Electronic Structure of Condensed Matter
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Lecture 6 - Part 1:
Kohn-Sham Calculations for Crystals: Plane Waves

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Lecture 6 - Part 1:
Kohn-Sham Calculations for Crystals: Plane Waves

OUTLINE

Calculations with Plane Waves
    Simple expressions for Bloch states, Schr. Eq.

Self-consistent Kohn-Sham calculation
    From output eigenvectors - find new density and potential
        Example of clever algorithm -- efficient in real space
    Repeat to self-consistency - determines density, total energy, . . .

Crucial aspects in the theory, algorithms, and actual computation
    Accurate “ab initio” pseudopotentials -- later
    Fast Fourier Transform (FFT) – introduction of grid in real space
    Later we will discuss modern advances in iterative algorithms

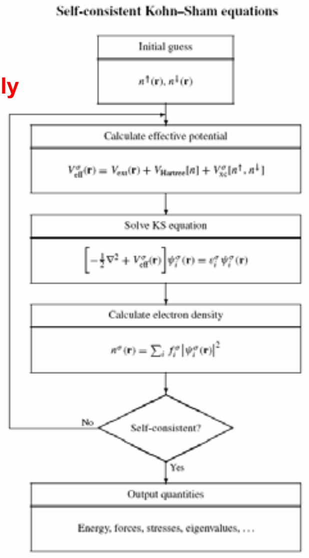
Tests for convergence -- MUST be done for calculations to be correct!

Examples

Recall the General Problem for Kohn-Sham calculations

Staring point:
Positions, types of atoms
and
Pseudopotential that is calculated separately
and not changed during the calculation

Each step is simple
in plane waves



Planes Waves

The good thing about plane waves I

It seems that you don’t have to think

EXCEPT – the cutoff and the pseudopotential

The bad thing about plane waves I

It seems that you don’t have to think

But you have to think if you want to get
the correct answer!

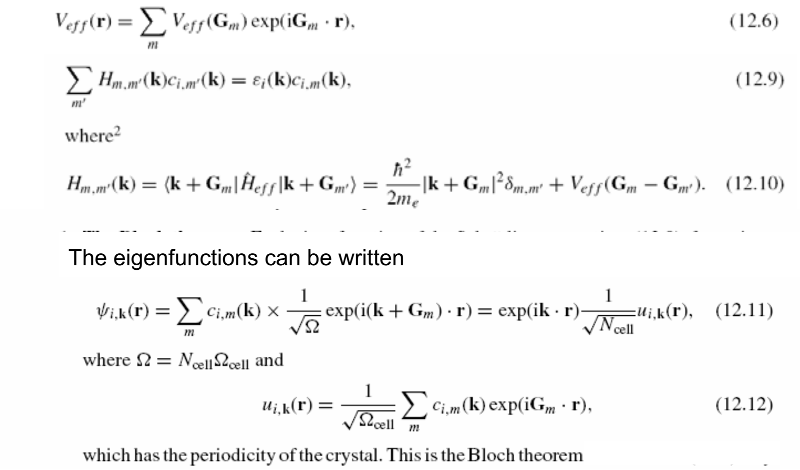
The good thing about plane waves II

You can go on to other things
phonons, structures, molecular dynamics, surfaces, ……
Plane waves can be VERY efficient – new algorithms, FFTs

This is why so many new developments have been done first with plane waves – later used with other methods

Kohn-Sham Equations in Planes Waves I

One electron Schrodinger-like Eq. – with a periodic potential V_{eff}
See lecture 2.



$$V_{eff}(\mathbf{r}) = \sum_m V_{eff}(\mathbf{G}_m)\exp(i\mathbf{G}_m\cdot\mathbf{r}), \qquad (12.6)$$

$$\sum_{m'} H_{m,m'}(\mathbf{k})c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k})c_{i,m}(\mathbf{k}), \qquad (12.9)$$

where[2]

$$H_{m,m'}(\mathbf{k}) = \langle \mathbf{k}+\mathbf{G}_m|\hat{H}_{eff}|\mathbf{k}+\mathbf{G}_{m'}\rangle = \frac{\hbar^2}{2m_e}|\mathbf{k}+\mathbf{G}_m|^2\delta_{m,m'} + V_{eff}(\mathbf{G}_m-\mathbf{G}_{m'}). \qquad (12.10)$$

