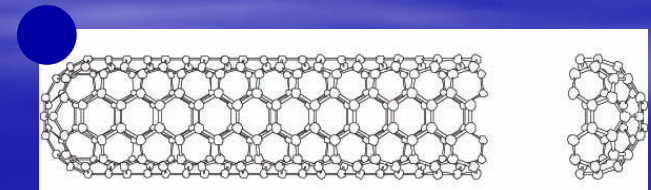


Overview of DFT and Plane wave Calculations

Oğuz Gülseren

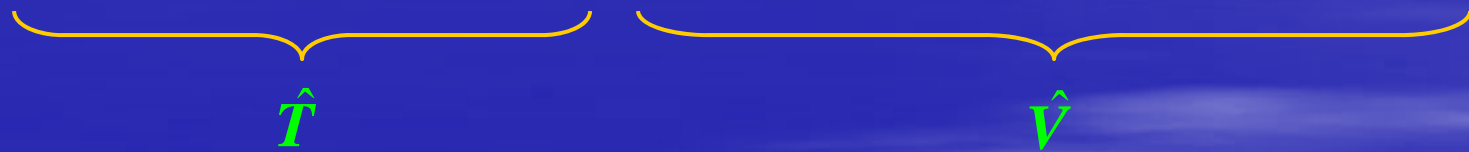


Eigenstates of electrons

- For optical absorption, etc., one needs the spectrum of excited states
- For thermodynamics and chemistry the lowest states are most important
- In many problems the temperature is low compared to characteristic electronic energies and we need only the ground state
 - Phase transitions
 - Phonons, etc.

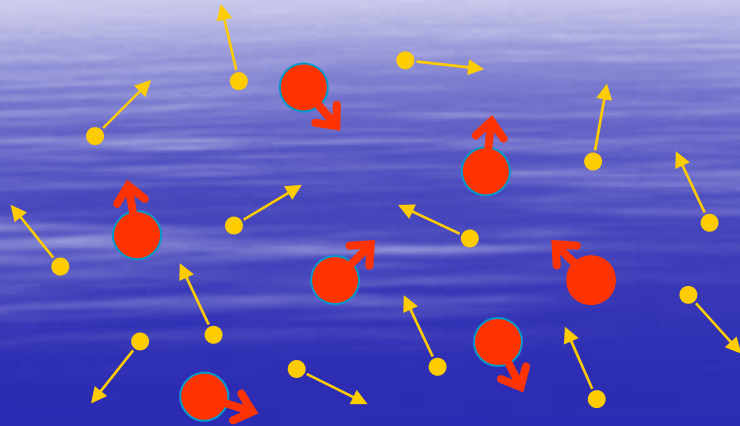
Time-independent and nonrelativistic Schrödinger equation:
 system consists of M nuclei and N electrons

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{m_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$



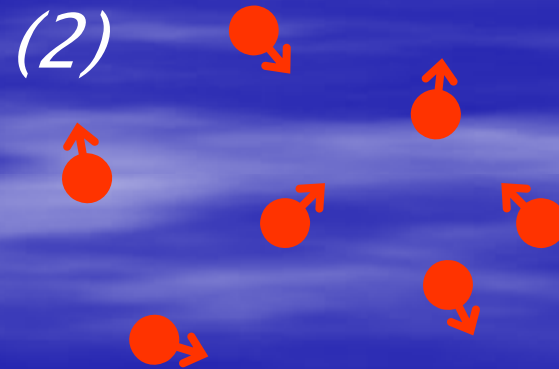
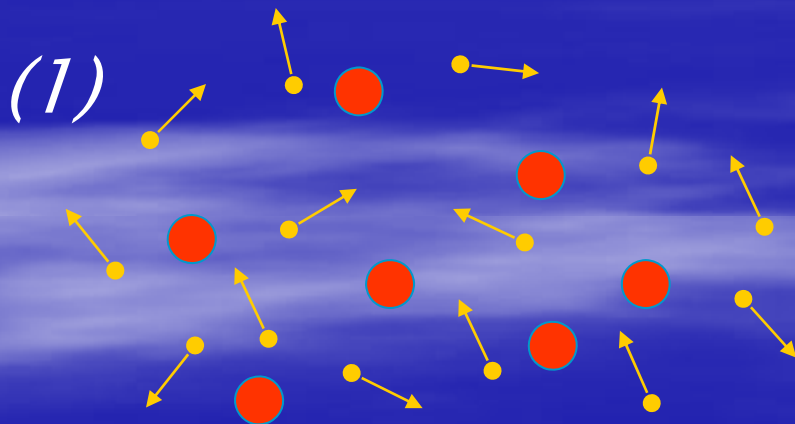
- elec
- nuc
- elec-nuc attraction
- elec-elec repulsion
- nuc-nuc repulsion

Born-Oppenheimer



$$\frac{m_n}{m_e} \gg 1$$

⇒ Nuclei are much slower than electrons



electronic/nuclear decoupling

$$\hat{H} = -\sum_{\mu} \frac{1}{2M_{\mu}} \nabla_{\mu}^2 - \sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_{i,\mu} \frac{Z_{\mu}}{r_{i\mu}} + \sum_{\mu,\nu>\mu} \frac{Z_{\mu}Z_{\nu}}{R_{\mu\nu}}$$

electrons

$$\hat{H}_{\{\vec{R}_{\mu}\}}^{el} = -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j>i} \frac{1}{r_{ij}} + V_{\{\vec{R}_{\mu}\}}^{ext}(\{\vec{r}_i\})$$

$$\hat{H}_{\{\vec{R}_{\mu}\}}^{el} \Psi_{n,\{\vec{R}_{\mu}\}}^{el}(\{\vec{r}_i\}) = E_n^{el}(\{\vec{R}_{\mu}\}) \Psi_{n,\{\vec{R}_{\mu}\}}^{el}(\{\vec{r}_i\})$$

nuclei

$$\hat{H} = -\sum_{\mu} \frac{1}{2M_{\mu}} \nabla_{\mu}^2 + E_n^{el}(\{\vec{R}_{\mu}\})$$

Classical => $\vec{F}_{\nu} = \frac{\partial}{\partial \vec{R}_{\nu}} E_0^{el}(\{\vec{R}_{\mu}\})$

First-principles calculations

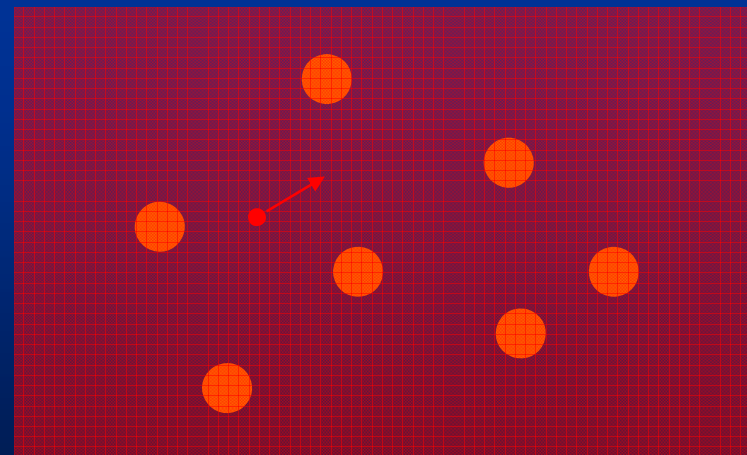
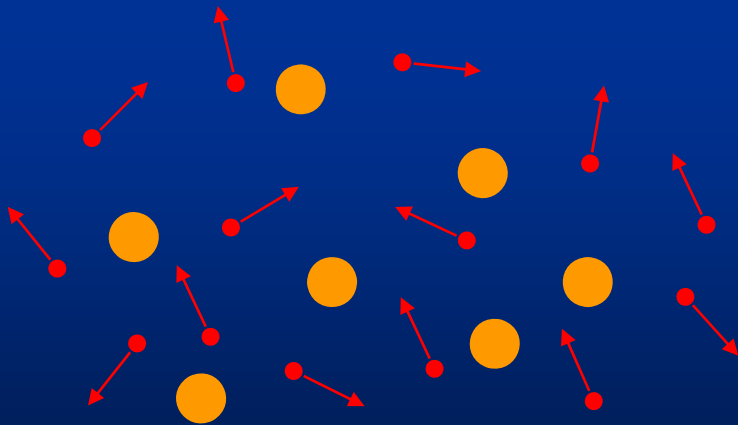
- *Fundamental laws of physics*
- *Set of “accepted” approximations*
to solve the corresponding equations on a computer
- *No empirical input*

PREDICTIVE POWER

Density-Functional Theory

1. $\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$ *particle density*

2. *As if non-interacting electrons in an effective (self-consistent) potential*



Density Functional Theory

- 1998 Nobel Prize in Chemistry to Walter Kohn
- **A prescription for replacing Schrödinger's Equation with similar, decoupled equations—which we can solve with fast computers and clever algorithms**
- Kohn-Sham Equations
- Applied Quantum Mechanics (other methods)
- An important long range for the field: protein folding

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

Density Functional Theory

- 1998 Nobel Prize in Chemistry to Walter Kohn
- A prescription for replacing Schrödinger's Equation with similar, decoupled equations—which we can solve with fast computers and clever algorithms
- **Kohn-Sham Equations**
- Applied Quantum Mechanics (other methods)
- An important long range for the field: protein folding

$$H\Psi_{nk} = \varepsilon_{nk} \Psi_{nk},$$

$$\text{where } H = K + V_{ne}(r) + V_{ee}(r) + V_{xc}(r)$$

and

$$K = -\frac{\hbar^2}{2m} \nabla^2,$$

$$V_{ne}(r) = -e^2 \sum_a \frac{Z_a}{|r - R_a|},$$

$$V_{ee}(r) = -e^2 \int \frac{\rho(r')}{|r - r'|} d^3r',$$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho},$$

$$\rho(r) = \sum_{nk} f_{nk} |\Psi_{nk}(r)|^2,$$

What's so great about DFT?

- **Normally**, we need to describe solids by a wavefunction of **all electrons**
- Then, we need to find solutions for more than **10^{23} electrons** and combine them
- This is still an **impossible task**

- In Density Functional Theory (DFT) we only need to find the **charge distribution** throughout our system
- Then, we can describe **single electrons** moving in a crystal mean field of all ions and other electrons
- In this way, we can calculate solids of up to a few **thousand atoms**
- And that is all we need, usually

Hohenberg - Kohn

$$\Psi(\{\vec{r}_i\}) \rightarrow \rho(\vec{r})$$

For our many-electron problem $\hat{H} = T + V_{ee} + \sum_{i=1}^N V_{ext}(\vec{r}_i)$

1. $E[\rho(\vec{r})] \equiv \int d^3\vec{r} V_{ext}(\vec{r}) \rho(\vec{r}) + F[\rho(\vec{r})] \geq E_{GS}$
(depends on nuclear positions) (universal functional)

2. $E[\rho_{GS}(\vec{r})] = E_{GS}$

PROBLEM:
Functional unknown!

Kohn - Sham

Independent particles in an effective potential

They rewrote the functional as:

$$E[\rho] = T_0[\rho] + \int d^3\vec{r} \rho(\vec{r}) [V_{ext}(\vec{r}) + \frac{1}{2}\Phi(\vec{r})] + E_{xc}[\rho]$$

*Kinetic energy for system
with no e-e interactions*

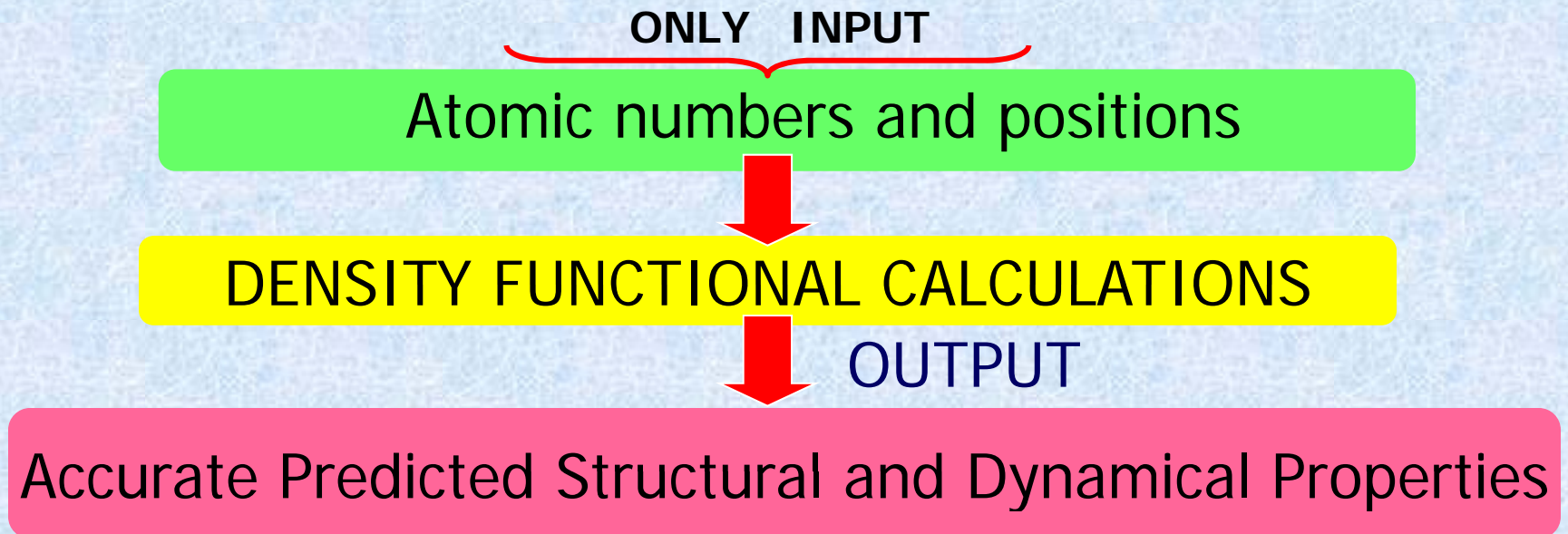
Hartree potential

*The rest:
exchange
correlation*

*Equivalent to independent
particles under the potential*

$$V(\vec{r}) = V_{ext}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$$

PREDICTION of MATERIALS PROPERTIES FROM FIRST-PRINCIPLES CALCULATIONS



Once the SCF wavefunctions, Ψ , are found, we can calculate:

1. Total Energy: $E = \langle \Psi | H | \Psi \rangle$
2. Hellmann-Feynman Forces:
3. Phonon Spectrum from Dynamical Matrix:

$$D_{\alpha\beta}(kk') = -\frac{1}{\sqrt{m(k)m(k')}} \frac{F_{\alpha}^{+}(k) - F_{\alpha}^{-}(k)}{u_{\beta}(k')}$$

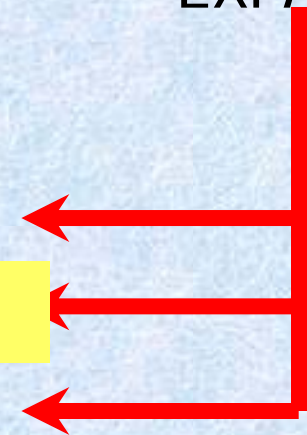
Density Functional Theory

Kohn and Sham showed that it is possible to introduce an effective one-electron wavefunctions, $\{\psi_i(\mathbf{r})\}$, which give rise to a set of self-consistent single-electron equations:

$$\left[-\frac{1}{2} \nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \Psi_i(\mathbf{r}) = \varepsilon_i \Psi_i(\mathbf{r}),$$

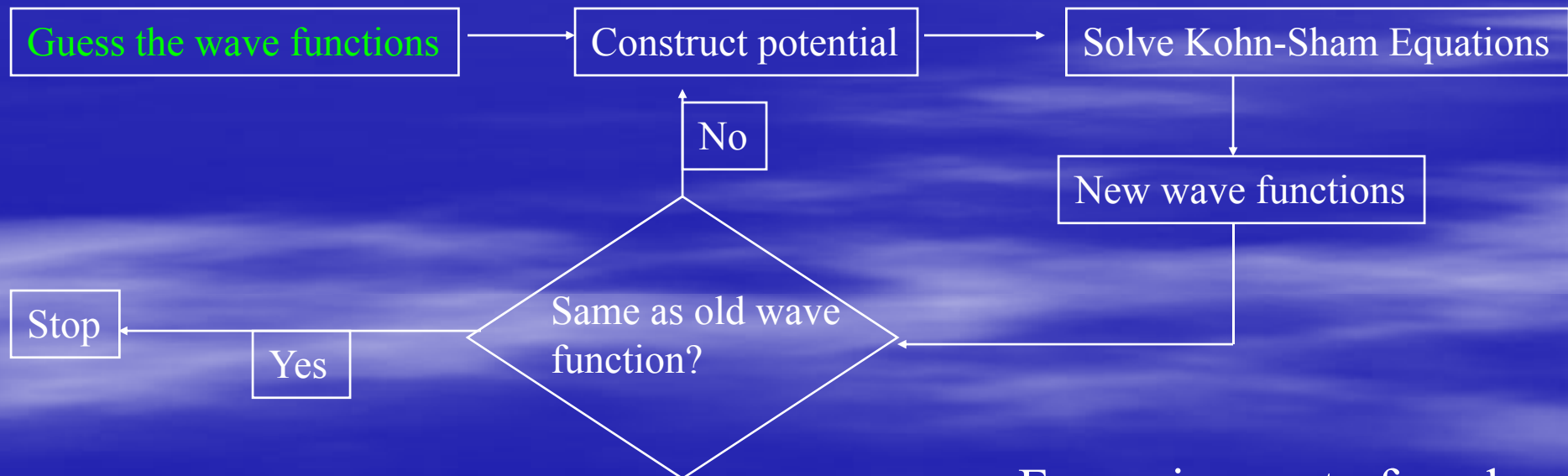
- Gaussians
- Numerical atomic orbitals
- Planewaves

