



The Plane-Wave Pseudopotential Method

*Eckhard Pehlke, Institut für Laser- und Plasmaphysik, Universität Essen,
45117 Essen, Germany.*

Starting Point: Electronic structure problem from physics, chemistry, materials science, geology, biology, ... which can be solved by total-energy calculations.

Topics of this talk:

- (i) how to get rid of the "core electrons":
the pseudopotential concept
- (ii) the plane-wave basis-set and its advantages
- (iii) supercells, Bloch theorem and Brillouin zone integrals

choices we have...

Treatment of electron-electron interaction

and decisions to make...

Hartree-Fock (HF)

Configuration-Interaction (CI)

Quantum Monte-Carlo (QMC)

Density-Functional Theory (DFT)

$$E_v[n] = T_0[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{XC}[n]$$

$$E_0 = \min_{\int n(\mathbf{r})d^3\mathbf{r}=N} E_v[n]$$

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{XC}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$
$$n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2, \quad v_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}$$

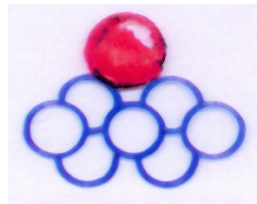
Problem: Approximation to XC functional.

decisions to make...

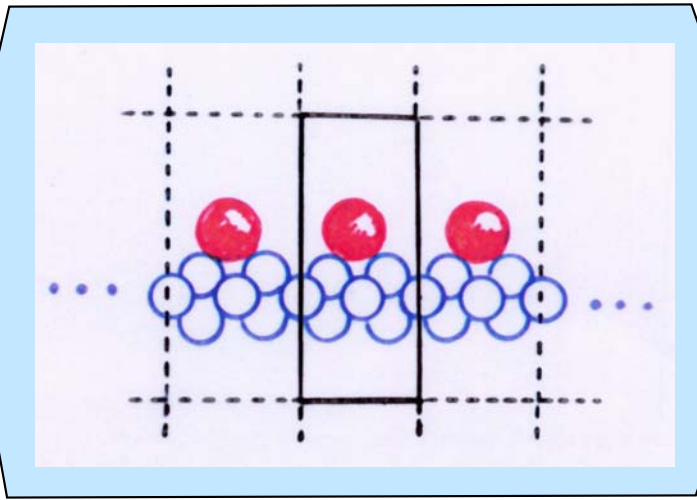
Simulation of Atomic Geometries

*Example: chemisorption site & energy of a particular atom on a surface = ?
How to simulate adsorption geometry?*

single molecule or cluster

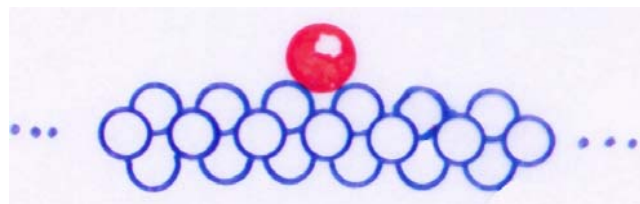


periodically repeated supercell, slab-geometry



Use Bloch theorem.
Efficient Brillouin zone integration schemes.

true half-space geometry, Green-function methods



decisions to make...

Basis Set to Expand Wave-Functions

linear combination of
atomic orbitals (LCAO)

$$\phi_{\mu\tau}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} u_{\mu}^{(\text{at})}(\mathbf{r} - \mathbf{R} - \boldsymbol{\tau})$$
$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{\mu, \tau} c_{\mu\tau}(\mathbf{k}) \phi_{\mu\tau}(\mathbf{k}, \mathbf{r})$$

plane waves (PW)

$$\psi(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{G}} c(\mathbf{k} + \mathbf{G}) \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k} + \mathbf{G})\cdot\mathbf{r}}$$

simple, unbiased,
independent of
atomic positions

augmented plane waves
(APW)

...

etc. etc.

I. The Pseudopotential Concept

Core-States and Chemical Bonding?