The eigenfunctions can be written

$$\psi_{i,\mathbf{k}}(\mathbf{r}) = \sum_m c_{i,m}(\mathbf{k}) \times \frac{1}{\sqrt{\Omega}}\exp(i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\frac{1}{\sqrt{N_{\text{cell}}}}u_{i,\mathbf{k}}(\mathbf{r}), \qquad (12.11)$$

where $\Omega = N_{\text{cell}}\Omega_{\text{cell}}$ and

$$u_{i,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}}\sum_m c_{i,m}(\mathbf{k})\exp(i\mathbf{G}_m\cdot\mathbf{r}), \qquad (12.12)$$

which has the periodicity of the crystal. This is the Bloch theorem

Kohn-Sham Equations in Planes Waves II

Matrix equation

(here we have omitted the constants h and m)

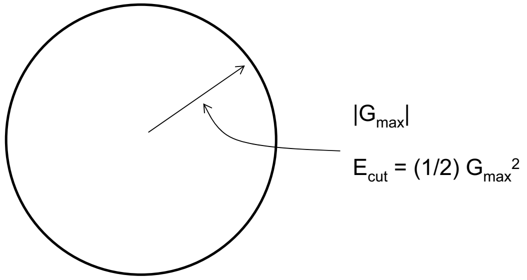
$$\begin{bmatrix} \tfrac{1}{2}(k)^2 & V_{eff}(G_1) & V_{eff}(G_2) & V_{eff}(G_3) & \ldots \\ V_{eff}(G_1) & \tfrac{1}{2}(k+G_1)^2 & V_{eff}(G_2-G_1) & V_{eff}(G_3-G_2) & \ldots \\ V_{eff}(G_2) & V_{eff}(G_2-G_1) & \tfrac{1}{2}(k+G_2)^2 & V_{eff}(G_3-G_2) & \ldots \\ V_{eff}(G_3) & V_{eff}(G_3-G_1) & V_{eff}(G_3-G_2) & \tfrac{1}{2}(k+G_3)^2 & \ldots \\ \ldots & \ldots & \ldots & \ldots & \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \end{bmatrix} = \varepsilon \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \end{bmatrix}$$

Straightforward approach – diagonalize – eigenvalues, vectors as functions of k
All modern codes use more efficient methods – see later

(NOTE: V_{eff} depends upon k in modern non-local potentials. This is a complication but it does not change the main points.)

Kohn-Sham Equations in Planes Waves III

Why work in Fourier Space? How many G vectors are needed?



These are the most important because the kinetic energy (diagonal of the matrix is large for larger G's.

Kohn-Sham Equations in Planes Waves - IV

What is V_{eff} ? We need the Fourier components V_{eff} (G)

Recall the key expressions of the Kohn-Sham approach

$$E_{KS} = T_s[n] + \int d\mathbf{r}\, V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\text{Hartree}}[n] + E_{II} + E_{xc}[n]. \qquad (7.5)$$

$E_{xc}[n]$ is the x-c energy - a functional of n

From variational principle to minimize energy:

$$V^{\sigma}_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \frac{\delta E_{\text{Hartree}}}{\delta n(\mathbf{r},\sigma)} + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r},\sigma)}$$
$$= V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V^{\sigma}_{\text{xc}}(\mathbf{r}). \qquad (7.13)$$

This is V_{eff} (r) for a general density = V_{KS}(r) for the correct n

(in general V depends on spin – not written explicitly here)

Easy to write in real space because Exc is expressed directly in real space.
Complicated in Fourier space – what do we do?