EXPAND



Calculating the Wave Function

- DFT (and other methods) iterate to self-consistency



For a given set of nuclear positions

Calculating the Wave Function

- DFT (and other methods) iterate to self-consistency

Guess the wave functions

$$H\Psi_{nk} = \epsilon_{nk} \Psi_{nk},$$

$$\text{where } H = K + V_{ne}(r) + V_{ee}(r) + V_{xc}(r)$$

and

$$K = -\frac{\hbar^2}{2m} \nabla^2,$$

$$V_{ne}(r) = -e^2 \sum_a \frac{Z_a}{|r - R_a|},$$

$$V_{ee}(r) = -e^2 \int \frac{\rho(r')}{|r - r'|} d^3r',$$

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho},$$

$$\rho(r) = \sum_{nk} f_{nk} |\Psi_{nk}(r)|^2,$$

Solve Kohn-Sham Equations

new wave functions

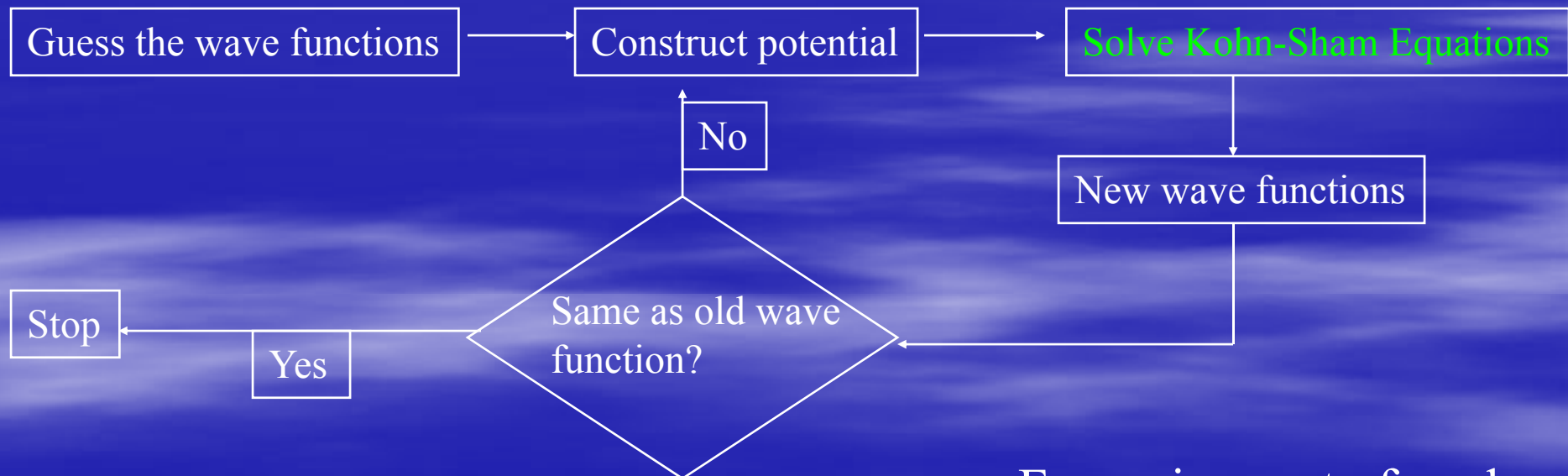
given set of nuclear positions

Stop

Yes

Calculating the Wave Function

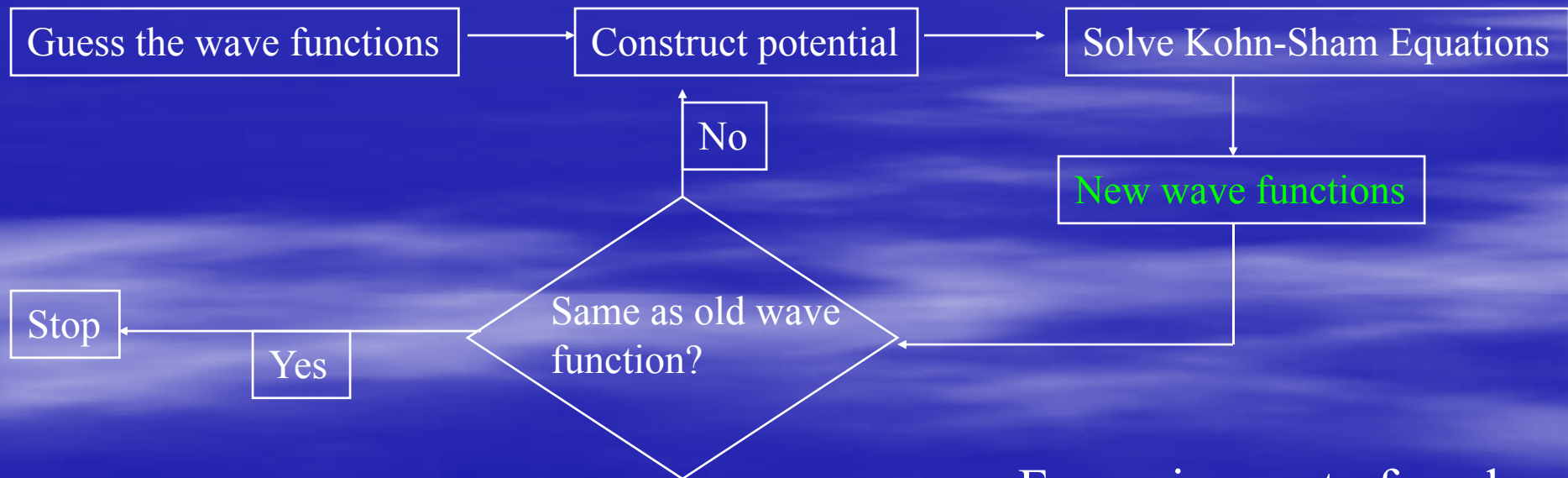
- DFT (and other methods) iterate to self-consistency



For a given set of nuclear positions

Calculating the Wave Function

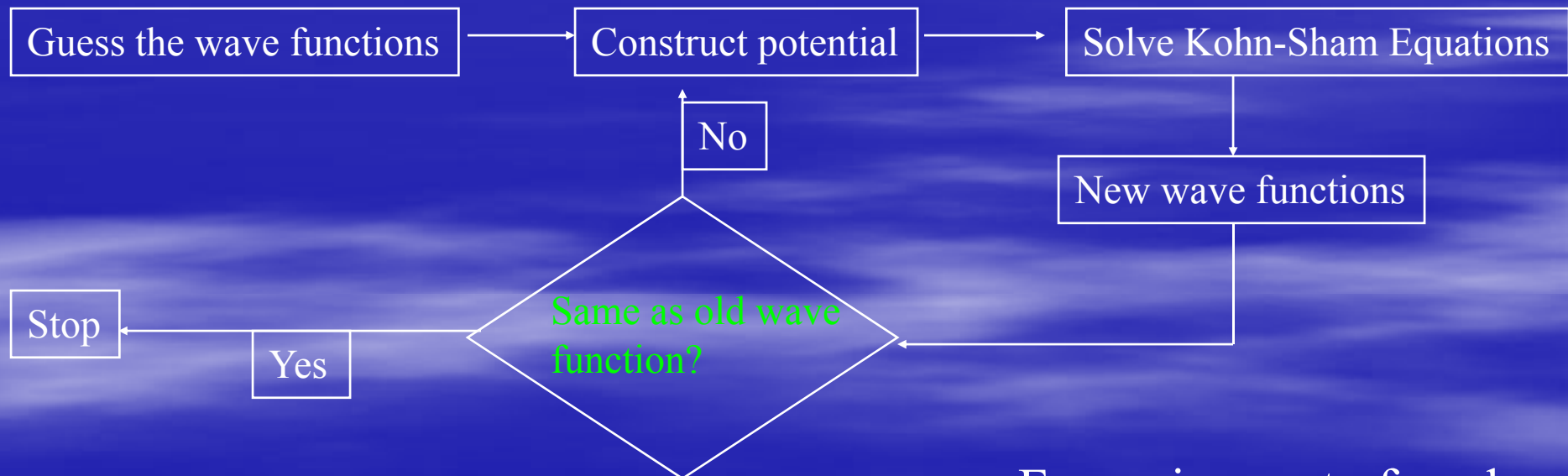
- DFT (and other methods) iterate to self-consistency



For a given set of nuclear positions

Calculating the Wave Function

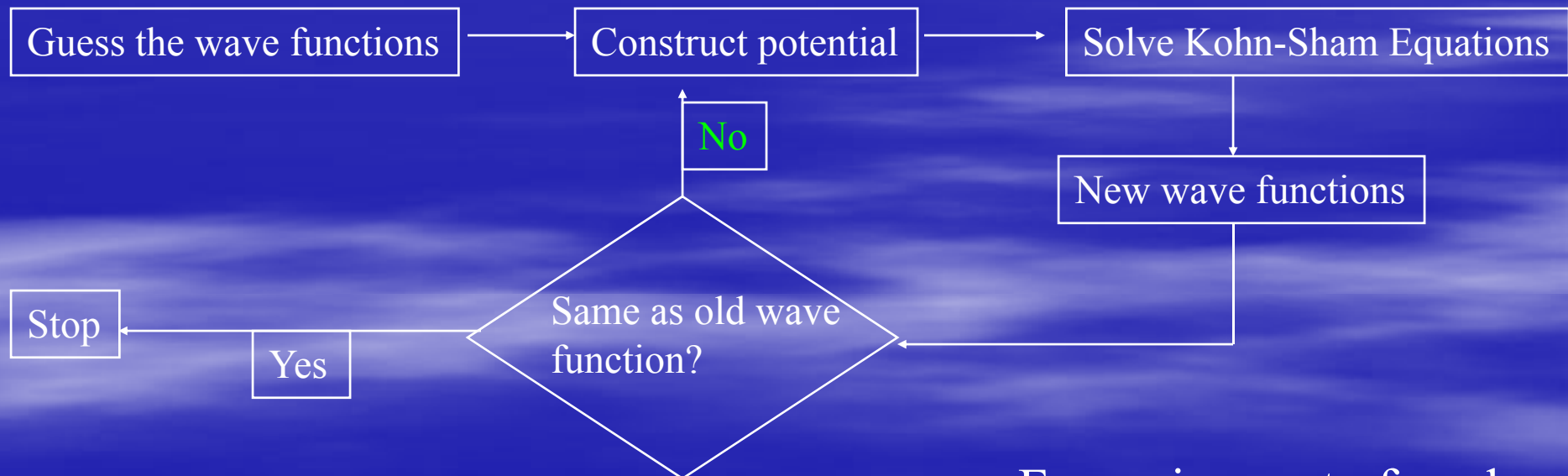
- DFT (and other methods) iterate to self-consistency



For a given set of nuclear positions

Calculating the Wave Function

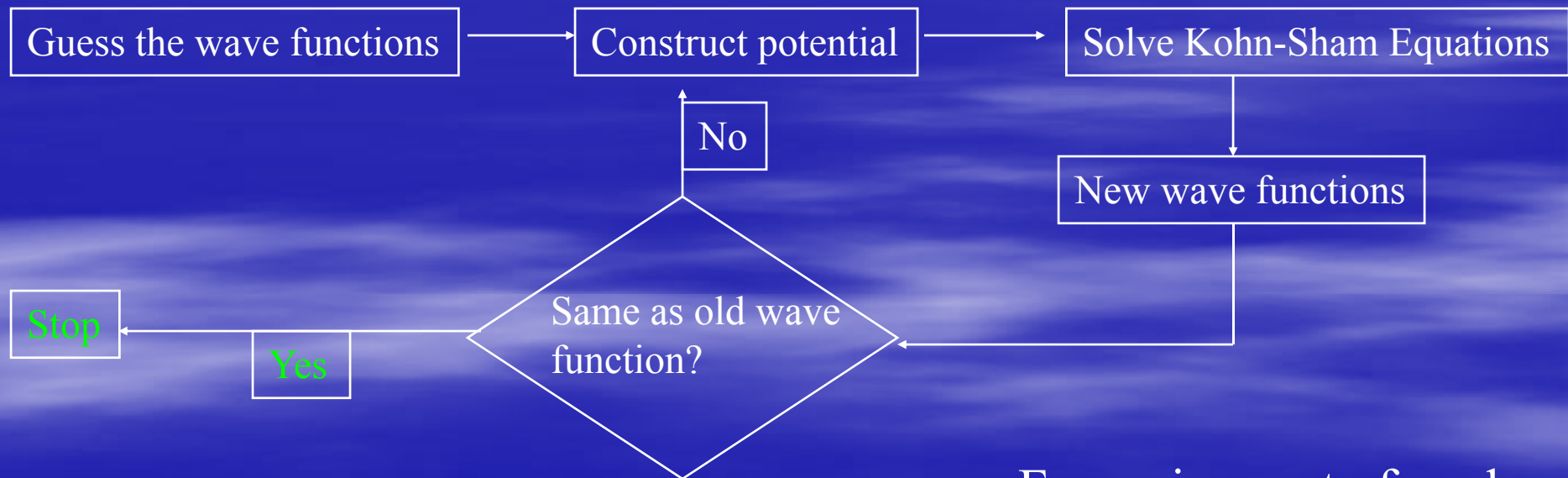
- DFT (and other methods) iterate to self-consistency



For a given set of nuclear positions

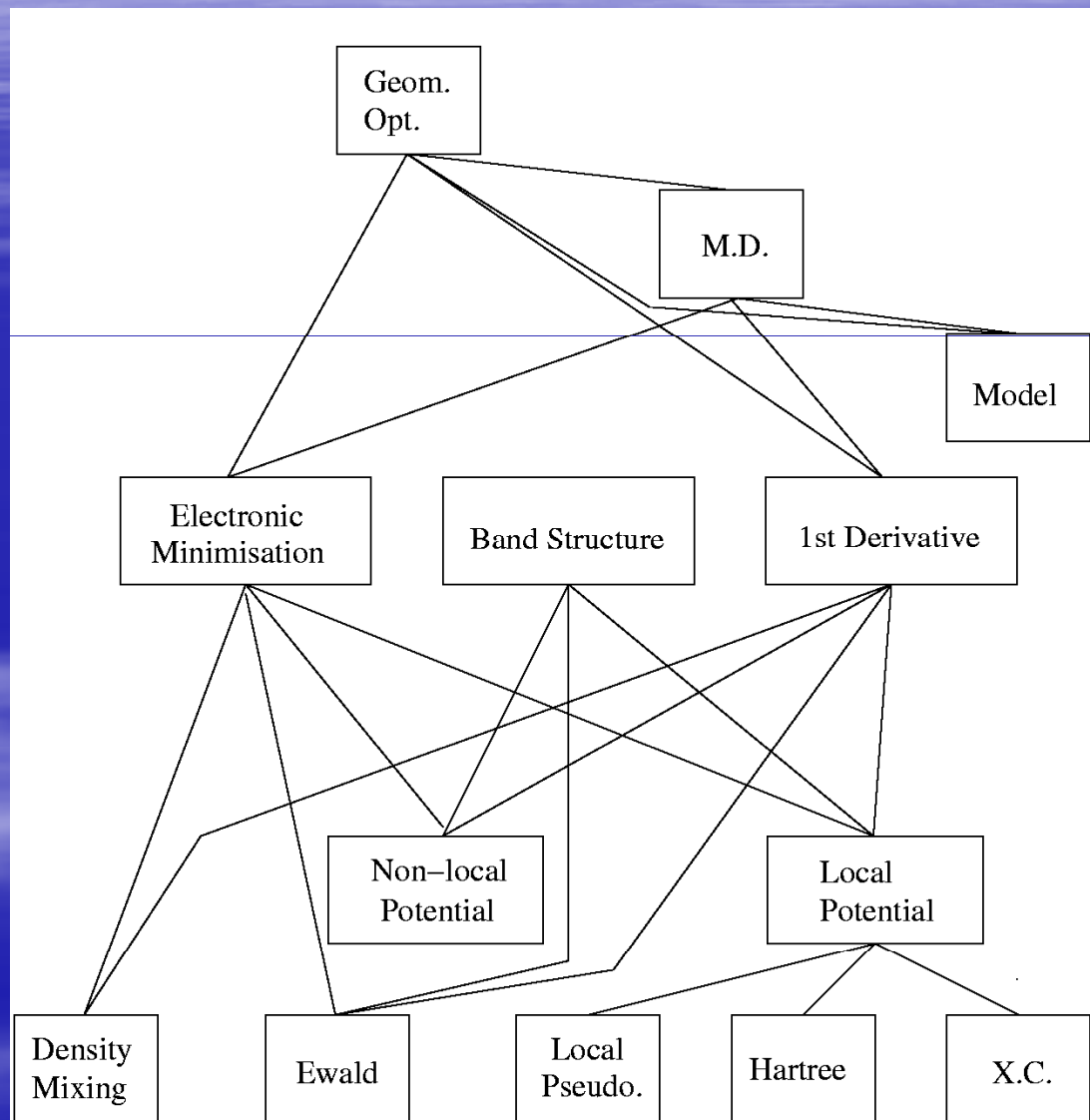
Calculating the Wave Function

- DFT (and other methods) iterate to self-consistency



For a given set of nuclear positions

Functional Modules



Overview

- Basis set – plane waves, the discerning choice!
- Grids, grids everywhere...
- Unit cells – when is a crystal not a crystal...?
- K-points and symmetry

The Starting Point

- The object is to find the single particle solutions to the Kohn-Sham equation.

$$\left(\nabla^2 + V_{eff} \right) |\psi_i\rangle = \epsilon_i |\psi_i\rangle$$

- The single particle orbitals (bands) can be represented in any complete basis set.

Basis Sets – Some Choices

- Linear combination of atomic orbitals (LCAO)
 - STO-xG
 - 6-31G
 - 6-311G*
 - 6-311G⁺⁺
- Real space grid
- Wavelets
- **Plane Waves**

VASP

Vienna Ab-initio Simulation
Package

<http://cms.mpi.univie.ac.at/vasp/>

VASP

- Implementing *ab initio* quantum mechanical molecular dynamics.

Input files

POSCAR
POTCAR
KPOINTS
INCAR

Output files

OUTCAR
OSZICAR
CONTCAR
CHGCAR
WAVECAR
EIGENVAL
PROCAR
XDATCAR
LOCPOT
DOSCAR

VASP input files

- **POSCAR:** Positions of ions
Bravais lattice
Periodic boundary conditions
- **POTCAR:** Pseudopotentials from VASP
- **KPOINTS:** Would be used for parallelization
- **INCAR:** Different parameters for different properties

POSCAR

```

Ge Bulk
5.6435
0.00000000 0.50000000 0.50000000
0.50000000 0.00000000 0.50000000
0.50000000 0.50000000 0.00000000
2
Direct
0.0000000000000000 0.0000000000000000 0.0000000000000000
0.2500000000000000 0.2500000000000000 0.2500000000000000
    
```

(Å)

$\vec{a}_1, \vec{a}_2, \vec{a}_3$

n atom

```

GaN-bulk
5.602
0.000000000 0.500000000 0.500000000
0.500000000 0.000000000 0.500000000
0.500000000 0.500000000 0.000000000
2 2
Selective dynamics
Direct
0.33333333 0.66666667 0.000 T T T
0.66666667 0.33333333 0.500 T F T
0.33333333 0.66666667 0.385 T T F
0.66666667 0.33333333 0.885 F F T
    
```

n_1, n_2

The ordering must be consistent with the POTCAR

POSCAR

pt 7 layer slab 15A vacuum

1.0000

2.812397014	0.0000000000	0.0000000000
-1.406198507	2.435607260	0.0000000000
0.0000000000	0.0000000000	28.7779000000

7

Selective dynamics

Cartesian

0.0000000000	1.623738173	0.0000000000	F F F
1.406198507	0.811869087	2.296312546	F F F
0.0000000000	0.0000000000	4.592625092	F F F
0.0000000000	1.623738173	6.888937638	T T T
1.406198507	0.811869087	9.185250185	T T T
0.0000000000	0.0000000000	11.481562731	T T T
0.0000000000	1.623738173	13.777875277	T T T

POTCAR

Choosing POTCAR file

LDA

GGA

PAW_LDA

PAW_GGA

PAW_PBE(VASP4.5)

Check following line in POTCAR

LEXCH= CA or 91

GGA=

LPAW= T

POTCAR

PAW_PBE Pt 05Jan2001

10.0000000000000000

parameters from PSCTR are:

VRHFIN =Pt: s1d9

LEXCH = PE

EATOM = 729.1171 eV, 53.5886 Ry

TITEL = PAW_PBE Pt 05Jan2001

LULTRA = F use ultrasoft PP ?

IUNSCR = 1 unscreen: 0-lin 1-nonlin 2-no

RPACOR = 2.330 partial core radius

POMASS = 195.080; ZVAL = 10.000 mass and valenz

RCORE = 2.500 outmost cutoff radius

RWIGS = 2.750; RWIGS = 1.455 wigner-seitz radius (au A)

ENMAX = 230.283; ENMIN = 172.712 eV

RCLOC = 1.896 cutoff for local pot

LCOR = T correct aug charges

LPAW = T paw PP

EAUG = 358.966

SYSTEM = Pt slab

Startparameter for this Run:

NWRITE = 2; LPETIM=F write-flag & timer

ISTART = 0 job : 0-new 1-cont 2-samecut

Electronic Relaxation 1

ENCUT = 400.0 eV(29.4 Ryd)

NELM = 80 number of electronic steps between two ionic steps

EDIFF = 1E-05 stopping-criterion for ELM

LPLANE = T

NPAR = 4

Ionic Relaxation

NSW = 100 number of steps for IOM

NBLOCK = 1 ; KBLOCK = 1

IBRION = 2 ionic relax: 0-MD 1-quasi-New 2-CG

ISIF = 2 stress and relaxation

ISYM = 1

IWAVPR = 1 prediction: 0-non 1-charg 2-wave 3-comb

LCORR = T Harris-correction to forces

Mass of Ions in am

ISMEAR = 1

SIGMA=0.08

Electronic Relaxation 2

IALGO = 38 algorithm

LDIAG = T sub-space diagonalisation

LREAL = F real-space projection

LELF = T

NBANDS = 52

INCAR

Plane Waves

Represent the orbital in Fourier space

$$\psi(\mathbf{r}) = \int \tilde{\psi}(\mathbf{g}) e^{i\mathbf{g}\cdot\mathbf{r}} d^3\mathbf{g}$$

For a periodic system (Bloch's Theorem)

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

Where the \mathbf{G} s are reciprocal lattice vectors and \mathbf{k} is a symmetry label in the 1st Brillouin zone.