Validity of the Frozen-Core Approximation

U. von Barth, C.D. Gelatt, Phys. Rev. B 21, 2222 (1980).

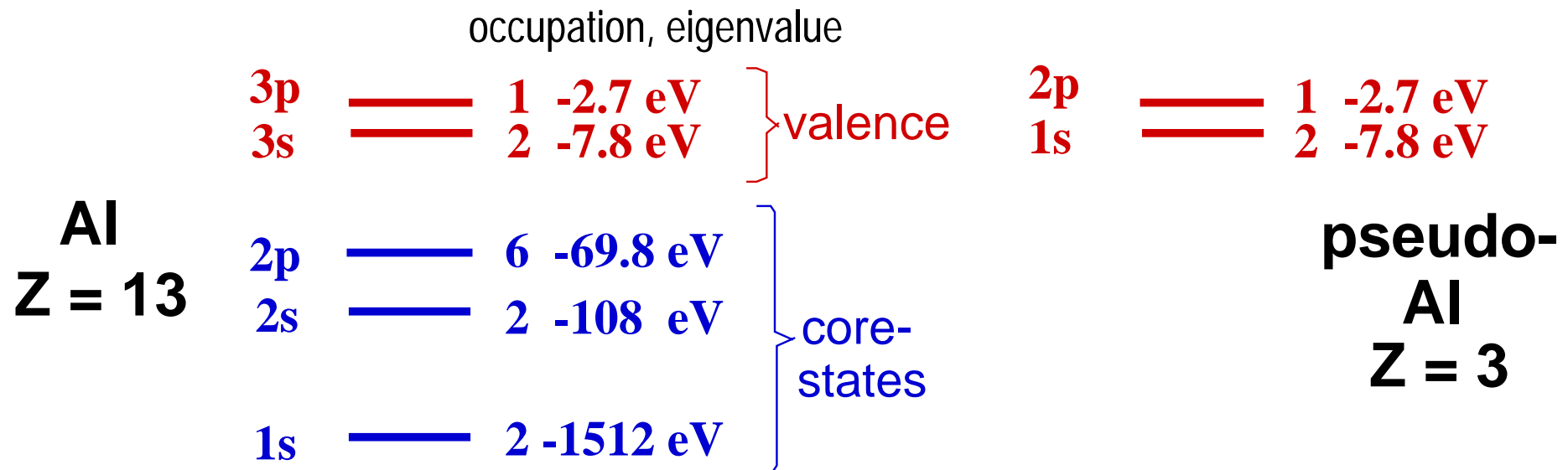
bcc \leftrightarrow fcc Mo, transformation energy 0.5 eV/atom
core kinetic energy change of 2.7 eV

but: error of **total energy** due to frozen-core approximation is small,
less than 2% of structural energy change

reason: frozen-core error of the total energy is of second order

$$\delta = \frac{1}{2} \int (\rho_c^0 - \rho_c) (v_{\text{eff}}^* - v_{\text{eff}}^0) d^3 \mathbf{r}$$

Remove Core-States from the Spectrum: Construct a Pseudo-Hamiltonian



$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}\right)\psi_j = \varepsilon_j\psi_j$$

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{(\text{ps})}\right)\psi_j^{(\text{ps})} = \varepsilon_j\psi_j^{(\text{ps})}$$

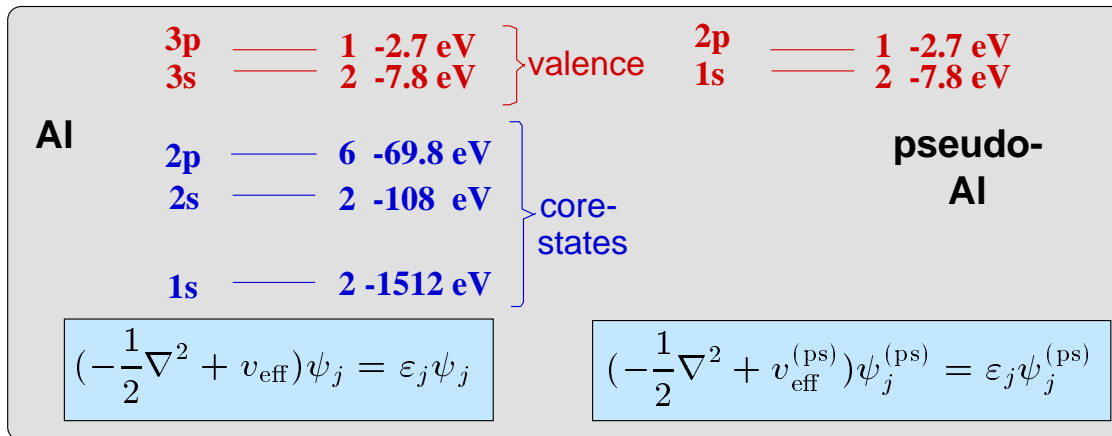
V. Heine, "The Pseudopotential Concept", in: Solid State Physics 24, pages 1-36,
Ed. Ehrenreich, Seitz, Turnbull (Academic Press, New York, 1970).