Use FFTs – next slide

Planes Waves and FFTs

In many cases it is convenient to have the option to choose which space to work in -- real or reciprocal

Examples:

Kinetic energy easy in reciprocal space:

$\Delta^2 \rightarrow |k + G|^2$

Density, Potential energy easy in real space:

$n(r) = |\psi(r)|^2$ $V(r) = \delta E_{xc}/\delta n(r)$

Suppose we have the wave functions in reciprocal space $\psi(G)$ and we want to find $n(r)$:

1. **FFT $\psi(G) \rightarrow \psi(r)$ on a grid in real space**
2. **$n(r) = |\psi(r)|^2$ and $V_{xc}(r) = V_{xc}[n]$**

If we want $n(G)$:

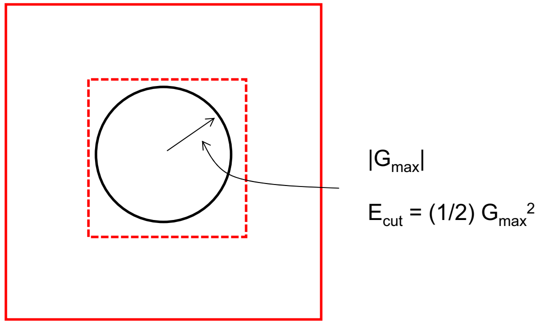
3. **FFT $n(r) \rightarrow n(G)$ and $V_{xc}(r) \rightarrow V_{xc}(G)$**

Using FFTs - Appendix M - section M.11

Key point: To avoid "aliasing" must perform the FFT on a grid that is double size in each direction - simple reasoning – $|\psi(r)|^2$ has Fourier components at twice the frequency of those in $\psi(r)$

How does on do the FFT

Use a cubic box of double size in each dimension!



Set every Fourier component of ψ equal to zero outside the circle
Then n(r) is given properly. Why?

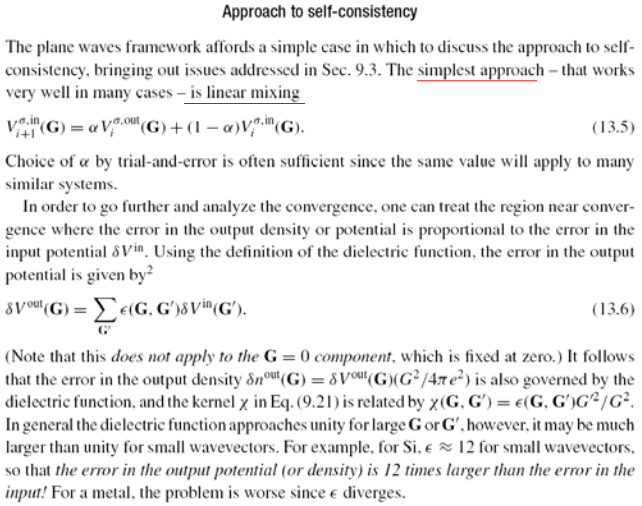
After getting new V(r), find new solution of $H\psi=\varepsilon\psi$ and make zro all components outside the sphere!

Despite the huge FFT grid it is still the most efficient approach!

Self-Consistency

This must be done in all methods – easiest to describe for plane waves

Solving the self-consistent equations for n and V_{eff}



Approach to self-consistency

The plane waves framework affords a simple case in which to discuss the approach to self-consistency, bringing out issues addressed in Sec. 9.3. The simplest approach – that works very well in many cases – is linear mixing

$$V_{i+1}^{\sigma,\mathrm{in}}(\mathbf{G}) = \alpha V_i^{\sigma,\mathrm{out}}(\mathbf{G}) + (1-\alpha)V_i^{\sigma,\mathrm{in}}(\mathbf{G}). \tag{13.5}$$

Choice of α by trial-and-error is often sufficient since the same value will apply to many similar systems.