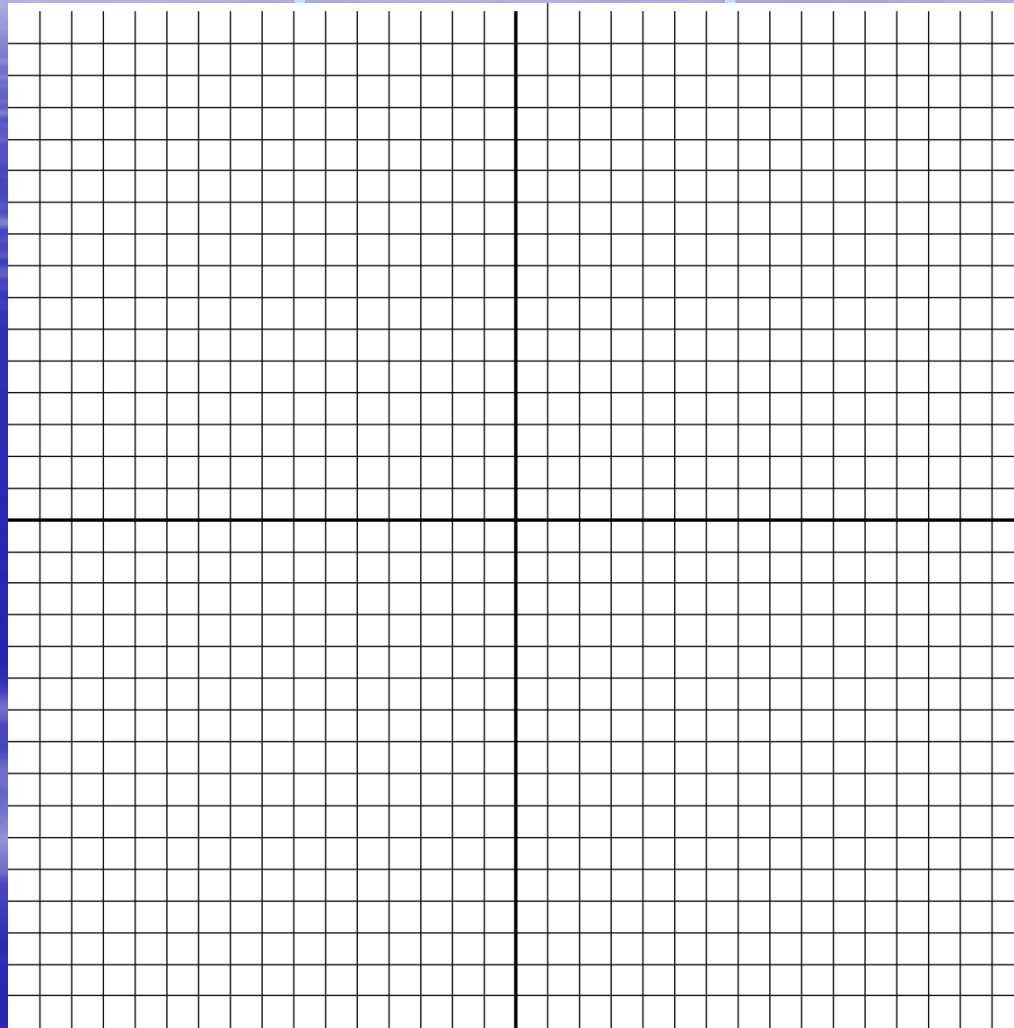
Why Plane Waves?

- Systematic convergence with respect to single parameter E_{cut}
- Non-local. Cover all space equally
 - Cheap forces (No Pulay term)
 - No basis-set superposition error
- Numerically efficient
 - Use FFTs to transform between real and reciprocal space
 - Calculation scales as $N_{\text{PW}} \ln N_{\text{PW}}$
- The obvious choice for periodic and works well for aperiodic systems

Disadvantages of Plane Waves

- Need lots of basis functions/atom
 - ‘Waste’ basis functions in vacuum regions
 - **But**, rapidly becomes more efficient than localised basis set due to better scaling
- Need pseudopotentials for tractability
 - To represent core features would require **huge** cut-off energy
 - **But**, Core features can be reconstructed
- Does not encode ‘local’ properties
 - **But**, can overcome this using projection analysis

Reciprocal Space



The Cut-off Energy

Limit the number of plane wave components to those such that

$$\frac{(\mathbf{G} + \mathbf{k})^2}{2} \leq E_{cut}$$

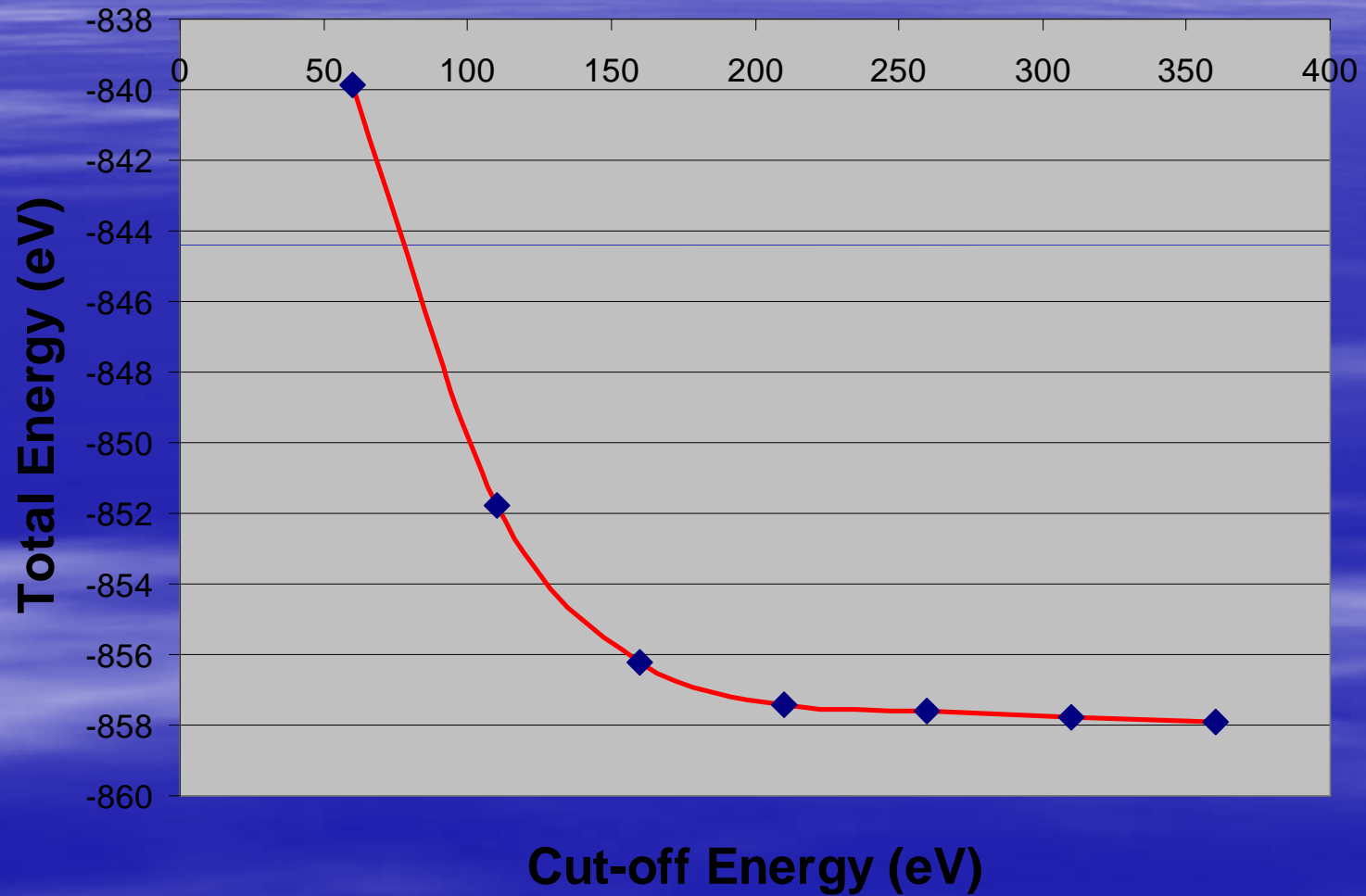
This defines a length scale

$$\lambda = \frac{\pi}{\sqrt{E_{cut}}}$$

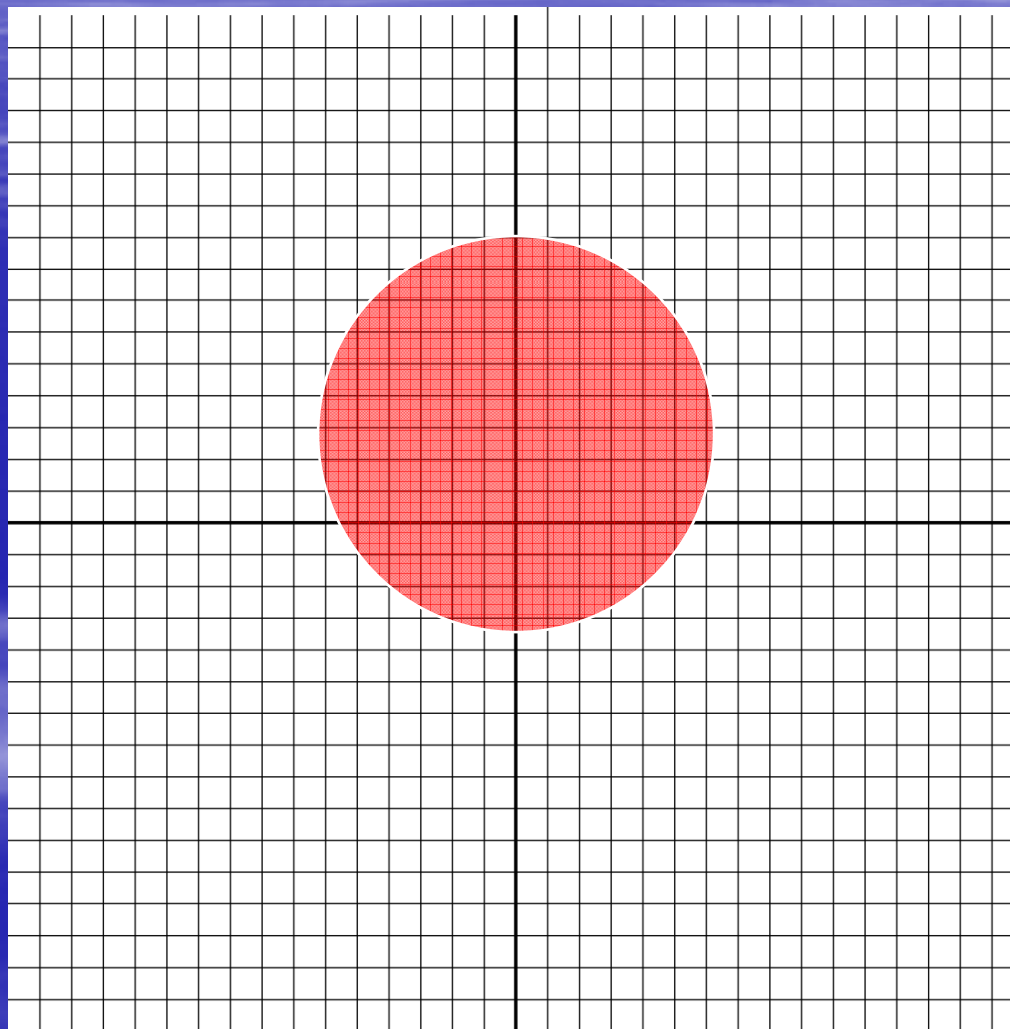
How to Choose a Cut-off Energy

- The minimum length scale depends on the elements in the system
- Variational principle \Rightarrow energy monotonically decreases to ground state energy as E_{cut} increases
- Converge required property with respect to cut-off energy

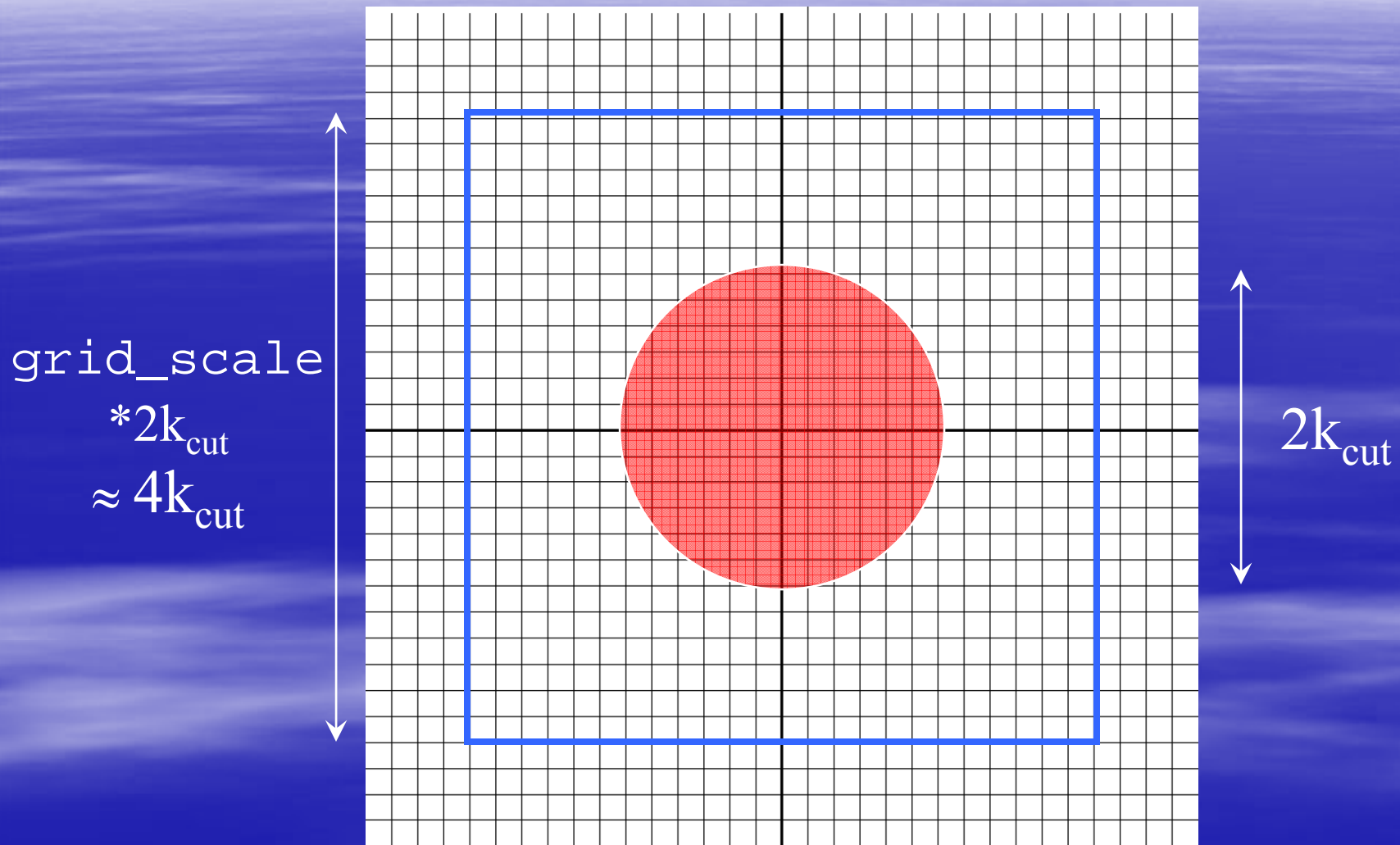
Convergence with E_{cut} (Si8)