Orthogonalized Plane Waves (OPW)

How to construct
 v (ps)

in principle ?

(actual proc. -> Martin Fuchs)



Definition of OPWs: $|OPW, \mathbf{k} + \mathbf{G}\rangle = |PW, \mathbf{k} + \mathbf{G}\rangle + \sum_c b_c(\mathbf{k} + \mathbf{G})|\psi_c\rangle$

with $b_c(\mathbf{k} + \mathbf{G}) = -\langle\psi_c|PW, \mathbf{k} + \mathbf{G}\rangle$

Expansion of eigenstate in terms of OPWs: $|\psi_{\mathbf{k}}\rangle = \sum_{\mathbf{G}} a(\mathbf{k} + \mathbf{G}) |OPW, \mathbf{k} + \mathbf{G}\rangle$

Secular equation: $\det \left(\langle OPW, \mathbf{k} + \mathbf{G} | \hat{H} - E | OPW, \mathbf{k} + \mathbf{G}' \rangle \right) = 0$

Re-interpretation: $\det \left(\langle PW, \mathbf{k} + \mathbf{G} | \hat{H}^{(\text{ps})} - E | PW, \mathbf{k} + \mathbf{G}' \rangle \right) = 0$

Pseudo-wavefunction: $|\psi_{\mathbf{k}}^{(\text{ps})}\rangle = \sum_{\mathbf{G}} a(\mathbf{k} + \mathbf{G}) |PW, \mathbf{k} + \mathbf{G}\rangle$

OPW-Pseudopotential:

$$\hat{v}^{(\text{ps}), \text{OPW}} = v + \sum_c (\varepsilon - \varepsilon_c) |\psi_c\rangle\langle\psi_c|$$

Pseudopotentials and Pseudo-wavefunctions

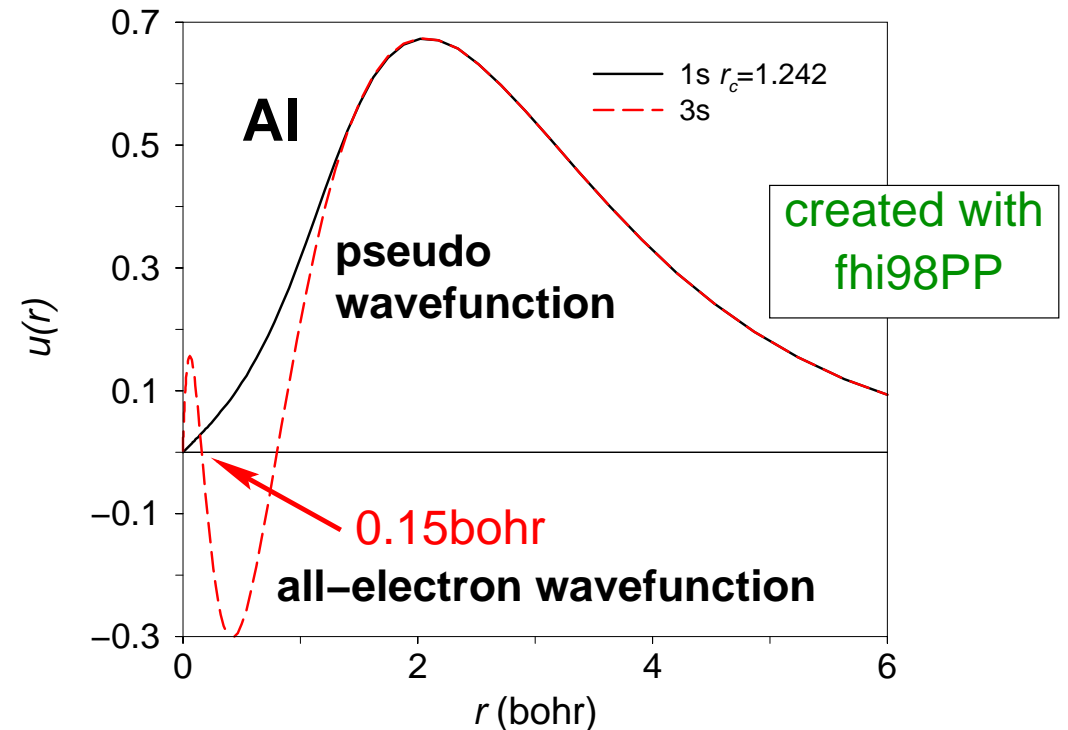
- Pseudopotentials are **softer** than all-electron potentials. (Pseudopotentials do not have core-eigenstates.)