In order to go further and analyze the convergence, one can treat the region near convergence where the error in the output density or potential is proportional to the error in the input potential δV^{in}. Using the definition of the dielectric function, the error in the output potential is given by[2]

$$\delta V^{\mathrm{out}}(\mathbf{G}) = \sum_{\mathbf{G}'} \epsilon(\mathbf{G},\mathbf{G}')\delta V^{\mathrm{in}}(\mathbf{G}'). \tag{13.6}$$

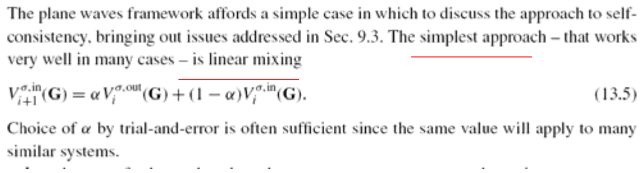
(Note that this *does not apply to the* $\mathbf{G}=0$ *component*, which is fixed at zero.) It follows that the error in the output density $\delta n^{\mathrm{out}}(\mathbf{G}) = \delta V^{\mathrm{out}}(\mathbf{G})(G^2/4\pi e^2)$ is also governed by the dielectric function, and the kernel χ in Eq. (9.21) is related by $\chi(\mathbf{G},\mathbf{G}') = \epsilon(\mathbf{G},\mathbf{G}')G'^2/G^2$. In general the dielectric function approaches unity for large $\mathbf{G}$ or $\mathbf{G}'$, however, it may be much larger than unity for small wavevectors. For example, for Si, $\epsilon \approx 12$ for small wavevectors, so that *the error in the output potential (or density) is 12 times larger than the error in the input!* For a metal, the problem is worse since ϵ diverges.

Analysis is very simple in Fourier components

Self-Consistency

This must be done in all methods – easiest to describe for plane waves

Solving the self-consistent equations for n and V_{eff}



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Choice of α by trial-and-error is often sufficient since the same value will apply to many similar systems.

There are better techniques from numerical analysis that can be used

The approach to self-consistency is most simply described in terms of Fourier components

The most difficulty is for small G which means large distances. For large cells there can be "charge sloshing", where electrons move in the cell (currents In a metal, polarization in an insulator. This slows down the convergence. Examples are calculations of surfaces – see later.

Tests for convergence

Sufficient number of G vectors – high enough E_{cut}

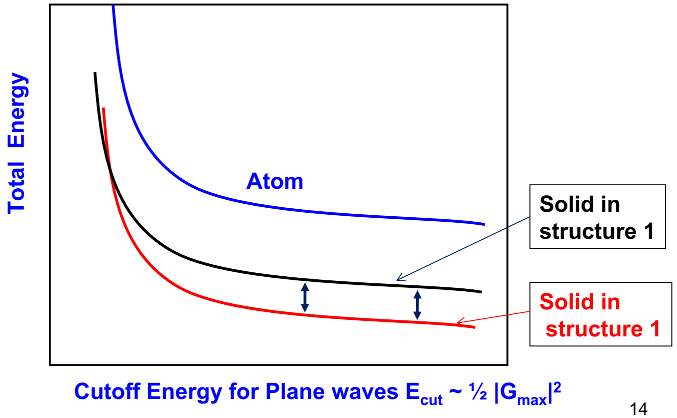
Sufficient number of points in the BZ

Sufficient number of iterations to convergence

Sufficient quality of the pseudopotential (later)

Test for convergence – Is E_{cut} large enough?

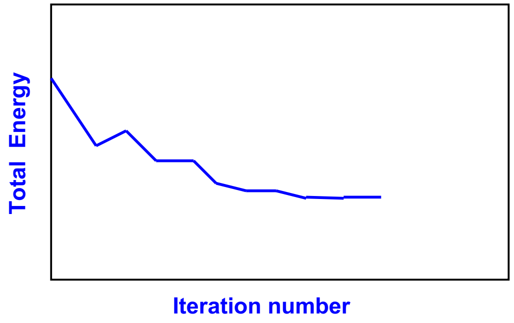
The total energy always decreases with increased number of plane waves
Why?
But differences may converge faster and my increase or decrease



Test for convergence – enough iterations?