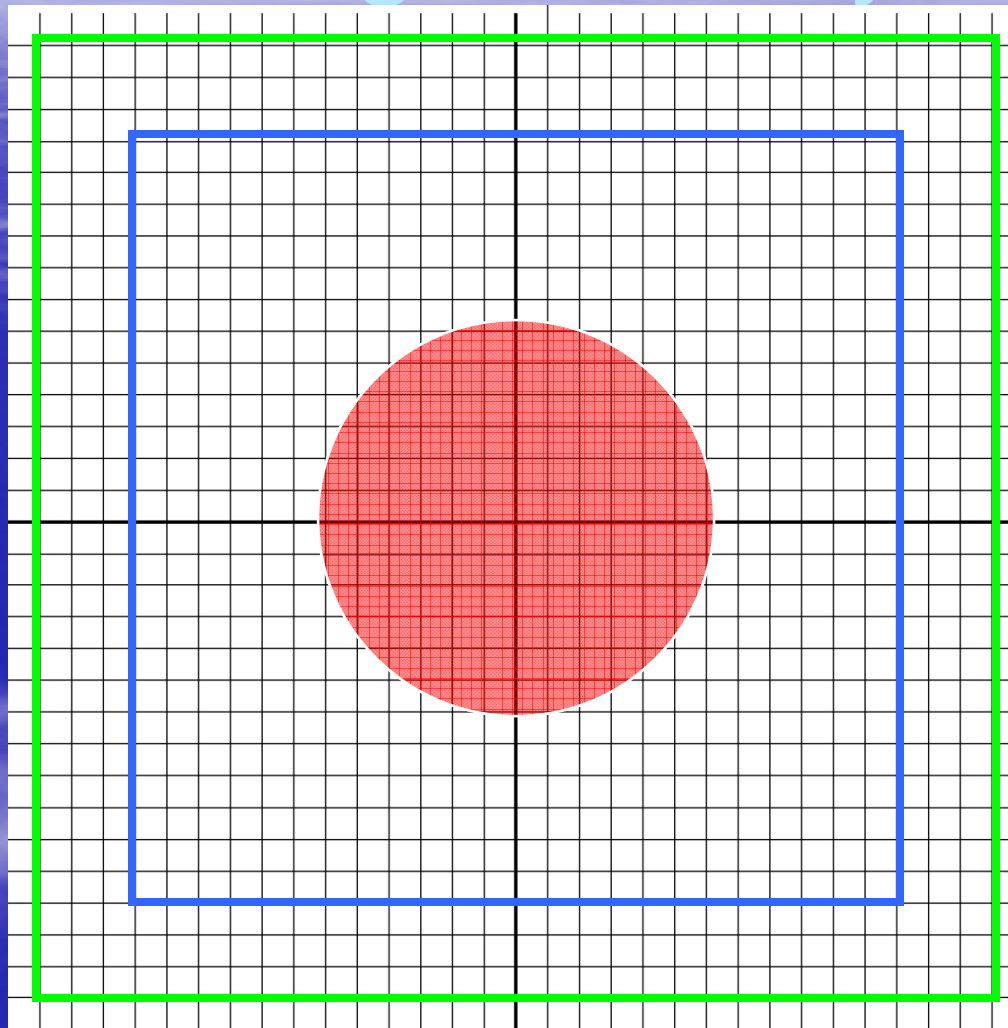
The Reciprocal Space Sphere



The FFT Grid



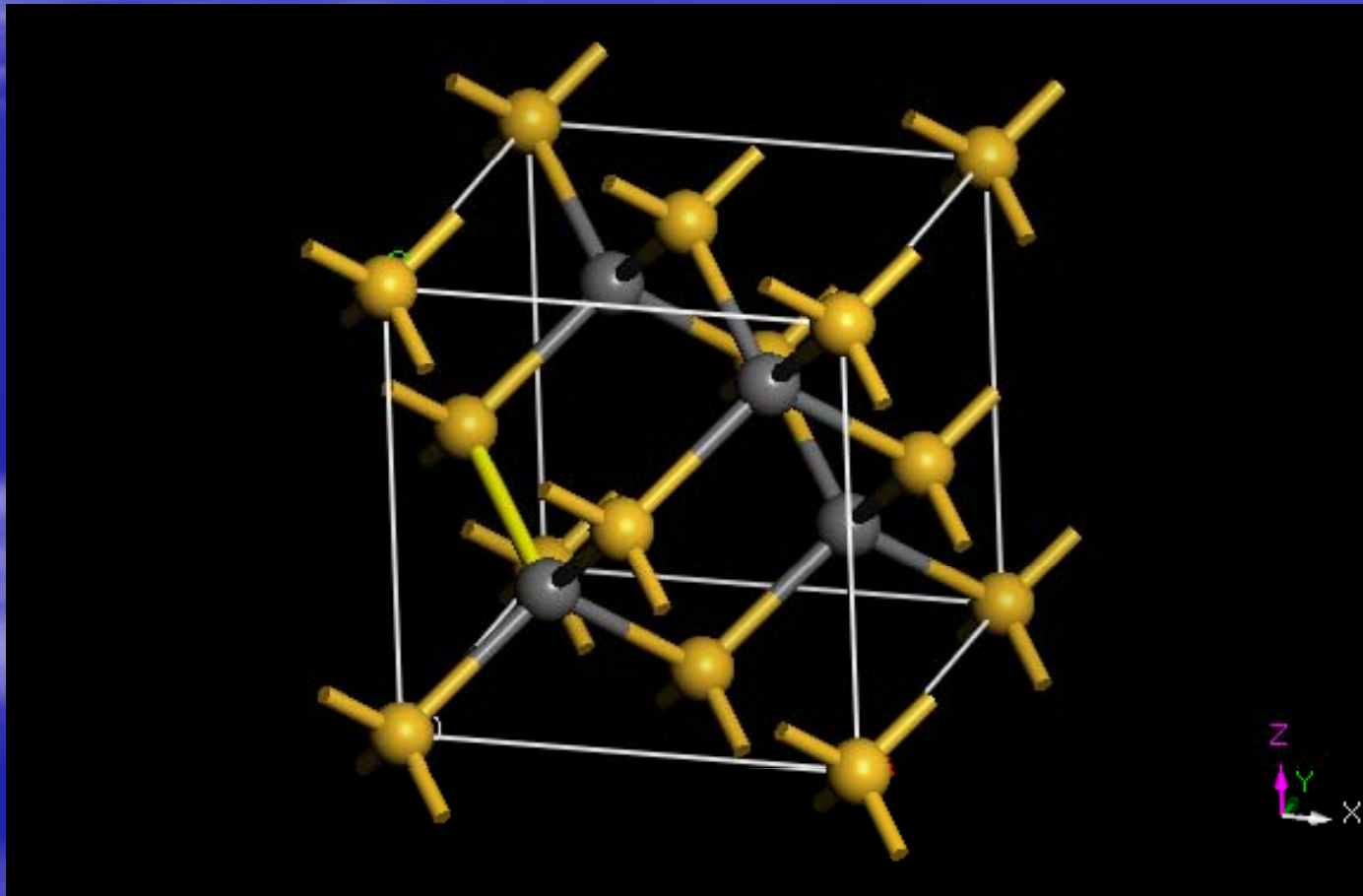
The Charge Density Grid



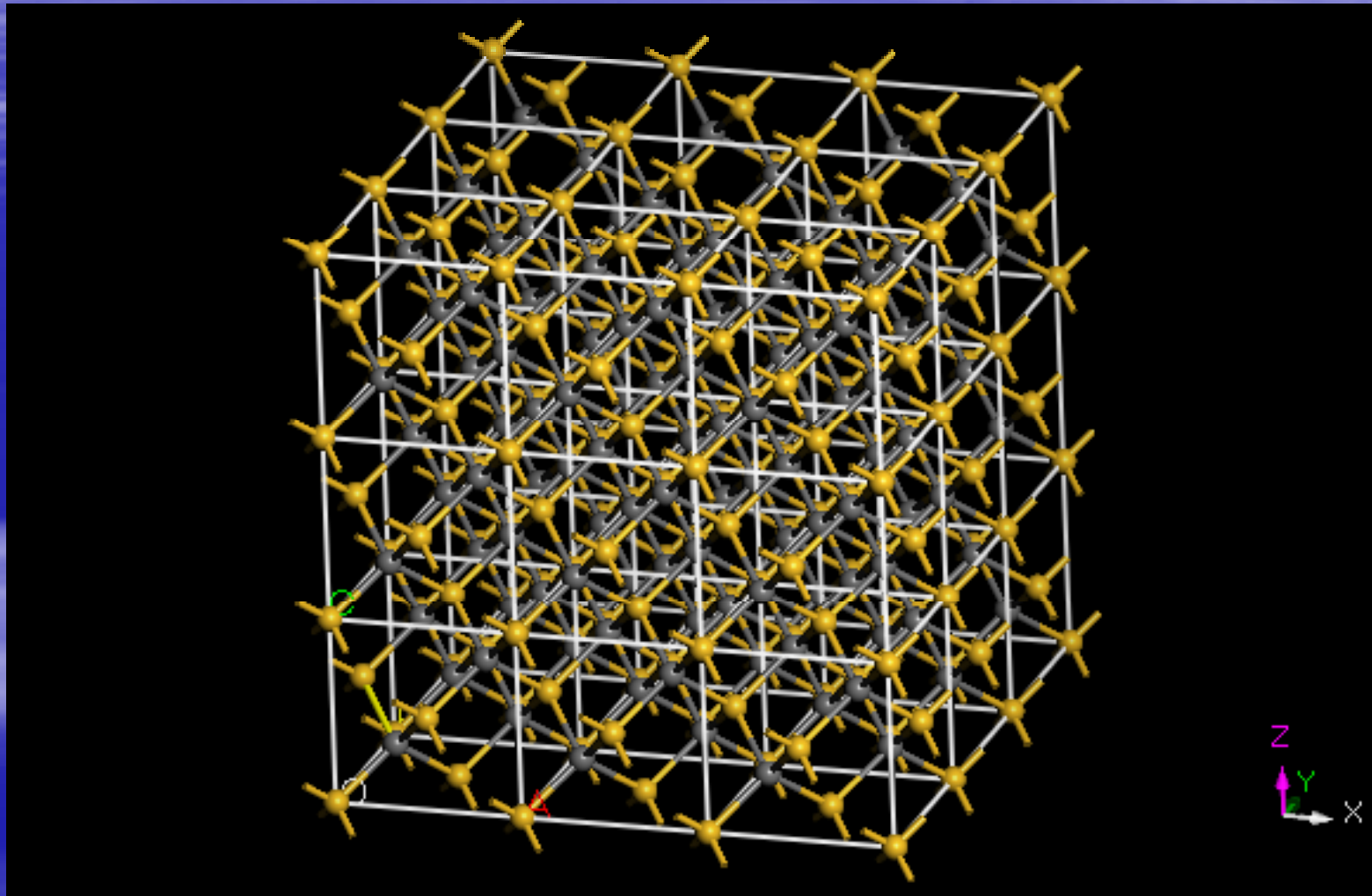
$2 * \text{fine_gmax}$

Periodic Systems

SiC beta 8-atom unit cell



SiC beta Crystal



KPOINTS

Automatic mesh

0

Monkhorst Pack

15. 15. 1.

0. 0. 0.

Now, Where Were We...?

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

For all $\frac{(\mathbf{G} + \mathbf{k})^2}{2} \leq E_{cut}$

And \mathbf{k} within the first Brillouin zone.

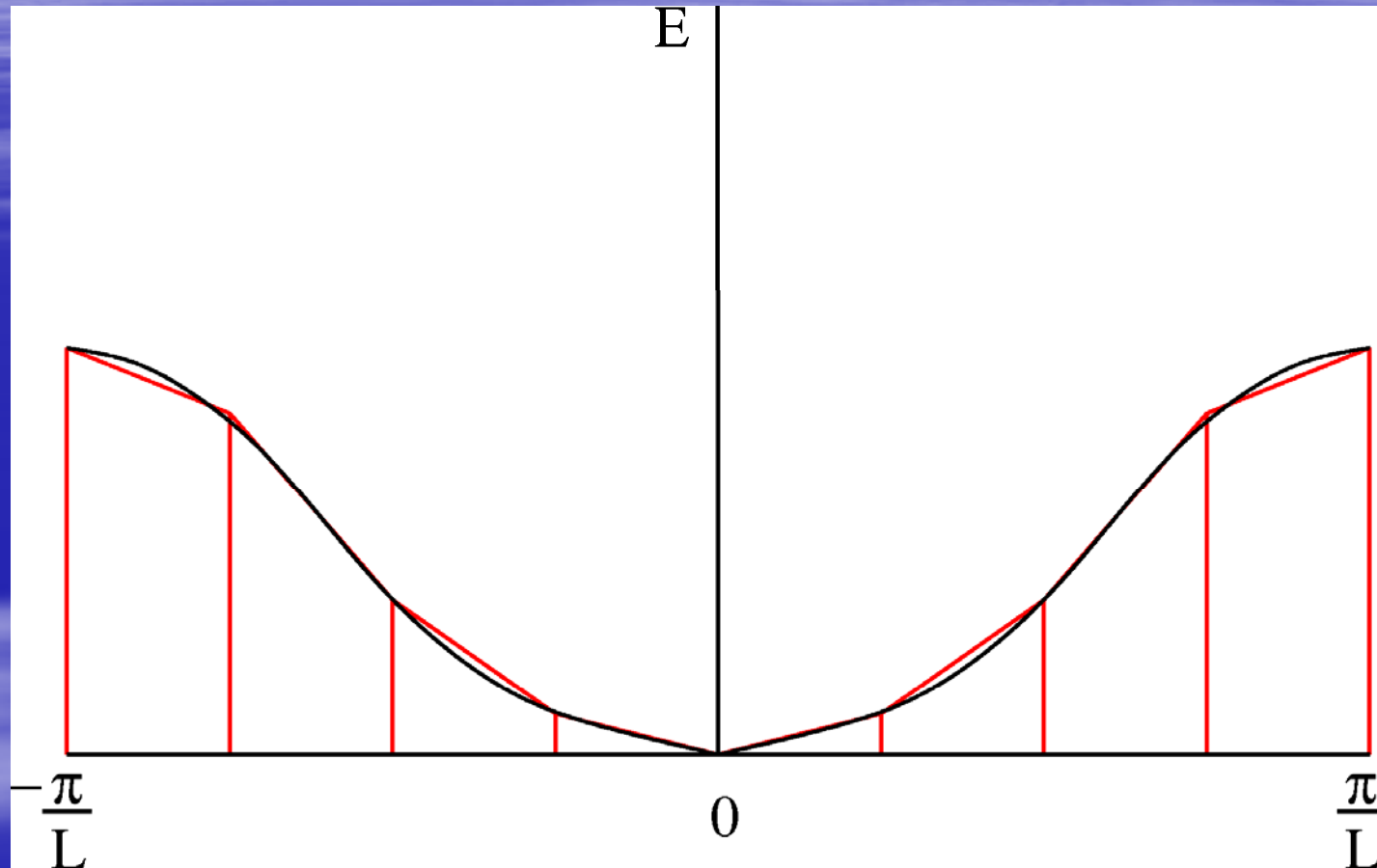
Integrating over the 1st Brillouin Zone

Observables are calculated as an integral over all k-points within the 1st Brillouin zone. For example:

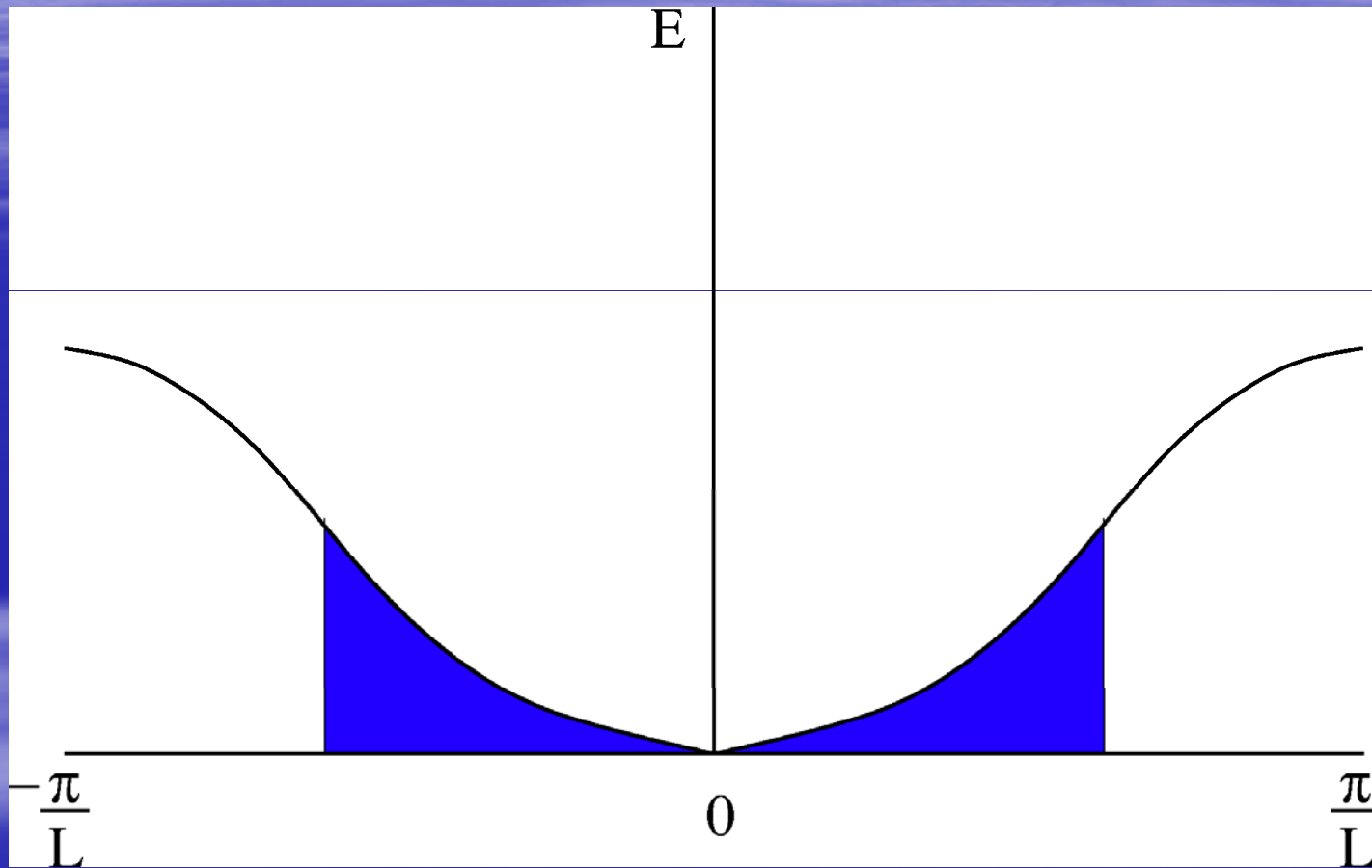
$$E_{tot} = \frac{1}{V_{BZ}} \int_{1stBZ} E(\mathbf{k}) d^3\mathbf{k}$$

$$n(r) = \frac{1}{V_{BZ}} \int_{1stBZ} n_{\mathbf{k}}(\mathbf{r}) d^3\mathbf{k}$$

Example Integration



K-points and Metals



Defining the k-point Grid

- Standard method is the Monkhorst-Pack grid. A regular grid in k-space.

Monkhorst, Pack. Phys. Rev. B 13 p. 5188 (1997)

- The symmetry of the cell may be used to reduce the number of k-points which are needed.
- Shifting the origin of the grid may improve convergence with k-points.

Moreno, Soler. Phys. Rev. B 45 p. 13891 (1992)

Probert. Phys. Rev. B

Monkhorst-Pack Grids for SC Cell

q	Number of Points (full grid)	Number of Points (Symmetrised)	R^2	Offset	Number of Points (Symmetrised Offset)	R^2 (Offset)
1	1	1	1.0	1/4,1/4,1/4	1	4.0
2	8	1	4.0	1/8,1/8,1/8	3	16.0
3	27	4	9.0	1/4,0,1/2	8	18.0
4	64	4	16.0	1/16,1/16,1/16	20	64.0

Monkhorst-Pack Grids for BCC Cell

q	Number of Points (full grid)	Number of Points (Symmetrised)	R^2	Offset	Number of Points (Symmetrised Offset)	R^2 (Offset)
1	1	1	0.75	0,1/4,1/2	1	2.0
2	8	2	3.0	1/4,1/4,1/4	2	4.0
3	27	4	6.75	1/2,1/2,1/2	5	9.0
4	64	6	12.0	1/8,1/8,1/8	8	16.0

Monkhorst-Pack Grids for FCC Cell

q	Number of Points (full grid)	Number of Points (Symmetrised)	R ²	Offset	Number of Points (Symmetrised Offset)	R ² (Offset)
1	1	1	0.5	0,1/2,1/2	1	1.0
2	8	2	4.0	0,0,0	2	4.0
3	27	4	4.5	1/2,1/2,1/2	6	9.0
4	64	10	16.0	0,0,0	10	16.0

Setting KPOINTS file

k-points for bulk	comment
0	automatic generation (= 0)
Monkhorst	Monkhorst or Gammapoint (centered)
11 11 11	mesh parameter
0 0 0	shift

“typical” values (never trust them!)

Metals (9x9x9)/atom

Semiconductors (4x4x4)/atom

For molecules or atoms (large supercells)

use 1 x 1 x 1 (Γ)

For surfaces (one long direction)

use 2-D Brillouin-zone, $n_{k1} \times n_{k2} \times 1$

VASP output files

- **OUTCAR:** Complete information of the simulation
 - Number of irreducible points
 - Final position of ions and forces
 - Time take to complete simulation
- **OSZICAR:** It contains the information about free energy (E_0) and about convergence speed.
- **CONTCAR:** It contains the positions of ion at the final ionic step in relaxations.

SYSTEM = Pt slab

Startparameter for this Run:

NWRITE = 2; LPETIM=F write-flag & timer

ISTART = 0 job : 0-new 1-cont 2-samecut

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LDIAG = T sub-space diagonalisation

LREAL = F real-space projection

LELF = T

NBANDS = 52

INCAR

GGA tag in INCAR:

(default is determined by POTCAR)

PB Perdew-Becke

PW Perdew-Wang 86

LM Langreth-Mehl-Hu

91 Perdew-Wang 91

PE Perdew-Burke-Ernzerhof (PBE)

RP revised PBE

If doing spin polarized PW91 calculations :

ISPIN = 2

MAGMON = (initial magnetic moment for each atom)

GGA = 91

VOSKOWN = 1

S.H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58, 1200(1980)

ALGO-tag

determine how the wavefunctions are optimized

Normal	IALGO = 38(blocked Davidson algorithm)
Very_Fast	IALGO = 48(RMM-DIIS)
Fast	IALGO = 38 for 5 initial steps than 48 after ions are moved: 38 for 1st step than 48

- ⊙ VASP4.5 does not support IALGO = 8 (preconditioned conjugated gradient) for copyright reasons
- ⊙ RMM-DIIS is 1.5 to 2 times faster, but Davidson is more stable.
- ⊙ Eigenstates can be missed using RMM-DIIS for large system.
- ⊙ If the Davidson algorithm is used for the first steps, there is practically no danger of missing eigenstates.