- **Cancellation Theorem:**

If the pseudizing radius is taken as about the core radius, then v (ps) is small in the core region.

$$\hat{v}^{(ps),OPW} |\Phi\rangle = v |\Phi\rangle - \sum_c |\psi_c\rangle \langle \psi_c | v | \Phi \rangle$$

V. Heine, *Solid State Physics* 24, 1 (1970).



- Pseudo-wavefunction is node-less.
- **Plane-wave basis-set feasible.**
- Justification of NFE model.

Computation of Total-Energy Differences

	Ge atom	slab, ~ 50 Ge atoms
all-electron atom: ($Z = 32$)	$E_{\text{total}} = -2096 \text{ H}$	$\sim 10^5 \text{ H}$
pseudo-atom: ($Z' = 4$)	$E_{\text{total}} = -3.8 \text{ H}$	$\sim 10^2 \text{ H}$
typical structural total-energy difference: (dimer buckling,...)		few 100 meV $\sim 10^{-2} \text{ H}$

II. The Plane-Wave Expansion of the Total Energy

J. Ihm, A. Zunger, M.L. Cohen, J. Phys. C 12, 4409 (1979).

M. Bockstedte, A. Kley, J. Neugebauer, M. Scheffler, CPC 107, 187 (1997).

Plane-Wave Expansion of Kohn-Sham-Wavefunctions

Translationally invariant system (supercell) --> Bloch theorem (k: Blochvector)

$$\psi_j(\mathbf{k}, \mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_j(\mathbf{k}, \mathbf{r})$$

Plane-wave expansion of Kohn-Sham states (G: reciprocal lattice vectors)

$$\psi_j(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{G}} \psi_j(\mathbf{k} + \mathbf{G}) \frac{e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}}{\sqrt{\Omega}}$$

Electron density follows from sum over all occupied states:

$$n(\mathbf{r}) = \sum_j^{\text{occ}} \int_{\Omega_{\text{BZ}}} |\psi_j(\mathbf{k}, \mathbf{r})|^2 \frac{d^3\mathbf{k}}{\Omega_{\text{BZ}}}$$

(for semiconductors)

Kohn-Sham equation in reciprocal space:

$$\sum_{\mathbf{G}'} \left\{ -\frac{1}{2} |\mathbf{k} + \mathbf{G}'|^2 \delta_{\mathbf{G},\mathbf{G}'} + v_{\text{eff}}(\mathbf{G}, \mathbf{G}') \right\} \psi_j(\mathbf{k} + \mathbf{G}') = \varepsilon_j(\mathbf{k}) \psi_j(\mathbf{k} + \mathbf{G})$$

Hohenberg-Kohn Functional in Momentum Space

Total-energy functional:

$$E_{\text{total}}(\{\tau + \mathbf{R}\}, [\psi_{j\mathbf{k}}]) = T_{\text{S}} + E_{\text{ps,loc}} + E_{\text{ps,non-loc}} + E_{\text{H}} + E_{\text{XC}} + E_{\text{Ion-Ion}}$$

Obtain individually convergent energy terms by adding or subtracting superposition of Gaussian charges at the atomic positions:

$$n^{\text{Gauss}}(\mathbf{r}) = \sum_{\mathbf{R},\tau} \frac{Z_{\tau}}{\pi^{3/2} r_{\text{Gauss},\tau}^3} e^{-|\mathbf{r}-\mathbf{R}-\tau|^2/r_{\text{Gauss},\tau}^2}$$

Define valence charge difference wrt. above Gaussian charge density:

$$\tilde{n}(\mathbf{r}) = n(\mathbf{r}) - n^{\text{Gauss}}(\mathbf{r})$$

The total energy can thus be written as the sum of individually well defined energies:

$$E_{\text{total}} = T_{\text{S}} + \tilde{E}_{\text{ps,loc}} + E_{\text{ps,non-loc}} + E_{\text{H}}[\tilde{n}] + E_{\text{XC}} + \tilde{E}_{\text{Ion-Ion}} - E_{\text{self}}$$

Hohenberg-Kohn Functional in Momentum Space (continued)