The total energy decreases as the potential and density improves -- Why?
But the algorithm to choose a new potential may not improve the potentail

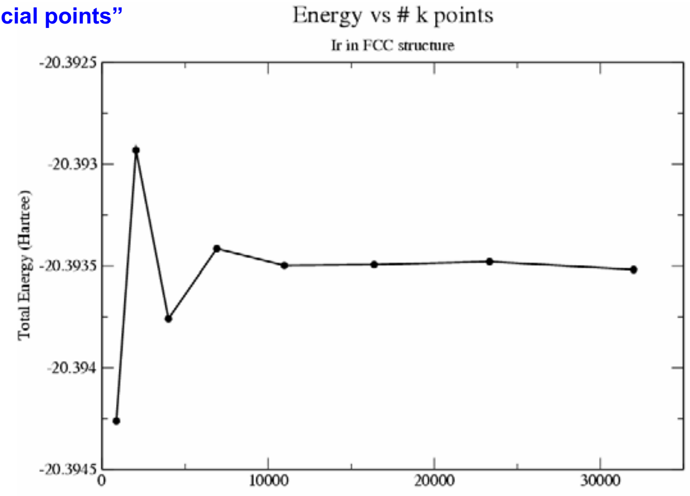
The energy is always above the converged result if is evaluated using a variational expression.



Example – FCC crystals
Ir in the close packed fcc structure

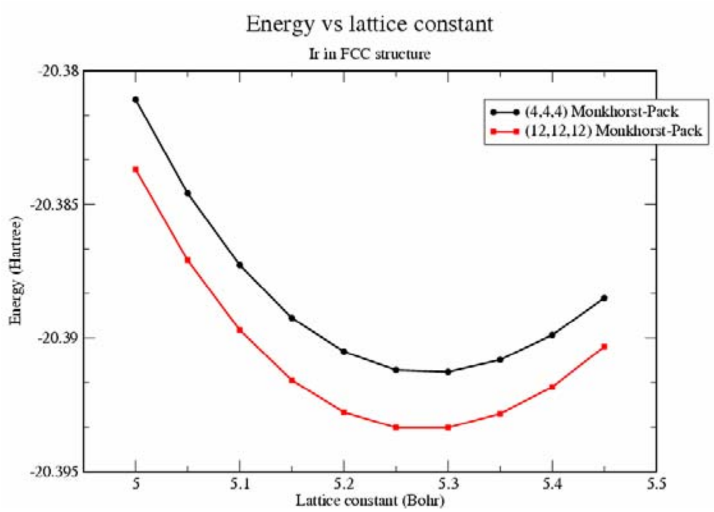
Calculations by Nithaya Chetty

Various sets of Monkhorst-Pack
"special points"



Exampl– FCC crystals
Ir in the close packed fcc structure

Calculations by Nithaya Chetty



Examples of results – tests on crystals

Table 13.1. Calculated properties of selected crystals using the local density approximation and various methods that involve plane waves: norm-conserving pseudopotentials (NCPPs), projector augmented waves (PAWs), "ultrasoft" pseudopotentials (USPPs) and linearized APWs (Ch. 17).

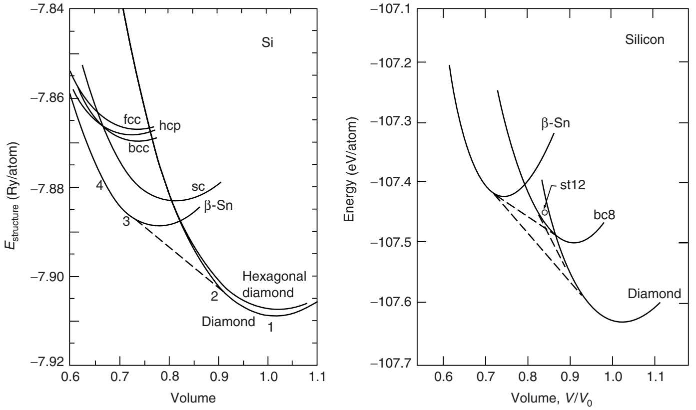
	C		Si		CaF_2		bcc Fe		
Method	*a*	*B*	*a*	*B*	*a*	*B*	*a*	*B*	*m*
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
* PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443	5.43	99	5.45	85–90	2.87[d]	172[d]	2.12[d]

* All methods agree if they are`done well.