Searching the optimal lattice parameter

(1) Automatic batch job

INCAR:

ISTART = 0

ICHARG = 2

initial charge-density from overlapping atoms

Sample unix bash script for volume scan

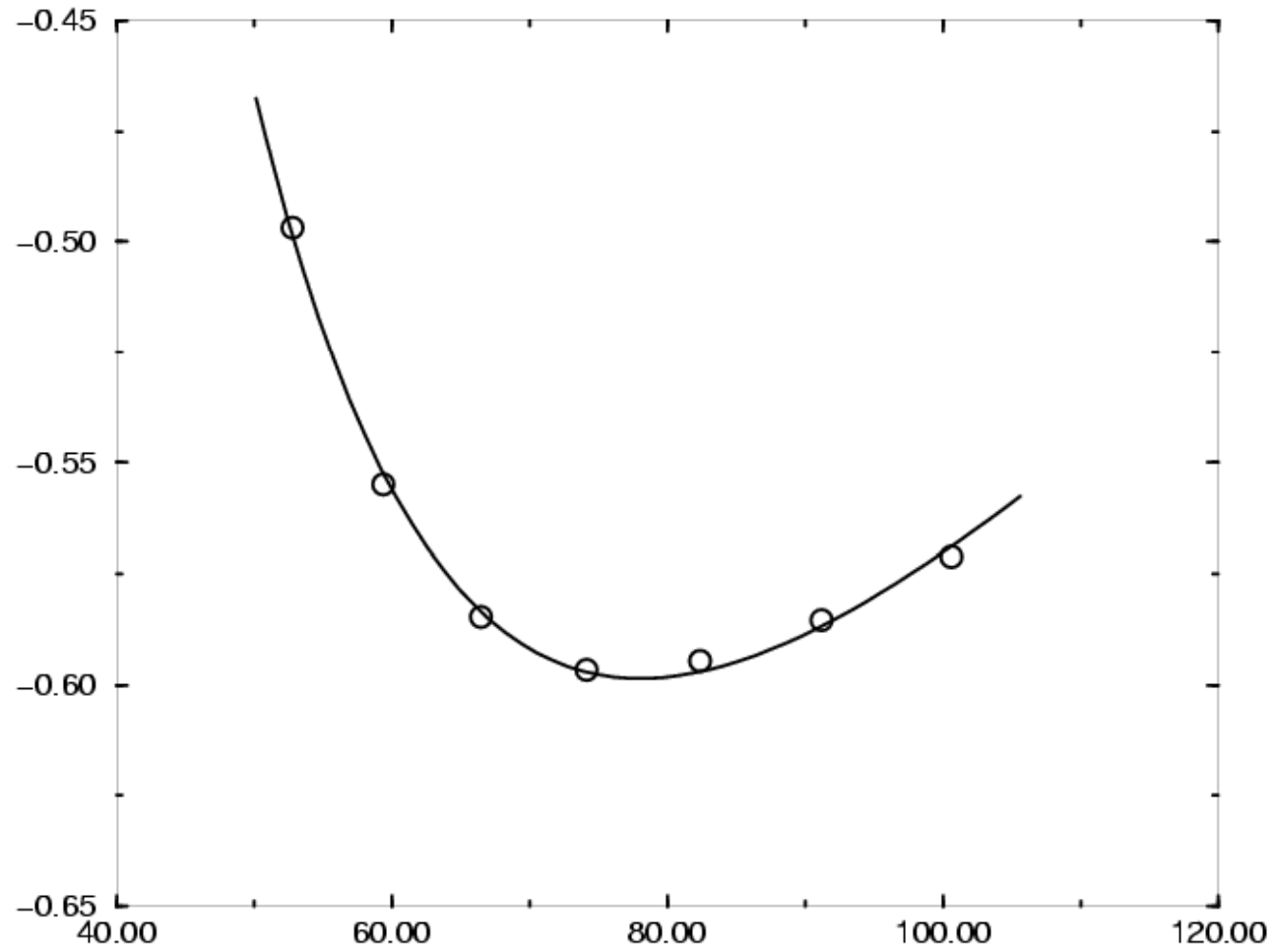
```
#!/bin/bash
for a in 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4
do
cat >POSCAR <<!
bcc Fe
$a
-0.5 0.5 0.5
0.5 -0.5 0.5
0.5 0.5 -0.5
1
direct
0.0 0.0 0.0
!
vasp
E=`tail -1 OSZICAR`
echo $a $E >> SUMMARY
done
```

Result of volume scan

2.3	1	F=	-.33734901E+01	E0=	-.33734901E+01	d	E	=0.000000E+00	mag	=0.111346E+00
2.4	1	F=	-.54258528E+01	E0=	-.54258528E+01	d	E	=0.000000E+00	mag	=0.713446E+00
2.5	1	F=	-.67487749E+01	E0=	-.67487749E+01	d	E	=0.000000E+00	mag	=0.136680E+01
2.6	1	F=	-.75334410E+01	E0=	-.75334410E+01	d	E	=0.000000E+00	mag	=0.169207E+01
2.7	1	F=	-.79469252E+01	E0=	-.79469252E+01	d	E	=0.000000E+00	mag	=0.193771E+01
2.8	1	F=	-.81030668E+01	E0=	-.81030668E+01	d	E	=0.000000E+00	mag	=0.211534E+01
2.9	1	F=	-.80790747E+01	E0=	-.80790747E+01	d	E	=0.000000E+00	mag	=0.226119E+01
3.0	1	F=	-.79505898E+01	E0=	-.79505898E+01	d	E	=0.000000E+00	mag	=0.253218E+01
3.1	1	F=	-.77562691E+01	E0=	-.77562691E+01	d	E	=0.000000E+00	mag	=0.264343E+01
3.2	1	F=	-.75101095E+01	E0=	-.75101095E+01	d	E	=0.000000E+00	mag	=0.274595E+01
3.3	1	F=	-.72343924E+01	E0=	-.72343924E+01	d	E	=0.000000E+00	mag	=0.283323E+01
3.4	1	F=	-.69416562E+01	E0=	-.69416562E+01	d	E	=0.000000E+00	mag	=0.290679E+01

Fe-bulk BCC

Volume vs. E



(2) Relaxing the structure

INCAR:

ISIF = 3

IBRION = 2

NSW = 40

PREC = high (VASP4.4)

ENMAX = 1.3*default value in POTCAR

EDIFF = 10E-5 (smaller than default value)

Ex.

diamond Si

from volume scan $a = 5.488 \text{ \AA}$

from structure relaxation $a = 5.465 \text{ \AA}$

(difference is due to the Pulay stress)

BCC Fe

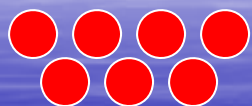
from volume scan $a = 2.849 \text{ \AA}$

from structure relaxation $a = 2.827 \text{ \AA}$

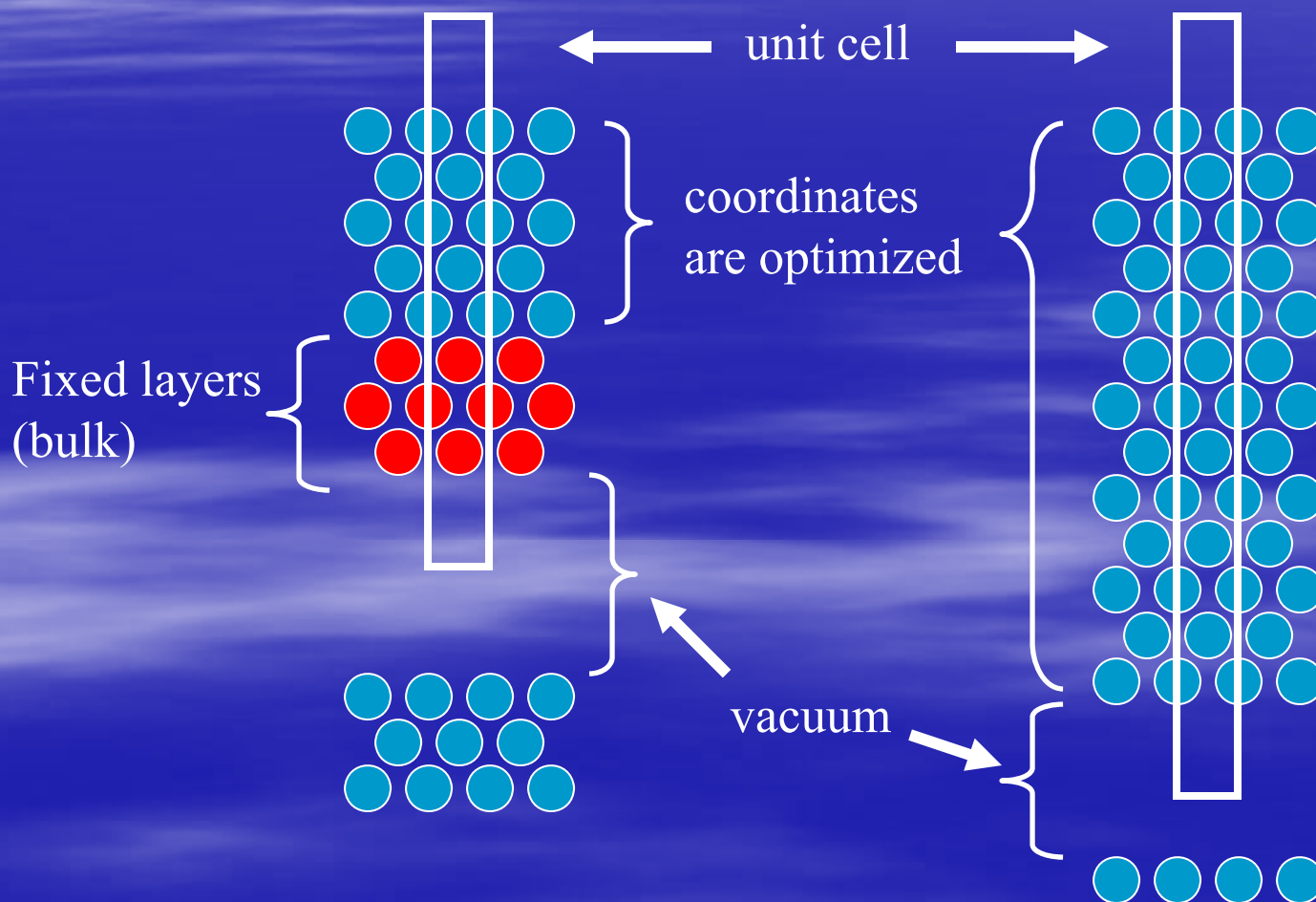
from FLAPW (WIEN97, volume scan) $a = 2.832 \text{ \AA}$

Building surfaces

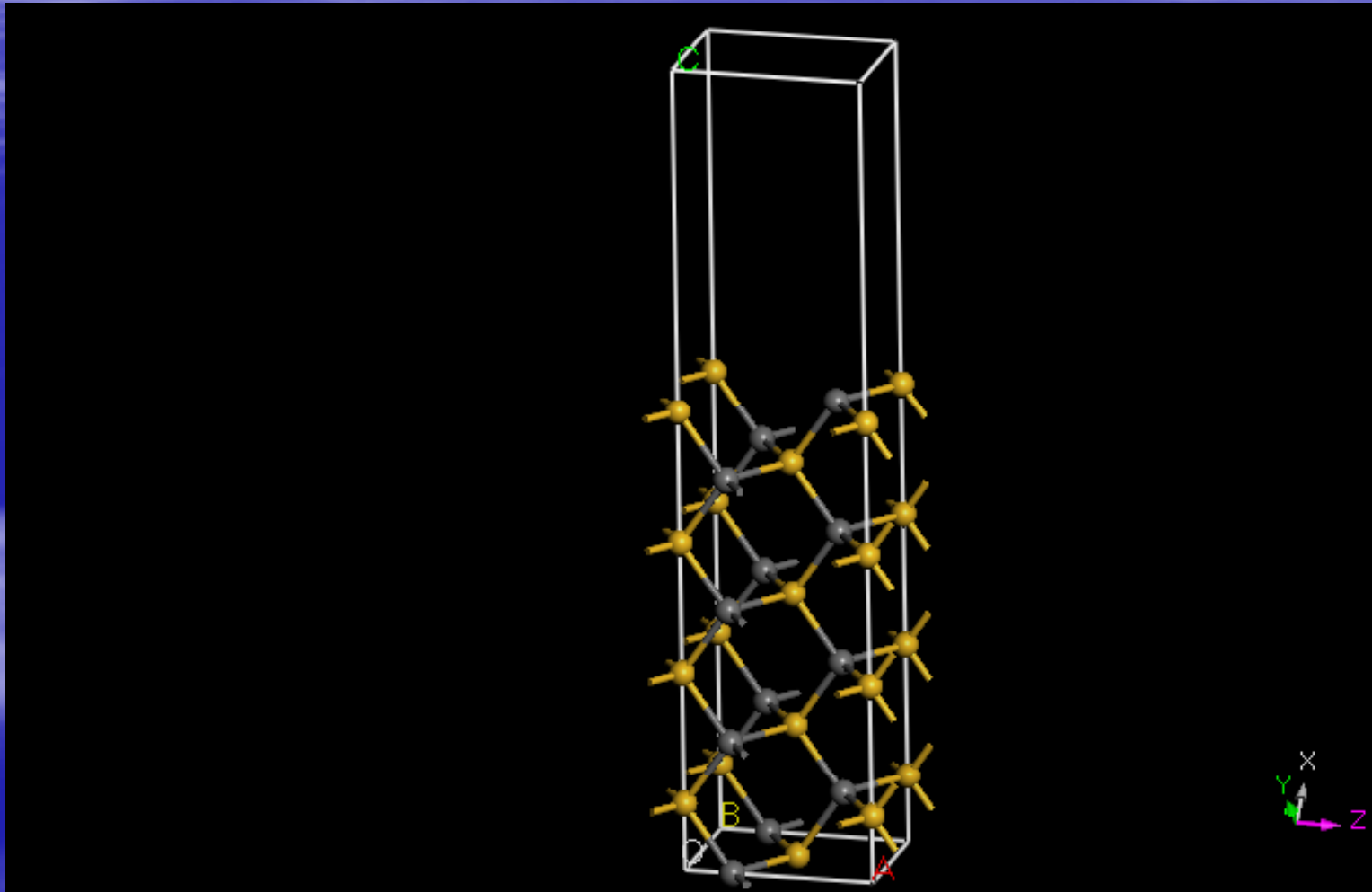
(1) asymmetric setup



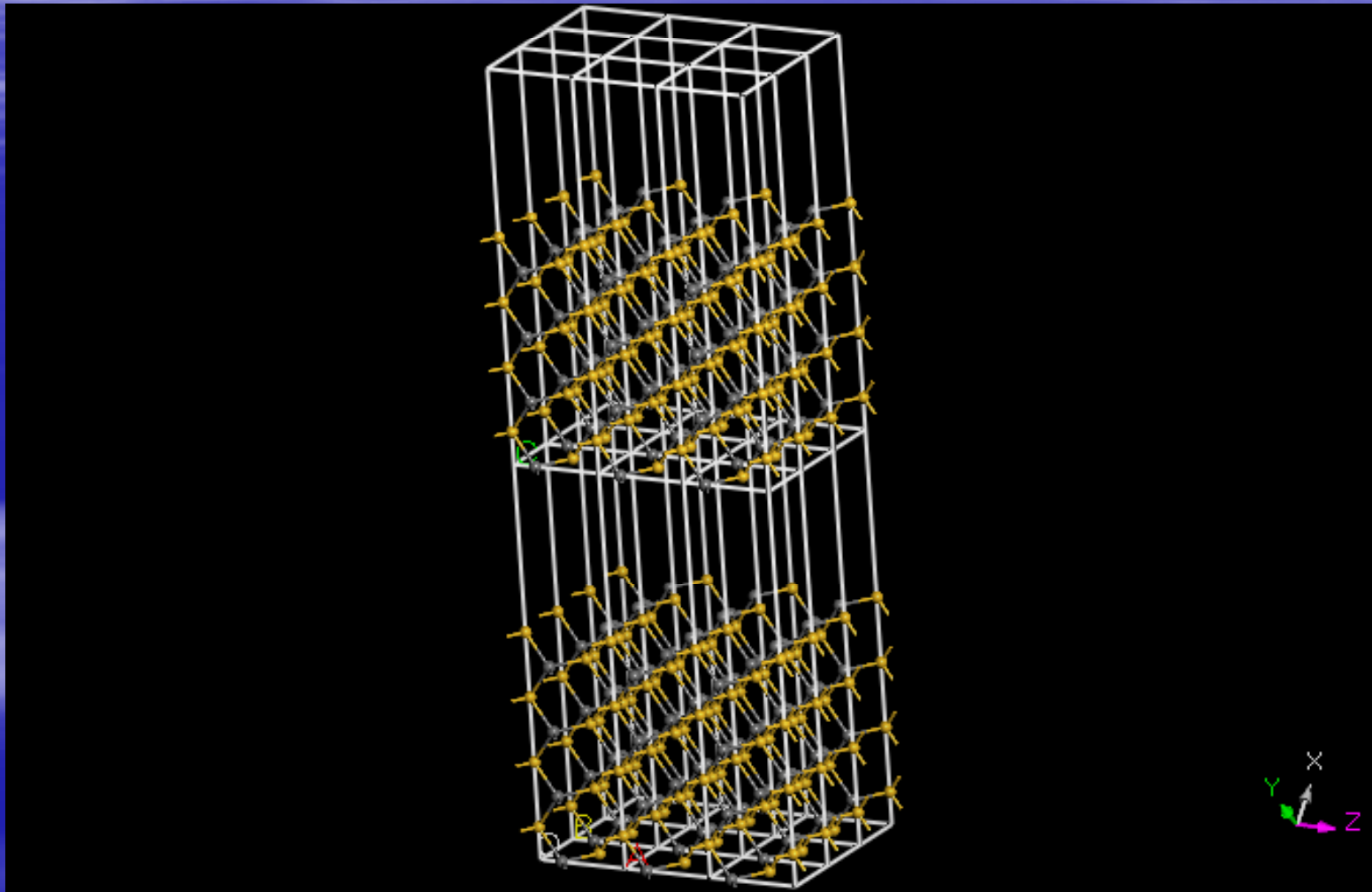
(2) symmetric setup



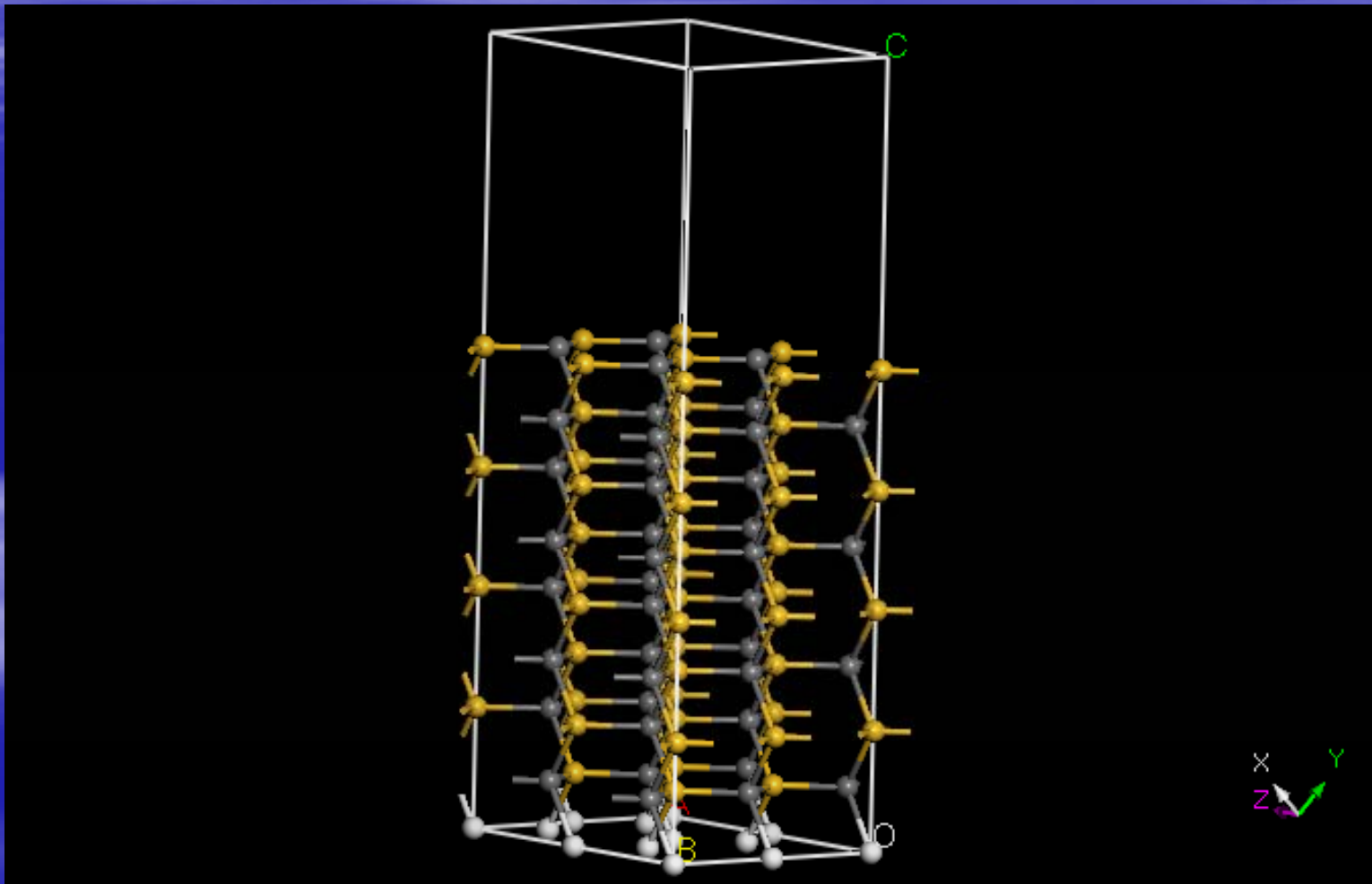
Surfaces – SiC (110)