- kinetic energy:

$$T_S = \sum_j^{\text{occ}} \int_{\Omega_{\text{BZ}}} \frac{d^3\mathbf{k}}{\Omega_{\text{BZ}}} \sum_{\mathbf{G}} \frac{|\mathbf{k} + \mathbf{G}|^2}{2} |\psi_j(\mathbf{k} + \mathbf{G})|^2$$

- local pseudopotential energy:
(only one kind of atoms)

$$\tilde{E}_{\text{ps,loc}} = \Omega \sum_{\mathbf{G}} S(\mathbf{G}) \tilde{v}_{\tau,\mathbf{G}} n_{\mathbf{G}}$$

with $\tilde{v}_{\tau}(r) = v_{\tau}^{\text{ps,ion}}(r) - \int \frac{n_{\tau}^{\text{Gauss,at}}(r')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$ and $S(\mathbf{G}) = \sum_{\tau} e^{i\mathbf{G}\cdot\tau}$ structure factor

- non-local pseudopotential energy

- Hartree energy:

$$E_{\text{H}}[\tilde{n}] = \frac{\Omega}{2} \sum_{\mathbf{G} \neq 0} \frac{4\pi}{|\mathbf{G}|^2} |\tilde{n}_{\mathbf{G}}|^2$$

- exchange-correlation energy:

$$E_{\text{XC}}^{\text{LDA}}[n + n^{\text{core}}] = \int_{\Omega} d^3\mathbf{r} (n(\mathbf{r}) + n^{\text{core}}(\mathbf{r})) \epsilon_{\text{XC}}^{\text{hom}}(n(\mathbf{r}) + n^{\text{core}}(\mathbf{r}))$$

- Ion-Ion Coulomb interaction: $\tilde{E}_{\text{Ion-Ion}} = \frac{1}{2} \sum_{\tau, \tau', \mathbf{R}: \tau \neq \tau' + \mathbf{R}} \frac{Z_{\tau} Z_{\tau'}}{|\tau - \tau' - \mathbf{R}|} \left(1 - \text{erf} \left(\frac{|\tau - \tau' - \mathbf{R}|}{\sqrt{r_{\text{Gauss},\tau}^2 + r_{\text{Gauss},\tau'}^2}} \right) \right)$

- Gaussian self energy: $E_{\text{self}} = \sum_{\tau} \frac{1}{\sqrt{2\pi}} \frac{Z_{\tau}^2}{r_{\text{Gauss},\tau}}$

Kinetic Energy Cut-Off and Basis-Set Convergence

Size of plane-wave basis-set limited by the kinetic-energy cut-off energy:

$$|\mathbf{k} + \mathbf{G}| \leq \sqrt{2E_{\text{cut}}}$$

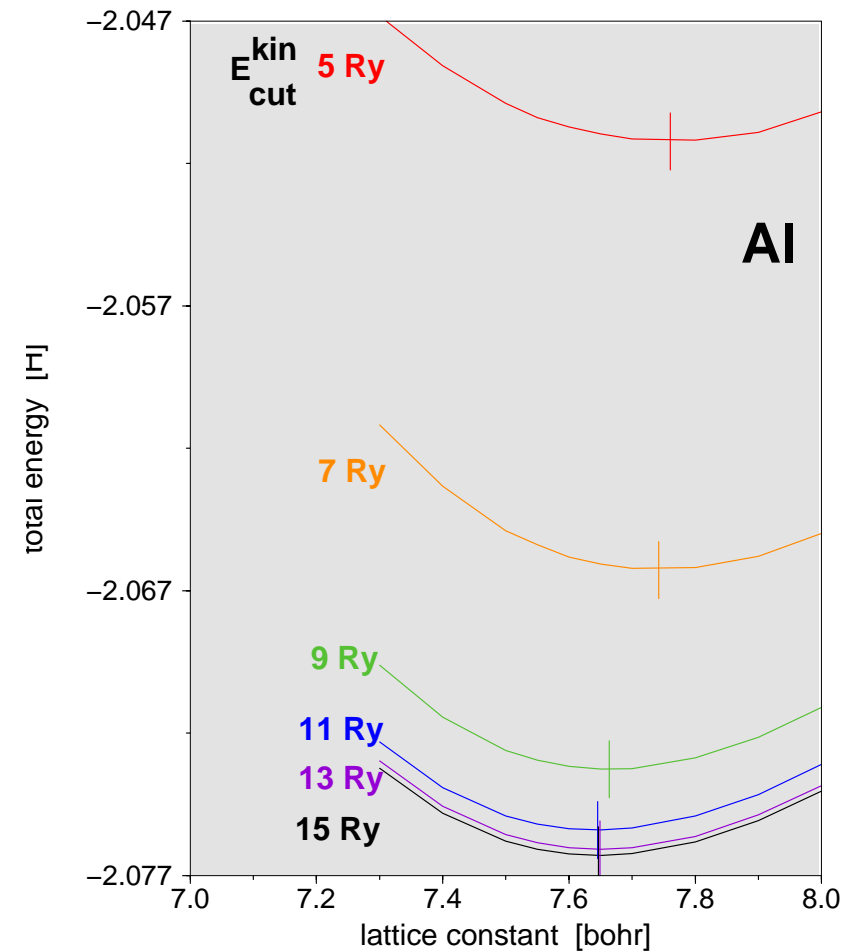
(Note: Conventionally, cut-off energy is given in Ry, then factor "2" is obsolete.)