* NCPP - "ab initio" norm-conserving pseudopotential

Examples of results - II

Transformation of silicon to metallic structures under pressure
Predictions from LDA

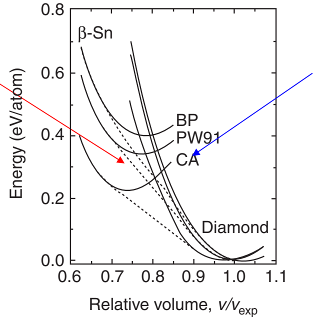


Results improved using improved functionals – next slide

Examples of results - IIa

Comparison of functionals LDA and various GGAs – See text for details

Close to experiment



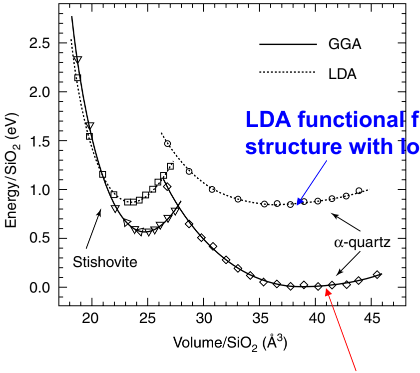
This is LDA.
CA means "Ceperley-Alder" who did the Quantum Monte Carlo calculations on the homogeneous electron gas that are now the basis for the LDA

Note – the energy is lower in all the GGAs than in LDA – the graphs have been shifted to give energy relative to Si in the diamond structure

Why do GGAs have this effect? – in the diamond structure the density is more inhomogneous – more homogeneous in the denser structures.
Thus the diamond structure is favored relative to the metallic structures.

Examples of results - III

SiO_2 – comparison of functionals



LDA functional finds wrong structure with lowest energy

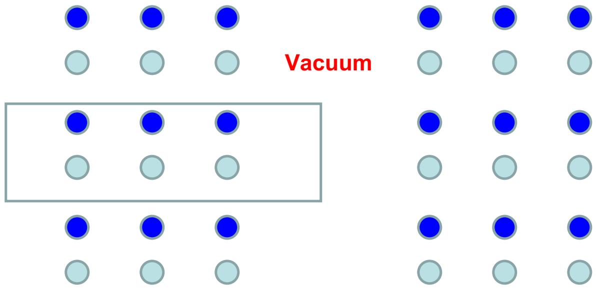
GGA functional leads to the lowest energy structure that agrees with experiment

D. R. Hamann, Phys. Rev. Lett., 76, 660, (199d).

How can surface energies and structures be calculated using plane waves?

Make a ”supercell” - large artificial cell – slab plus vacuum

Two surface s per cell



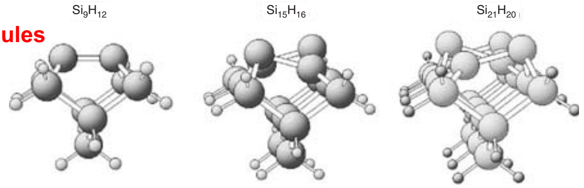
Many plane waves needed just to make wavefunction in vacuum zero!

But still plane waves are efficient with modern methods!

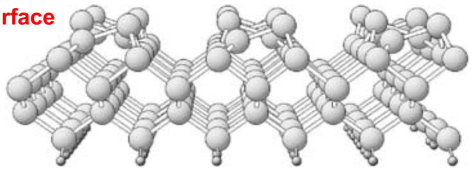
Examples of results - IV

Calculations on difficult cases – large cells - isolated systems?? Yes
Smart algorithms – later in course – Chapter 18, App. L and M
Fast computers

molecules



Surface



Continued in part II