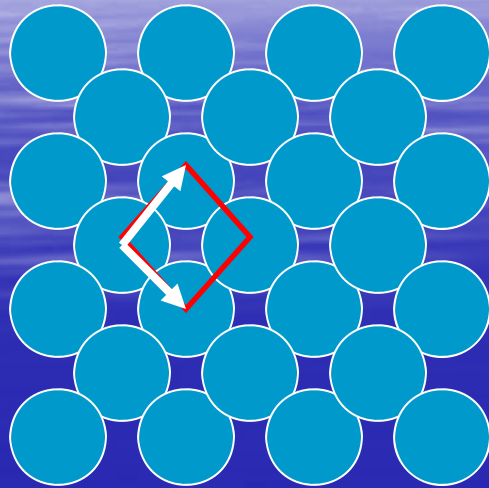
SiC (110) Surface Slabs



Reducing interactions – H termination



FCC (100)



fcc - (100) surface - 5 layers

3.55

.500000	.500000	.000000
-.500000	.500000	.000000
.000000	.000000	5.000000

Selective Dynamics

Cartesian

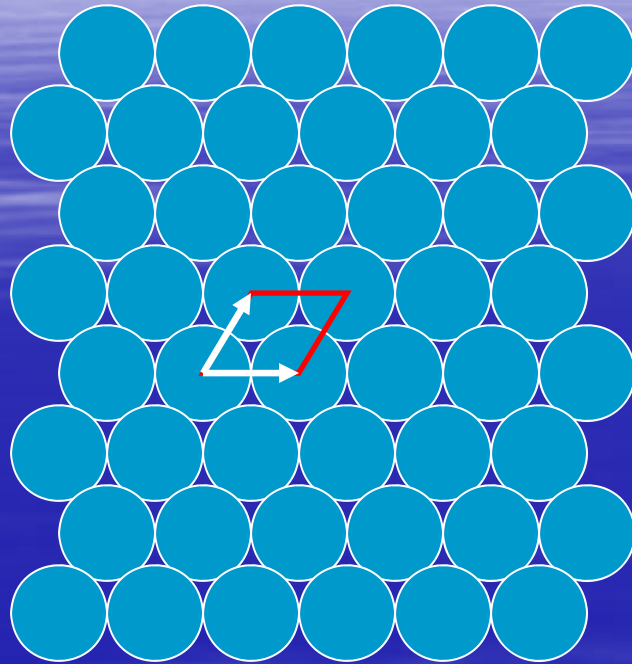
.00000	.00000	.00000	F	F	F
.00000	.50000	.50000	F	F	F
.00000	.00000	1.00000	F	F	F
.00000	.50000	1.50000	T	T	T
.00000	.00000	2.00000	T	T	T

or

Direct

.00000	.00000	.00000	F	F	F
.50000	.50000	.16667	F	F	F
.00000	.00000	.33333	F	F	F
.50000	.50000	.50000	T	T	T
.00000	.00000	.66667	T	T	T

FCC (111)



fcc - (111) surface - 5 layers

3.55

.707106	.000000	.000000
-.353553	.612372	.000000
.000000	.000000	5.1961524

Selective Dynamics

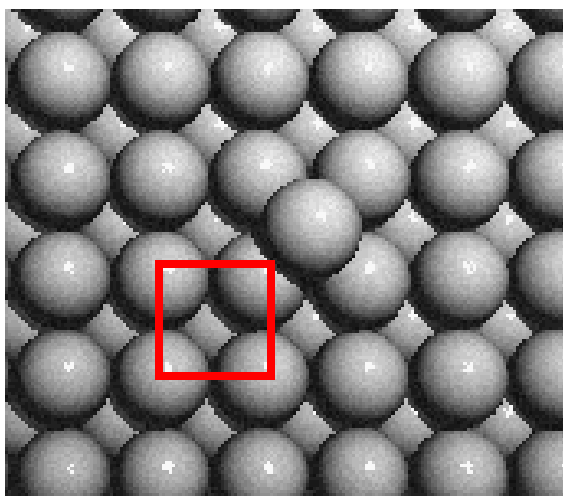
Cartesian

.00000	.00000	.00000	F	F	F
.00000	.40825	.57735	F	F	F
.00000	.20412	1.15470	F	F	F
.00000	.00000	1.73205	T	T	T
.00000	.40825	2.30940	T	T	T

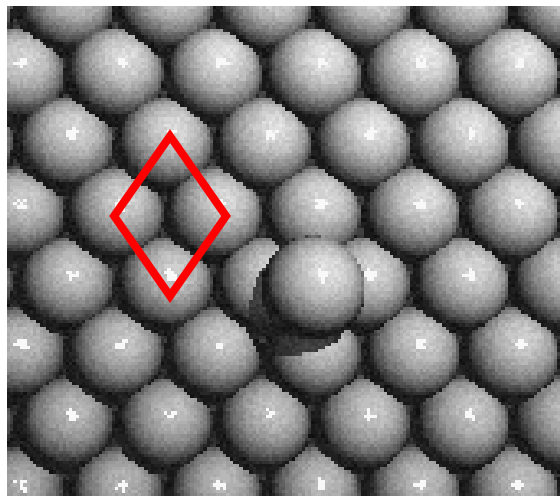
or

Direct

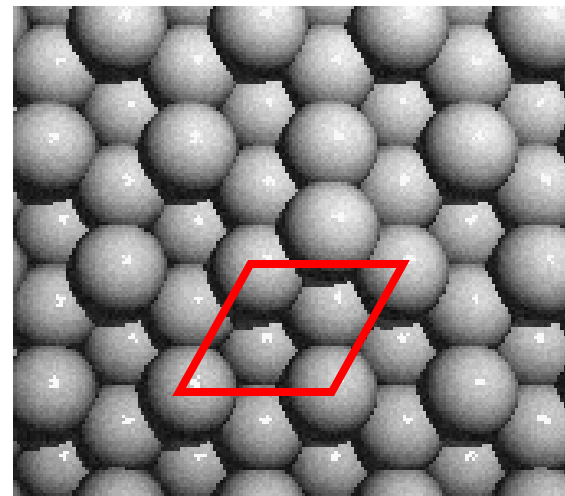
.00000	.00000	.00000	F	F	F
.33333	.66667	.11111	F	F	F
.66667	.33333	.22222	F	F	F
.00000	.00000	.33333	T	T	T
.33333	.66667	.44444	T	T	T



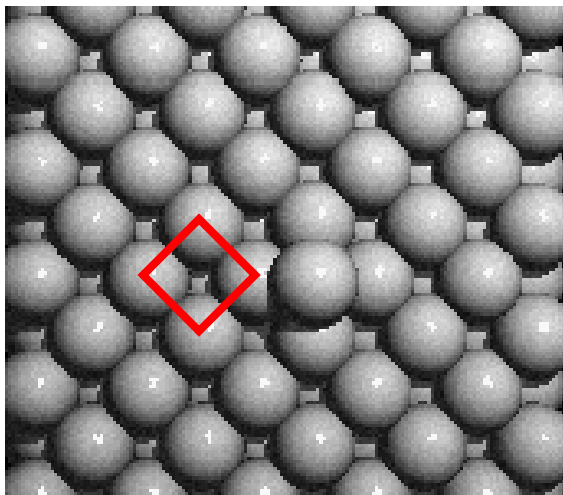
BCC(100)



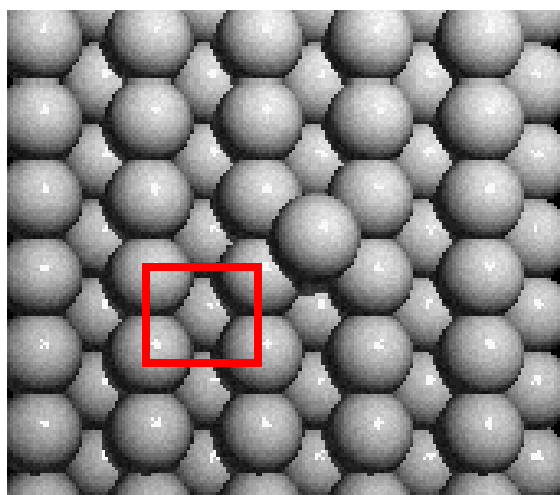
BCC(110)



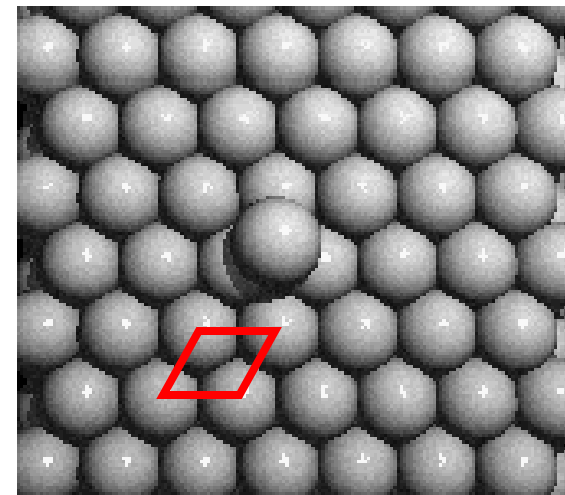
BCC(111)



FCC(100)



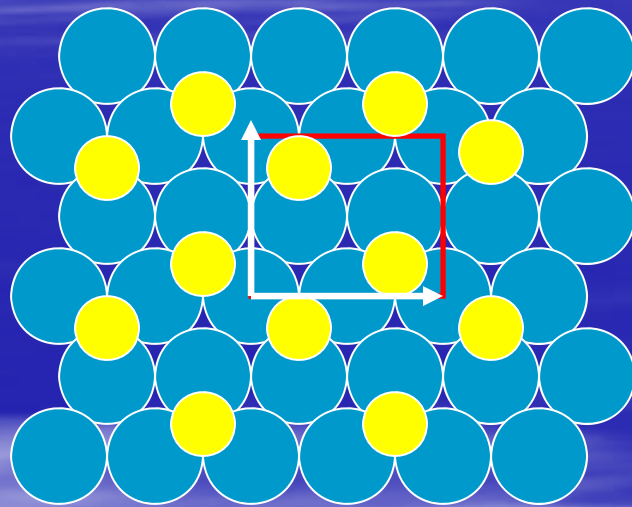
FCC(110)



FCC(111)

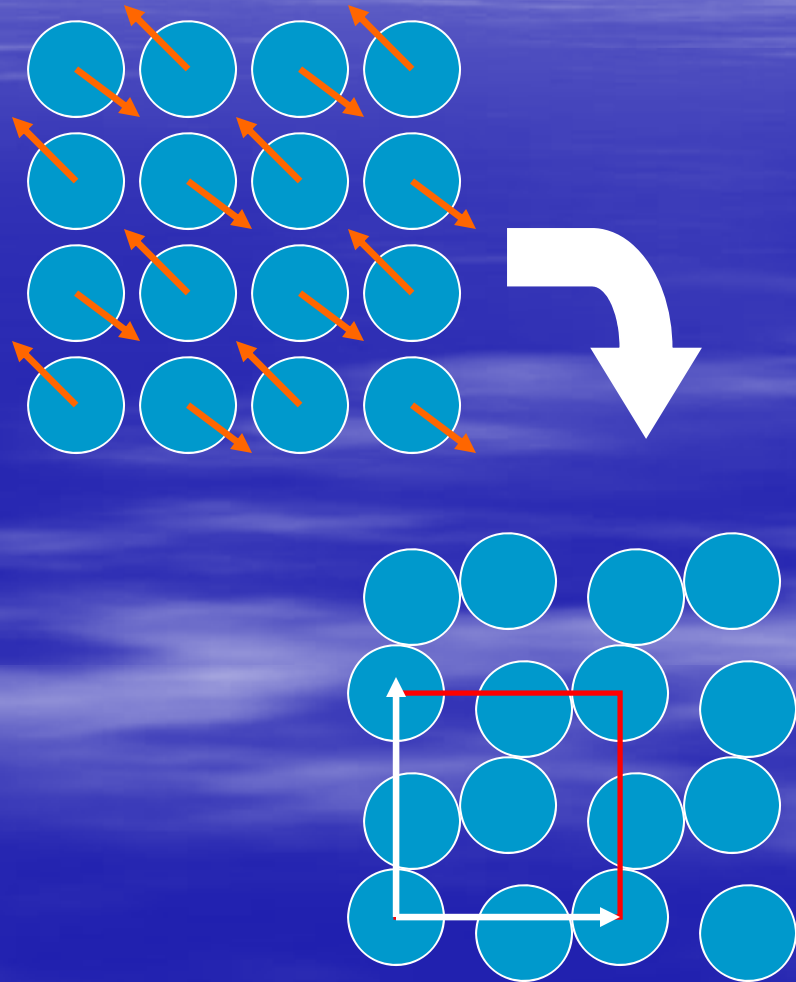
Adsorbing atoms / molecules

Ex. FCC (111) c(2x4)



Surface reconstruction

Ex. BCC (100) p(2x2)



Surface energy

$$\sigma = \frac{1}{2} (E_{surf} - N_{atom} \times E_{bulk})$$

Geometry

getting relaxed structure from CONTCAR

$$\text{Relaxation of surface layers : } \frac{d_i - d_{idea}}{d_{idea}} \times 100\%$$

Heat of formation of overlayers of A on substrate B

$$H_{n(A)} = \frac{E_{slab(B)+2n(A)} - (E_{slab(B)} + 2nE_{bulk(A)})}{2}$$

(Should use the same energy cutoff for each calculation)

Local Density of states

INCAR:

RWIGS = γ Å (works only for NPAR = 1 or serial version)

LORBIT = 11 (only for PAW)

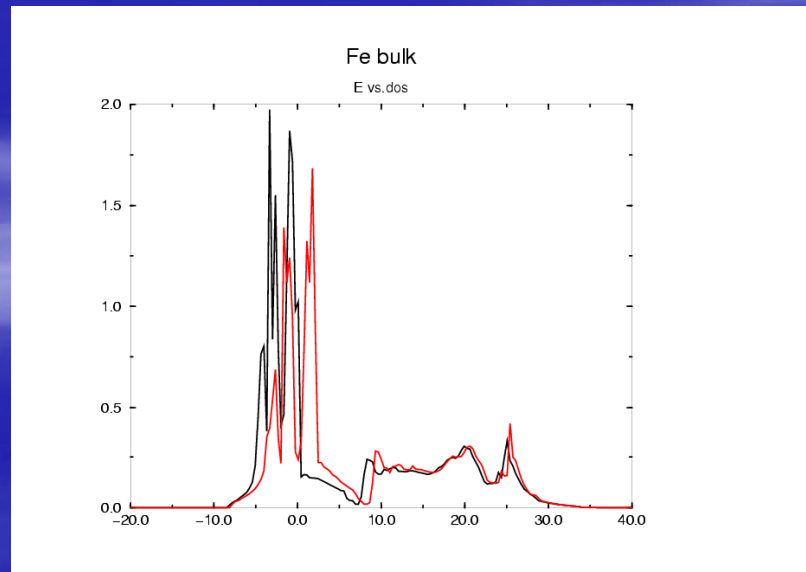
ISMEAR = -5 (use tetrahedron for DOS calculations)

NPAR = 1

Output file :

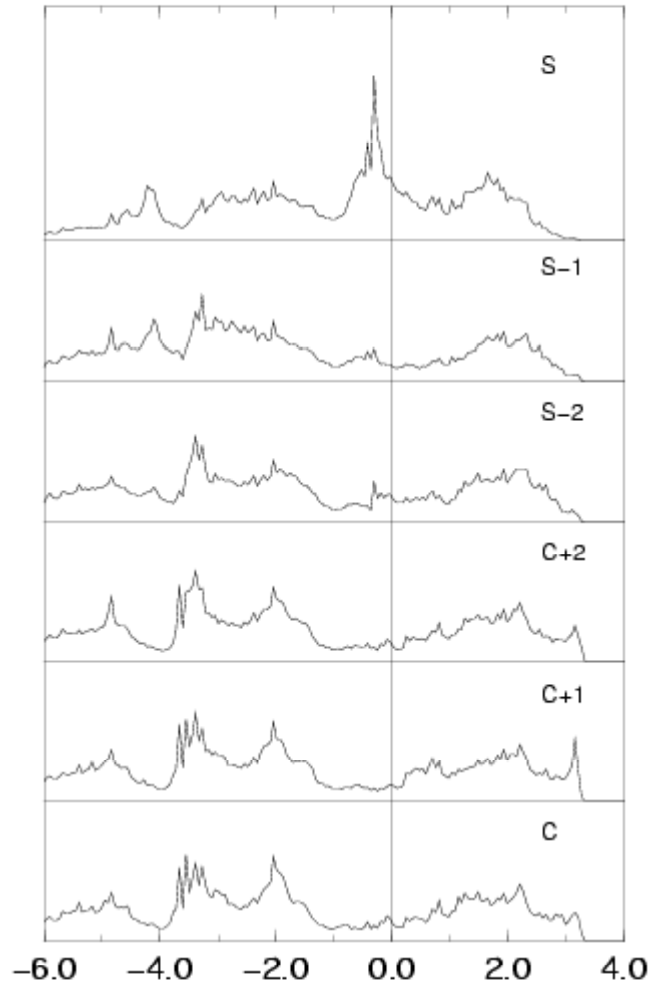
DOSCAR (energy, s-dos, p-dos, d-dos for each atom)

PROCAR (dos for each band and k-point)



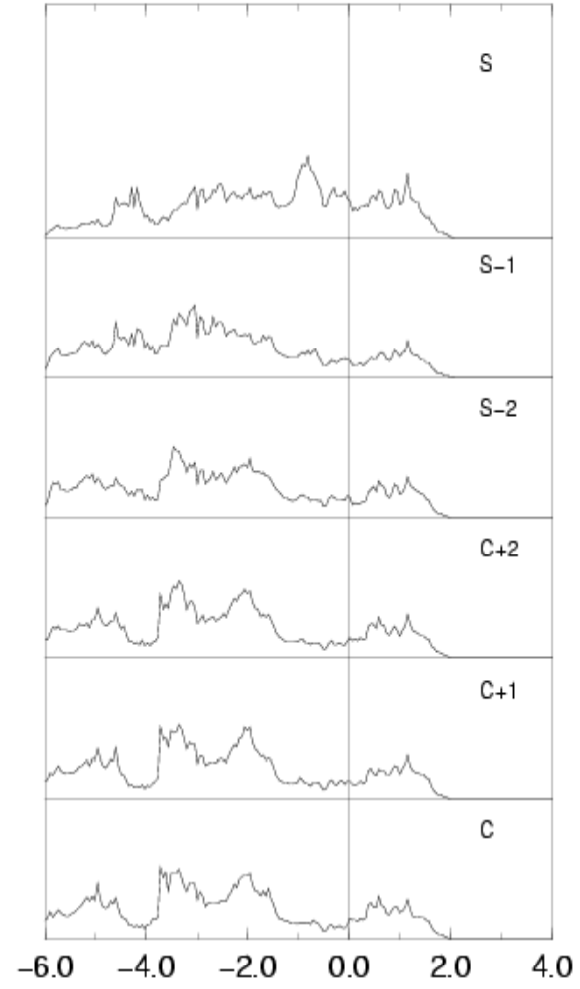
tot-dos

w15-100 k20



tot-dos

w13-100 c2x2 k16



LORBIT-tag

Available up from VASP version 3.2. In VASP.3.2 ORBIT can be either `.TRUE.` or `.FALSE.`. In VASP.4.X LORBIT can also take integer values:

logical	integer	RWIGS line in INCAR	files written
<code>.FALSE.</code>	0	line required	DOSCAR and PROCAR file
	1	line required	DOSCAR and extended PROCAR file
<code>.TRUE.</code>	2	line required	DOSCAR and PROOUT file
	10	not read	DOSCAR and PROCAR file
	11	not read	DOSCAR and PROCAR file with phase factors
	12		not supported

VASP.4.6 behaviour:

integer	RWIGS line in INCAR	files written
0	line required	DOSCAR and PROCAR file
1	line required	DOSCAR and lm decomposed PROCAR file
2	line required	DOSCAR and lm decomposed PROCAR file + phase factors
5	line required	PROOUT file
10	not read	DOSCAR and PROCAR file
11	not read	DOSCAR and lm decomposed PROCAR file
12	not read	DOSCAR and lm decomposed PROCAR file + phase factors

Band structure (after selfconsistent run)

1. Setup a k-point list along specific axis in KPOINTS
2. Set ICHARG = 11, read charge density from CHGCAR
3. Set FFT grid parameter manually to same value, to make sure that CHGCAR file is read properly (NGX, NGY, NGZ, NGXf, NGYf, NGZf)
4. Analyze and plot data in EIGENVAL after job done

Ex.