Efficient calculation of convolutions:

$$\begin{array}{ccc} \psi_{j,\mathbf{k}}(\mathbf{G}) & \xrightarrow{\text{red arrow}} & (v_{\text{loc}} \psi_{j,\mathbf{k}})(\mathbf{G}) \\ \downarrow \text{FFT} & & \uparrow \text{FFT}^{-1} \\ \psi_{j,\mathbf{k}}(\mathbf{r}_n) & \xrightarrow{\text{mult.}} & v_{\text{loc}}(\mathbf{r}_n) \psi_{j,\mathbf{k}}(\mathbf{r}_n) \end{array}$$

Real space mesh fixed by sampling theorem.

Basis-set convergence of total energy:



Advantages of Plane-Wave Basis-Set

- (1) basis set is independent of atom positions and species, unbiased
- (2) forces acting on atoms are equal to Hellmann-Feynman forces, no basis-set corrections to the forces (no Pulay forces)
- (3) efficient calculation of convolutions, use FFT to switch between real space mesh and reciprocal space
- (4) systematic improvement (decrease) of total energy with increasing size of the basis set (increasing cut-off energy): can control basis-set convergence

Remark: When the volume of the supercell is varied, the number of plane-wave component varies discontinuously. Basis-set corrections are available (G.P. Francis, M.C. Payne, J. Phys. Cond. Matt. 2, 4395 (1990).)

III. Brillouin Zone Integration and Special k-Point Sets

- (i) General Considerations
- (ii) Semiconductors & Insulators
- (iii) Metals

D.J. Chadi, M.L.Cohen, Phys. Rev. B 8, 5747 (1973).

H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13, 5188 (1976).

R.A. Evarestov, V.P. Smirnov, phys. stat. sol. (b) 119, 9 (1983).

The Brillouin Zone Integration

Make use of supercells and exploit translational invariance; apply Bloch theorem.
Charge density and other quantities are represented by Brillouin-zone integrals:

$$n(\mathbf{r}) = \sum_j^{\text{occ}} \int_{\Omega_{\text{BZ}}} |\psi_j(\mathbf{k}, \mathbf{r})|^2 \frac{d^3\mathbf{k}}{\Omega_{\text{BZ}}} \quad (\text{for semiconductors / insulators})$$

Smooth integrand => approximate integral by a weighted sum over special points:

$$n(\mathbf{r}) \approx \sum_j^{\text{occ}} \sum_{n=1}^{N_{\text{kpt}}} w_n |\psi_j(\mathbf{k}_n, \mathbf{r})|^2$$

This is the "trick" by which we get rid of the many degrees of freedom from the crystal electrons!

Special Points for Efficient Brillouin-Zone Integration

Calculate integrals of the type $\bar{f} = \int_{\Omega_{\text{BZ}}} f(\mathbf{k}) \frac{d^3\mathbf{k}}{\Omega_{\text{BZ}}}$ with

- $f(\mathbf{k})$ periodic in reciprocal space, $f(\mathbf{k} + \mathbf{G}) = f(\mathbf{k})$,
- $f(\mathbf{k})$ symmetric with respect to all point group symmetries.

