted)
  - Number of plane waves may change discontinuously when cell size changed – increase Ecut by 20-30% to get a smooth E-V curve
Speed up the SCF calculation

- Number of iterations should be small (fast converge)
- Each iteration should be fast

**Diagram:**

1. **Guess density** $n(r)$
2. Construct effective potential
   
   $$V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{H}[n] + V_{SC}[n]$$
3. Solve KS equation
   
   $$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r)\right] \psi_i(r) = \varepsilon \psi_i(r)$$
4. Calculate new density and compare
   
   $$n(r) = \sum |\psi_i(r)|^2$$
5. **Efficiency diagonalization method**
   - Conjugate gradient minimization
6. **Mixing scheme**
   - Linear
   - Anderson
   - Broyden
7. **Self-consistent?**
   - **Yes**
     - Obtain output: Total energy, Force, Eigenvalues, ...
   - **No**

Apirath – DFT: basic and practice - 6/5/07
Computational time and Memory

- Conventional matrix diagonalization (standard LAPACK routine)
  - CPU time scales as $O(N_{basis}^3)$
  - Memory storage scales as $O(N_{basis}^2)$

- Conjugate gradient minimization
  - CPU time scales as $O(N_{electron} N_{basis} \ln N_{basis})$

- k point sampling
  - CPU time and memory scale linearly with the number of k points
Other way to determine the KS ground states

- Direct minimization of KS functional
  - Damped second order
  - Preconditioned conjugate gradient
  - Direct Inversion of Iterative Subspace (DIIS)

- Car-Parrinello molecular dynamics
Summary

- Periodic solid – consider only one unit cell
- Plane wave basis set – unbiased, no basis correction to forces, switch between real space and reciprocal space via FFT, control the accuracy with energy cutoff
- Pseudopotentials – reduce the number of plane waves required
- FFT – allow the calculation to scale well with system size
- Brillouin zone integration – approximate by sum over special k points
- Accuracy – always test the convergence of $E_{\text{cut}}$ and k-points