KPOINTS file for band structure

k-points for band structure

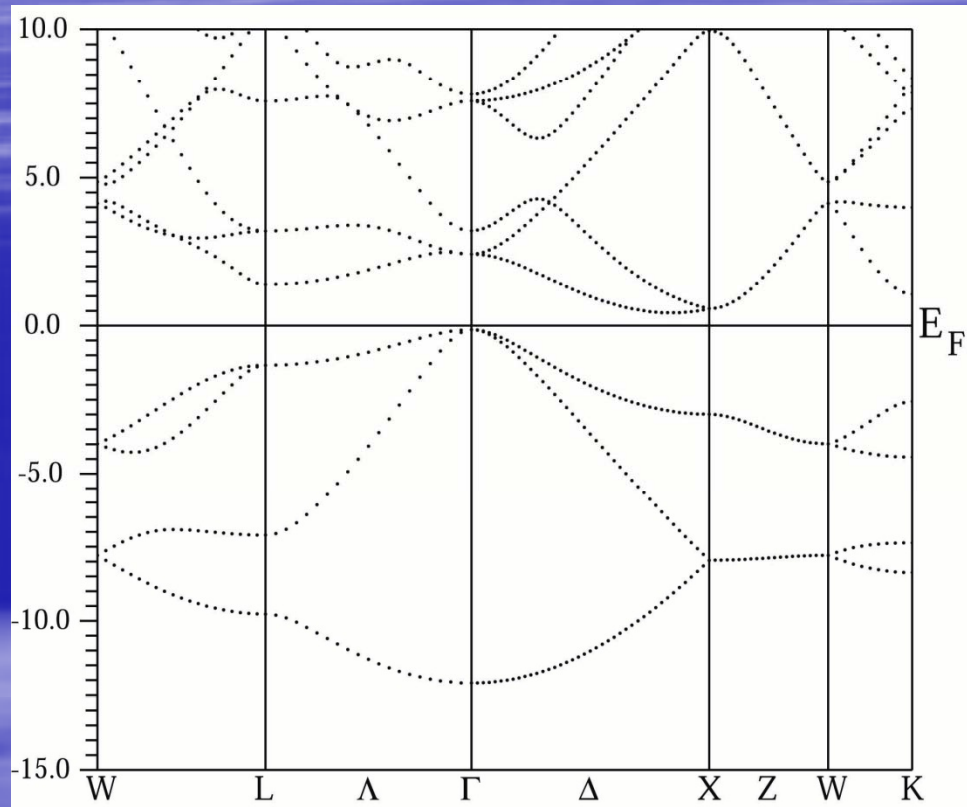
161

C

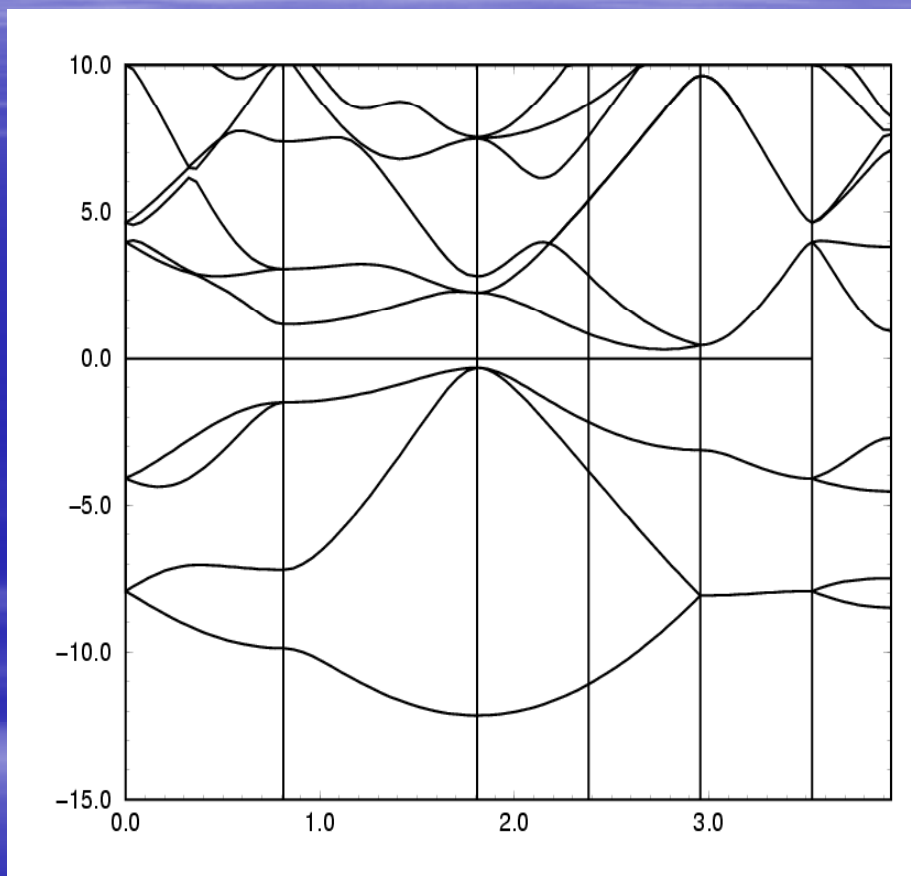
.00000	.00000	.00000	1.00000
.02500	.00000	.00000	1.00000
.05000	.00000	.00000	1.00000

...

Si-bulk Band Structure



WIEN2k



VASP

using 2-D Brillouin-zone for surfaces
to get projected bandstructure

Ex. K-points along line Γ -X-M- Γ

k-points for surface band structure

13

R

.00000	.00000	.00000	1.00000
.12500	.00000	.00000	1.00000
.25000	.00000	.00000	1.00000
.37500	.00000	.00000	1.00000
.50000	.00000	.00000	1.00000
.50000	.12500	.00000	1.00000
.50000	.25000	.00000	1.00000
.50000	.37500	.00000	1.00000
.50000	.50000	.00000	1.00000
.37500	.37500	.00000	1.00000
.25000	.25000	.00000	1.00000
.12500	.12500	.00000	1.00000
.00000	.00000	.00000	1.00000

Work function

INCAR:

LVTOT = .TRUE.

Output file :

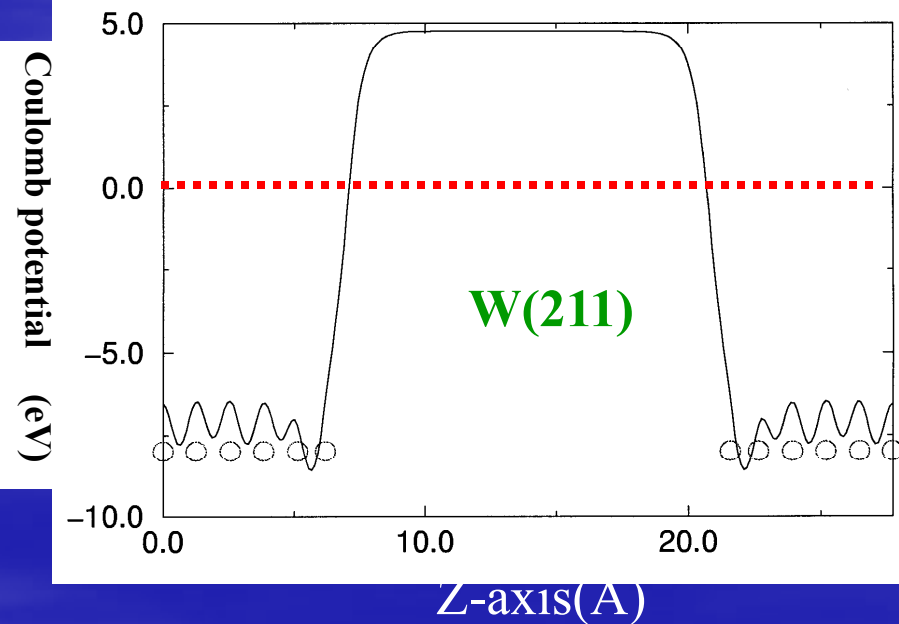
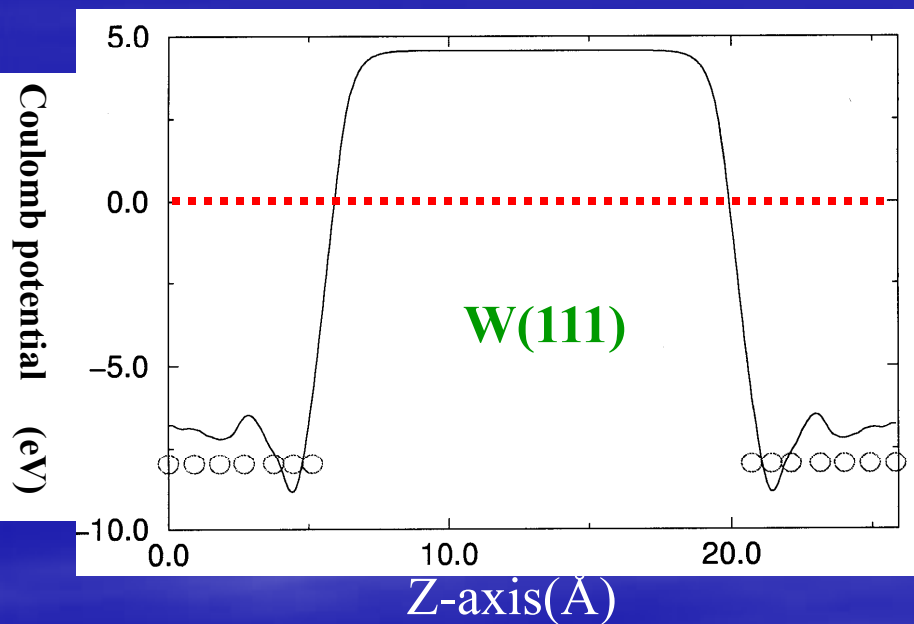
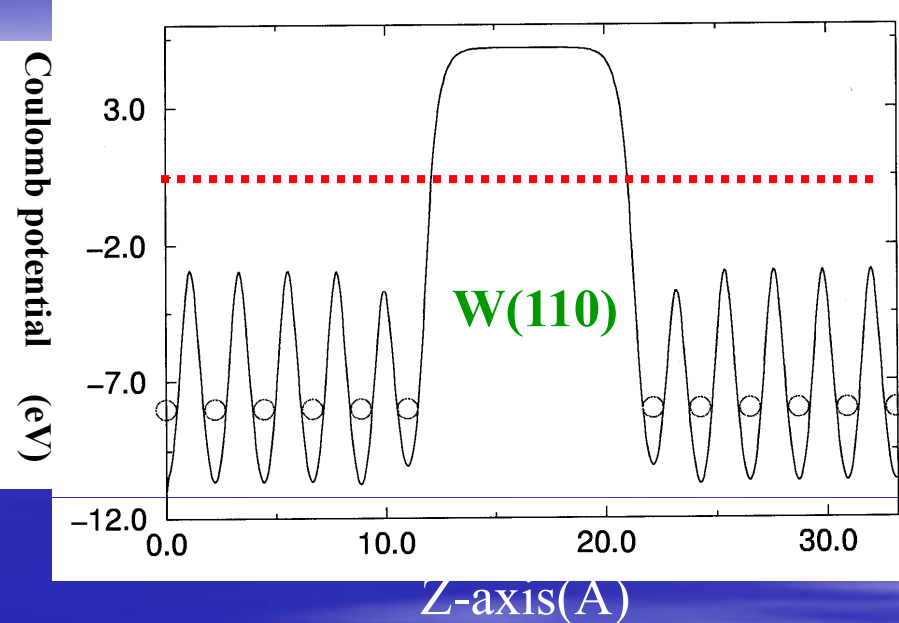
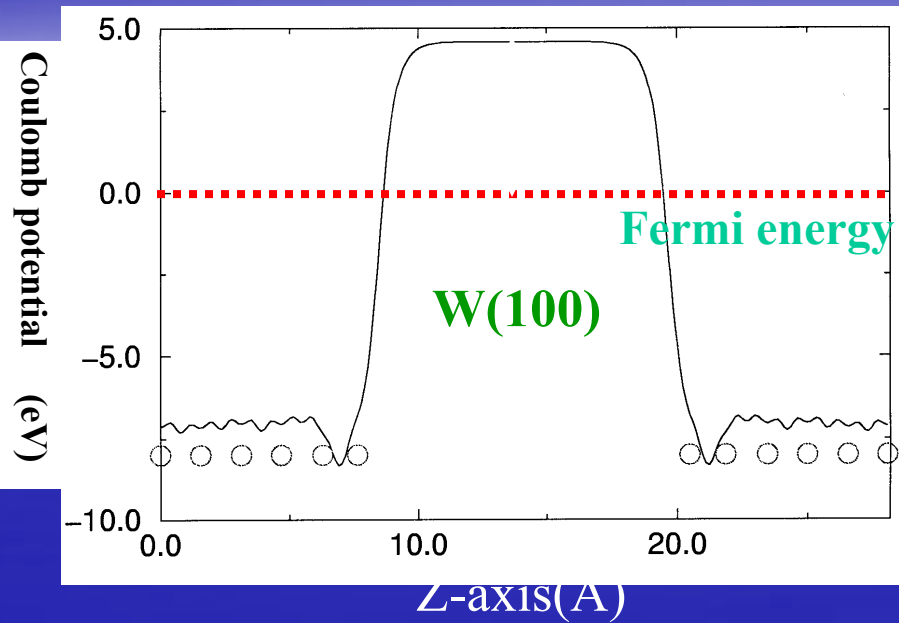
LOCPOT (same format as CHGCAR)

```
WRITE(IU,FORM) (((V(NX,NY,NZ),NX=1,NGX),NY=1,NGY),NZ=1,NGZ)
```

LOCPOT only contain electrostatic part of potential, if exchange correlation potential is to be included, change one line in main.F :

```
! comment out the following line to add exchange correlation  
! INFO%LEXCHG=-1
```

1. Search “E-fermi” in OUTCAR to get fermi-level
2. Analyze and plot data in LOCPOT



Surface adsorption

Ex. CO/Ni(111)

POSCAR:

Ni - (111)

3.53

```
.707106 .000000 .000000
-.353553 .612372 .000000
.000000 .000000 5.1961524
```

5 1 1

Selective Dynamics

Direct

```
.00000 .00000 .00000 F F F
.33333 .66667 .11111 F F F
.66667 .33333 .22222 F F F
.00000 .00000 .33333 T T T
.33333 .66667 .44444 T T T
.33333 .66667 .54029 T T T
.33333 .66667 .60299 T T T
```

INCAR:

EXMAX = 400

ISMEAR = -5

LORBIT = 1

NPAR = 1

RWIGS = 1.40 1.29 1.11

LVTOT = .TRUE.

IDIPOL = 3

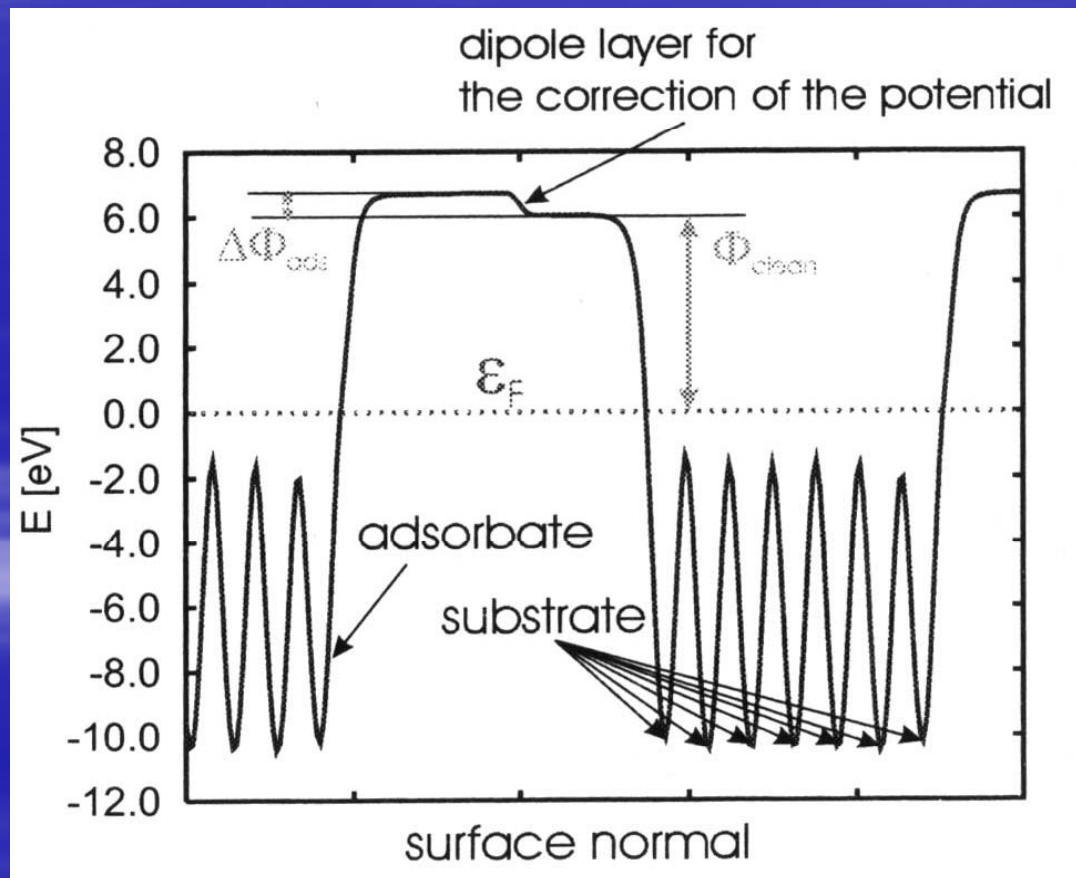
LDIPOL = .TRUE.

(dipol corrections)

Adsorption energy

$$E_{ads} = E_{total} - E_{clean} - E_{CO} \quad (\text{use the same energy cutoff})$$

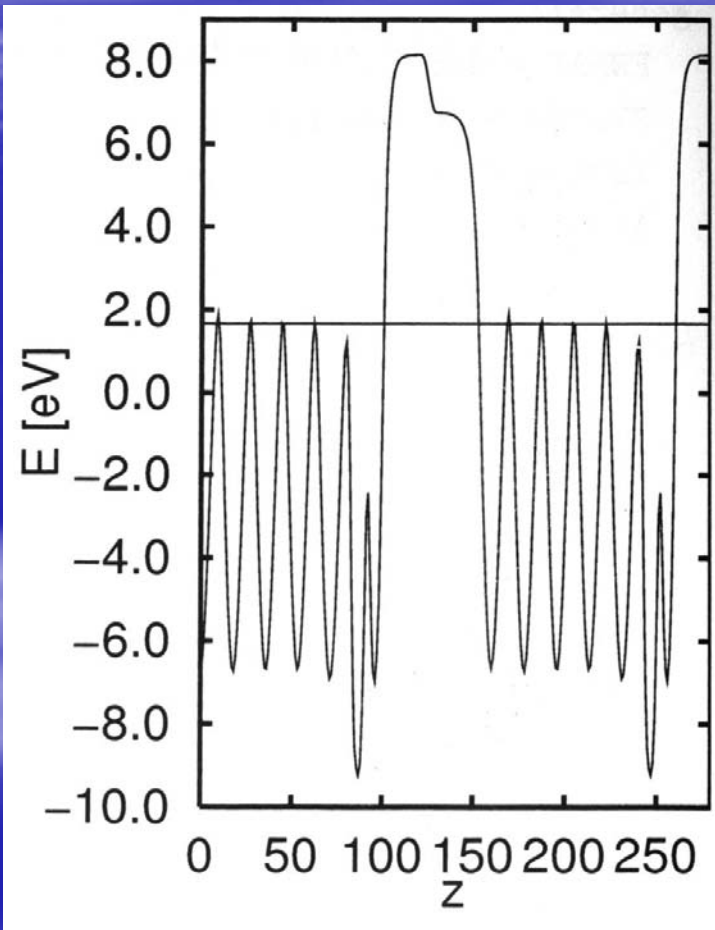
Dipole correction



Result of CO/Ni(111)

$$\begin{aligned} E_{clean} &= -25.730 \text{ eV (270eV)} \\ &= -25.741 \text{ eV (400eV)} \end{aligned}$$

$$\begin{aligned} E_{ads} &= E_{total} - E_{clean} - E_{CO} \\ &= -40.830 + 25.741 + 14.833 \\ &= -0.256 \text{ eV} \end{aligned}$$



$$\mathcal{E}_F = 1.66 \text{ eV}$$

Vacuum-potential at 8.15 / 6.76 eV

$$\Phi_{CO} = 6.49 \text{ eV} \quad \Phi_{clean} = 5.10 \text{ eV}$$

But in Ni(111) calculation

$$\Phi_{clean} = 5.24 \text{ eV}$$

due to too small vacuum in CO/Ni(111)