Expand $f(\mathbf{k})$ into a FOURIER series: $f(\mathbf{k}) = \bar{f} + \sum_{m=1}^{\infty} f_m A_m(\mathbf{k})$

with $A_m(\mathbf{k}) = \frac{1}{|G_0|} \sum_{\alpha \in G_0} e^{i\mathbf{k} \cdot (\alpha \mathbf{R}_m)}$ and $A_0(\mathbf{k}) = 1$

Choose special points \mathbf{k}_i ($i=1, \dots, N$) and weights w_i such that

$$\sum_{i=1}^N w_i A_m(\mathbf{k}_i) = \delta_{m,0} \quad \text{for } m = 0, 1, \dots, M-1$$

for M as large as possible. The real-space vectors \mathbf{R}_m are assumed to be ordered according to their length.

Then:

$$\sum_{i=1}^N w_i f(\mathbf{k}_i) = \bar{f} + \underbrace{\sum_{m=M}^{\infty} f_m \sum_{i=1}^N w_i A_m(\mathbf{k}_i)}_{\text{error of BZ integration scheme}}$$

error of BZ integration scheme

Special k-Points for 2D Square Lattice

Let point group be C_4 (not C_{4v}).

Lattice vector $\mathbf{a}_1 = a\mathbf{e}_x$, $\mathbf{a}_2 = a\mathbf{e}_y$

\mathbf{k}_i	w_i	N	M
$(\frac{1}{4} \frac{1}{4})$	1	1	3
$(\frac{1}{4} 0) (\frac{1}{2} \frac{1}{4})$	$\frac{1}{2} \frac{1}{2}$	2	6
$(0 0) (\frac{1}{5} \frac{2}{5})$	$\frac{1}{5} \frac{4}{5}$	2	4
$(\frac{1}{8} \frac{1}{8}) (\frac{1}{8} \frac{3}{8}) (\frac{3}{8} \frac{1}{8}) (\frac{3}{8} \frac{3}{8})$	$\frac{1}{4} \frac{1}{4} \frac{1}{4} \frac{1}{4}$	4	12
$(\frac{1}{6} 0) (\frac{1}{6} \frac{1}{3}) (\frac{1}{3} \frac{1}{6}) (\frac{1}{2} 0) (\frac{1}{2} \frac{1}{3})$	$\frac{2}{9} \frac{2}{9} \frac{2}{9} \frac{1}{9} \frac{2}{9}$	5	15
$(\frac{1}{20} \frac{3}{20}) (\frac{3}{20} \frac{9}{20}) (\frac{5}{20} \frac{5}{20})$	} $\frac{1}{5} \frac{1}{5} \frac{1}{5} \frac{1}{5} \frac{1}{5}$	5	16
$(\frac{7}{20} \frac{1}{20}) (\frac{9}{20} \frac{7}{20})$			

Monkhorst-Pack Special k-Points

Equally spaced k-point mesh in reciprocal space:

$$\mathbf{k}_{i_1, i_2, i_3} = u_{i_1}^{(1)} \mathbf{a}_1^* + u_{i_2}^{(2)} \mathbf{a}_2^* + u_{i_3}^{(3)} \mathbf{a}_3^*, \quad i_1 = 1, \dots, l^{(1)}, \quad i_2 = 1, \dots, l^{(2)}, \quad i_3 = 1, \dots, l^{(3)}$$

and

$$u_i = \frac{2i - l - 1}{2l} .$$

Restrict k-point set to points in the irreducible part of the Brillouin zone.

Weight of each point \sim number of points in the star of the respective wave vector:

Weights:

$$w_{\mathbf{k}} = \frac{|\text{star}(\mathbf{k})|}{l^{(1)} l^{(2)} l^{(3)}}$$

H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13, 5188 (1976).

Why Few k-Points Already Work Fine for Semiconductors

Semiconductors and insulators: always integrate over **complete bands!**

$$n(\mathbf{r}) = \sum_j^{\text{occ}} \int_{\Omega_{\text{BZ}}} |\psi_j(\mathbf{k}, \mathbf{r})|^2 \frac{d^3\mathbf{k}}{\Omega_{\text{BZ}}}$$

Introduce Wannier-functions for the j-th band: $\psi_j(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N_{\mathbf{R}}}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_j(\mathbf{r} - \mathbf{R})$

True charge density from the j-th band: $n_j(\mathbf{r}) = \frac{1}{N_{\mathbf{R}}} \sum_{\mathbf{R}} |w_j(\mathbf{r} - \mathbf{R})|^2$