Other new feature and advantages

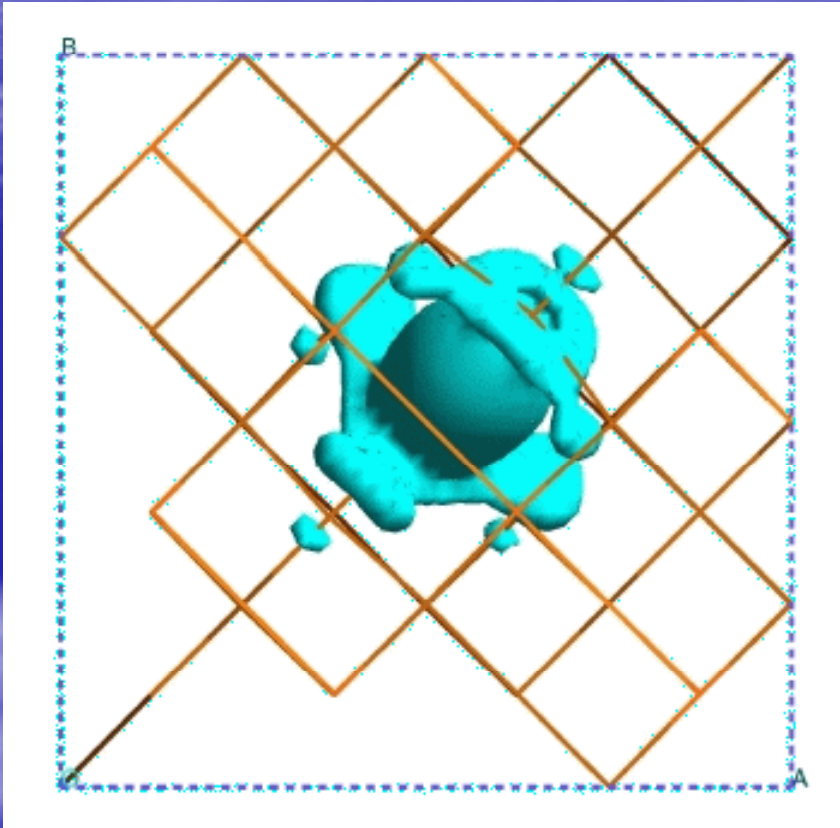
VASP4.5

- ⊙ non-collinear magnetic structure and spin orbital coupling
- ⊙ PREC=Low/Medium/Normal/Accurate/High
- ⊙ single precision WAVCAR (smaller)
- ⊙ new MPI communication layer and FFT routines

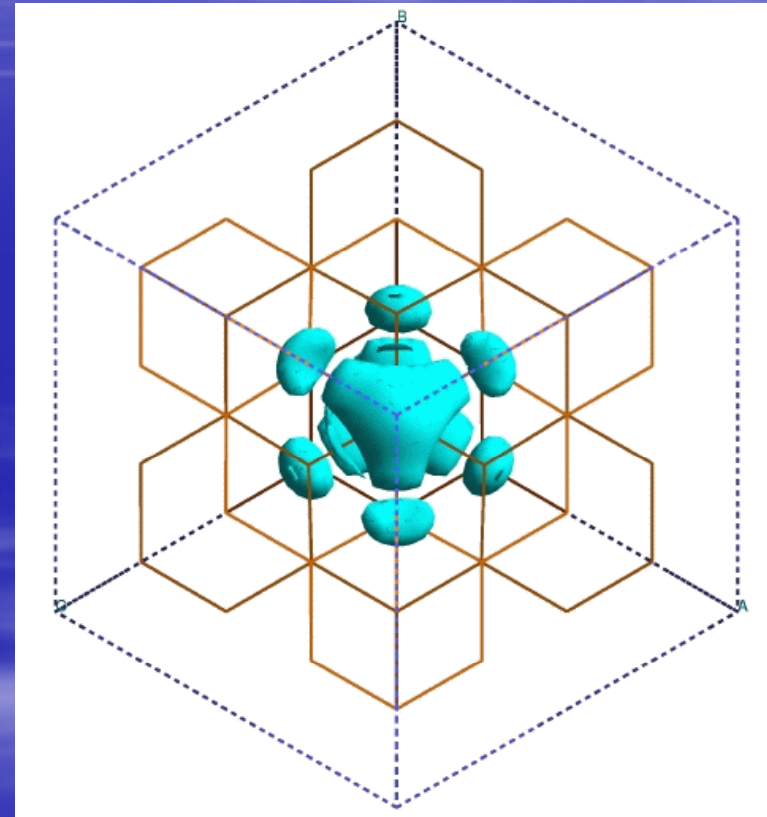
VASP4.6

- ⊙ support L(S)DA+U calculations
- ⊙ report orbital moment
- ⊙ new output file “vasprun.xml”
used in new vasp utility “p4v” (python for vasp)

Defects – H defect in Si Bond Centre Site (64 Si cell)

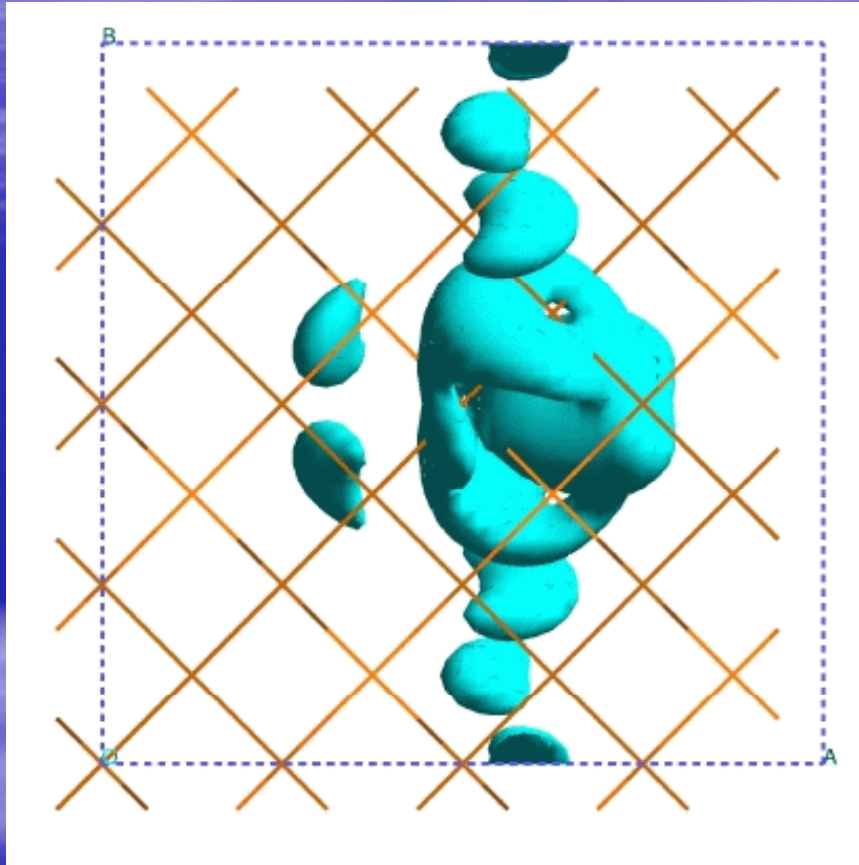


001 direction

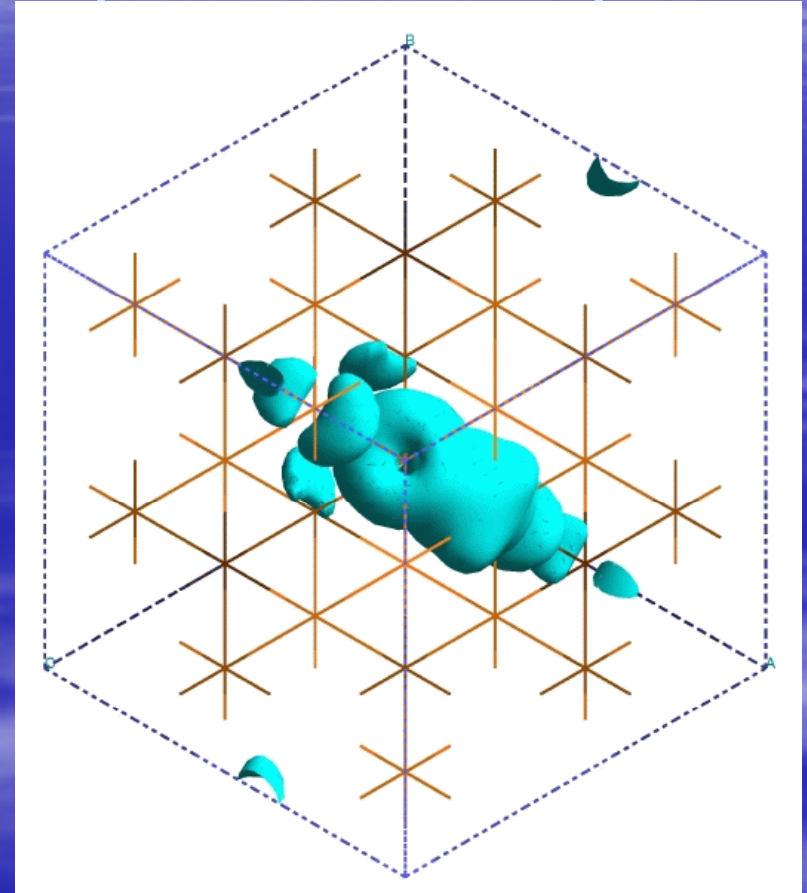


111 direction

Defects – H defect in Si Tetrahedral Site (64 Si cell)

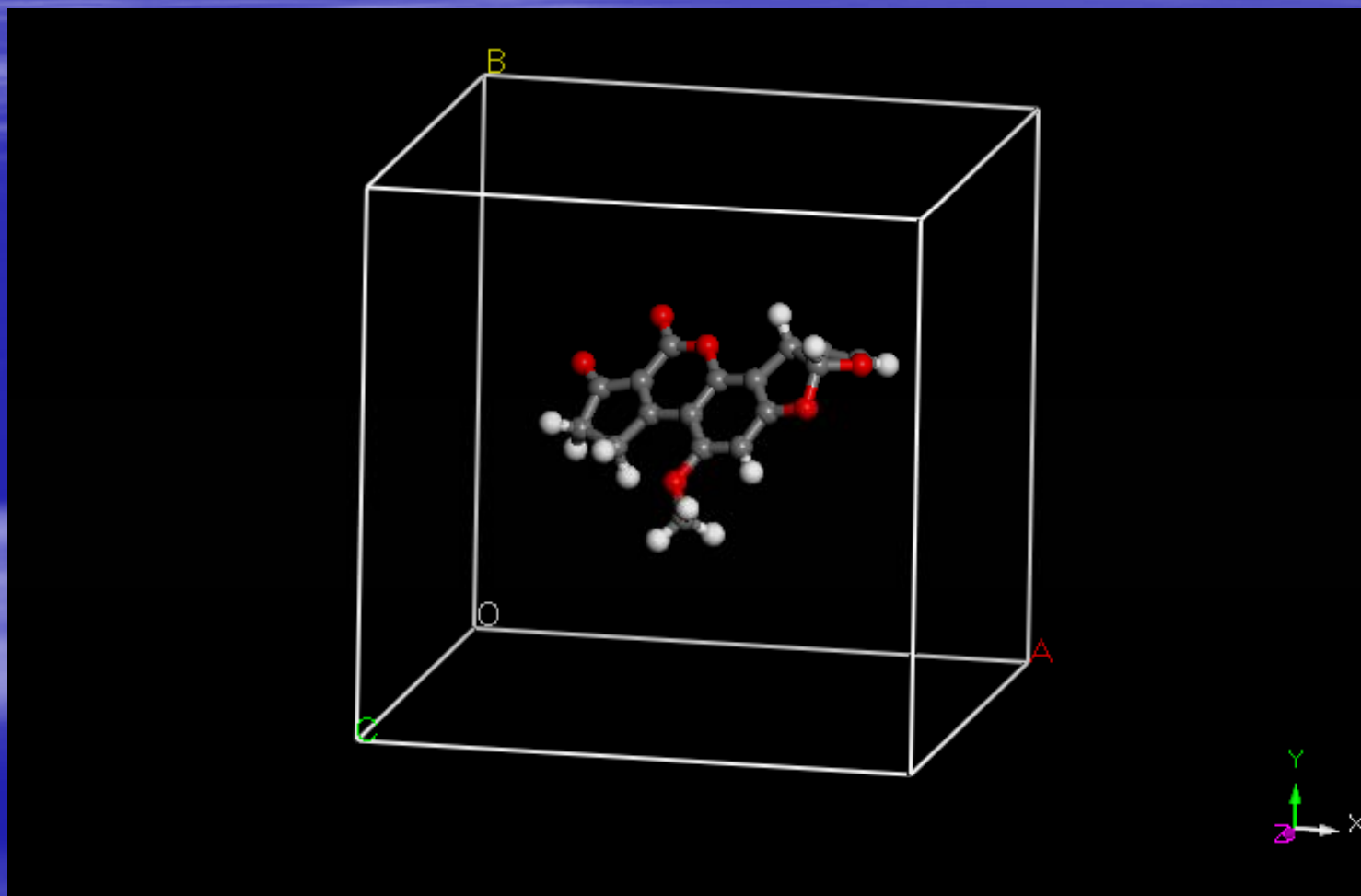


001 direction

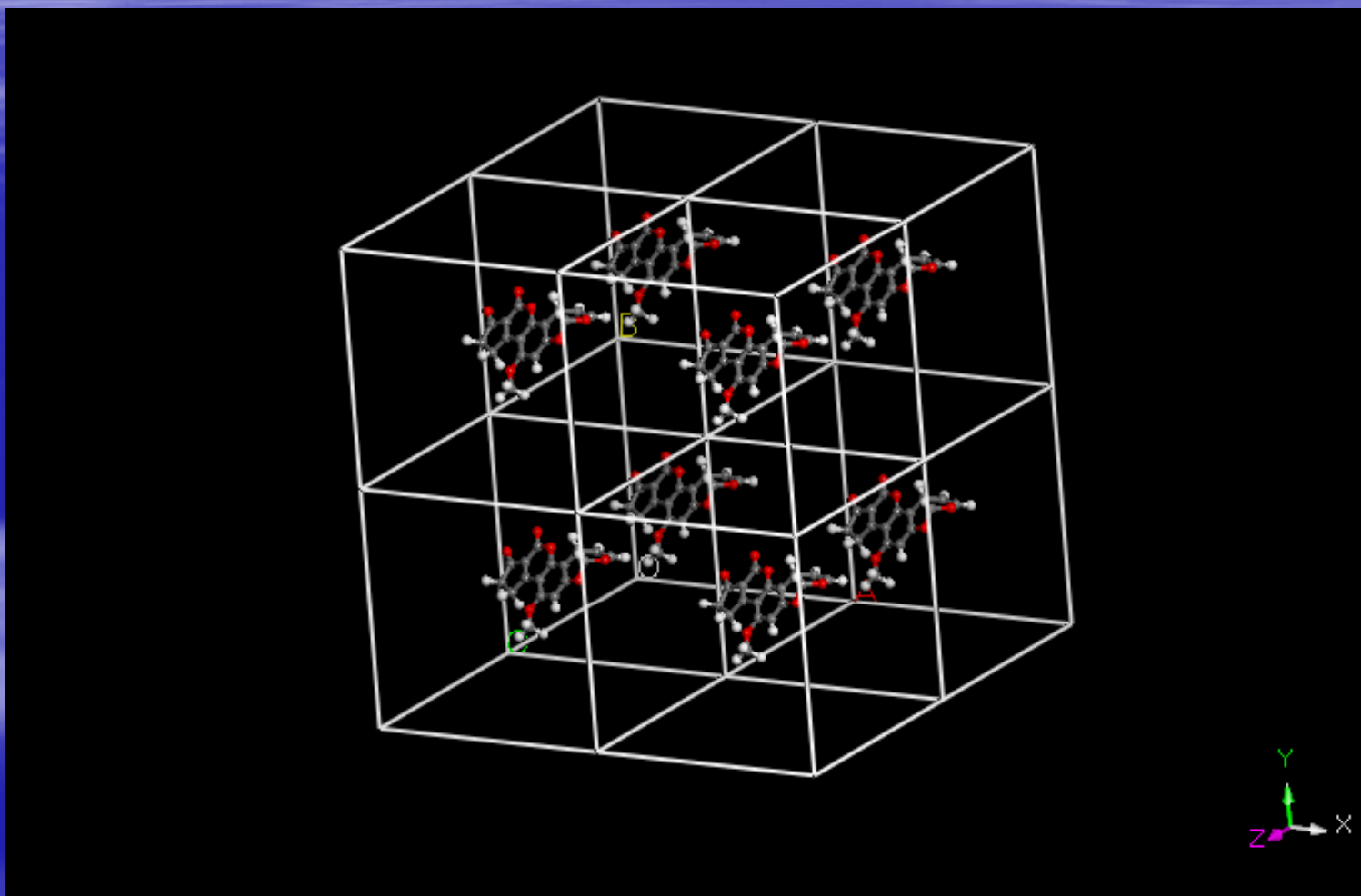


111 direction

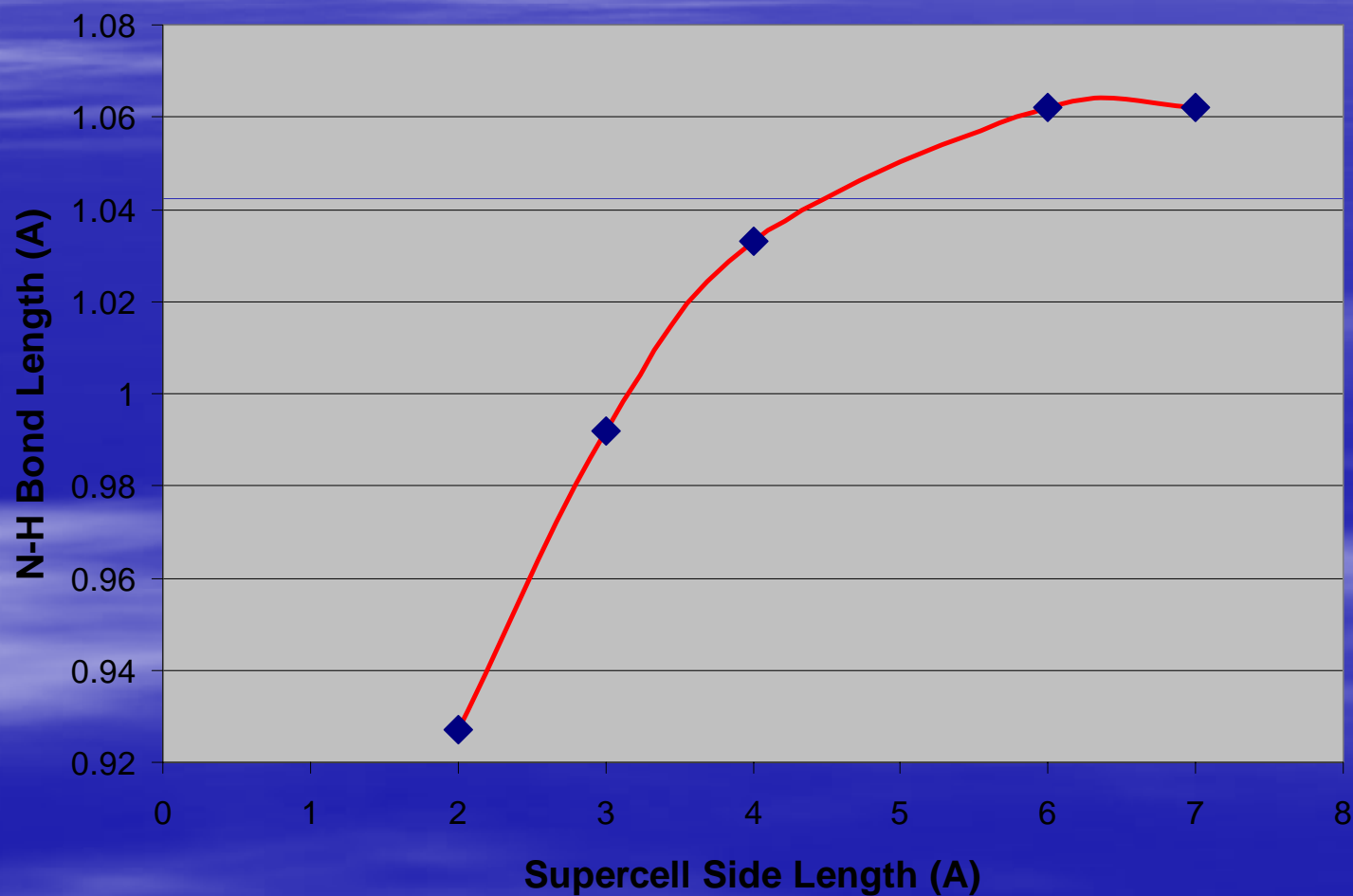
Molecules (Aflatoxin B1)



Aflatoxin B1 “Crystal”



Convergence with Supercell Size (NH₃)



Summary

- **Bands** – single particle solutions to Kohn-Sham equation
- **Plane wave basis set** – bands represented on reciprocal space grid within cut-off
- **Supercells** – approximating aperiodic system with a periodic one
- **K-points** – integration grid in 1st Brillouin zone