Approximate charge density (from sum over special k-points):

$$\tilde{n}_j(\mathbf{r}) = \sum_{i=1}^N w_i \left(\frac{1}{|G_0|} \sum_{\alpha \in G_0} |\psi_j(\alpha \mathbf{k}_i, \mathbf{r})|^2 \right) = \frac{1}{N_{\mathbf{R}}} \sum_{\mathbf{R}} \sum_{\mathbf{R}'} \sum_{i=1}^N w_i A_{\mathbf{R}-\mathbf{R}'}(\mathbf{k}_i) w_j^*(\mathbf{r}-\mathbf{R}') w_j(\mathbf{r}-\mathbf{R})$$

$$\tilde{n}_j(\mathbf{r}) = n(\mathbf{r}) + \frac{1}{N_{\mathbf{R}}} \sum_{\mathbf{R}} \sum_{\mathbf{R}', |\mathbf{R}-\mathbf{R}'| > C_M} \left(\sum_{i=1}^N w_i A_{\mathbf{R}-\mathbf{R}'}(\mathbf{k}_i) \right) w_j^*(\mathbf{r}-\mathbf{R}') w_j(\mathbf{r}-\mathbf{R})$$

**Error of integration scheme = overlap of Wannier functions with distance $> C_M$.
Even faster convergence (due to the more localized atomic orbitals) for total charge density.**

... And Why Metals Need Much More k-Points

Metals: partially filled bands; k-points have to sample the shape of the Fermi surface.

$$n(\mathbf{r}) = \sum_j \int_{\Omega_{\text{BZ}}} f_{\text{F}} \left(\frac{\varepsilon_j(\mathbf{k}) - \mu}{k_{\text{B}}T} \right) |\psi_j(\mathbf{k}, \mathbf{r})|^2 \frac{d^3\mathbf{k}}{\Omega_{\text{BZ}}}$$

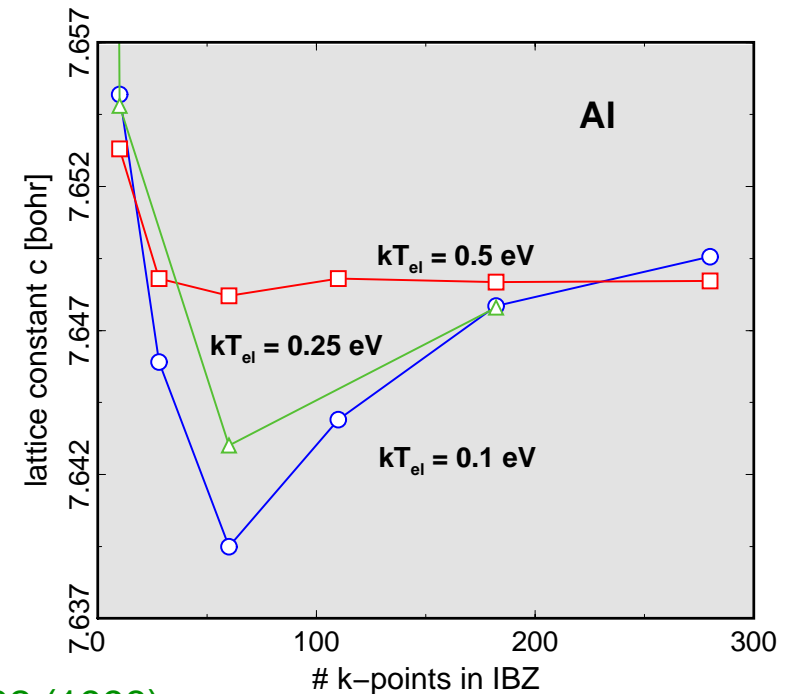
"Smearing" of Fermi surface in order to improve convergence with number of k-points, e.g. by choosing an artificially high electron temperature (0.1 eV).

Extrapolate to zero temperature by averaging the free energy A and the inner energy E :

$$A(T) = E_0 - \frac{1}{2}\gamma T^2 + \dots$$

$$E(T) = E_0 + \frac{1}{2}\gamma T^2 + \dots$$

$$E_0 \approx (A(T) + E(T))/2$$



M. Lindenblatt, E.P.

- Respective corrections to the forces. F. Wagner, Th. Laloyaux, M. Scheffler, Phys. Rev. B 57, 2102 (1998).
- For some quantities and materials "smearing" can lead to serious problems. M.J. Mehl, Phys. Rev. B 61, 1654 (2000).

Summary: The Plane-Wave Pseudopotential Method

- (1) Born-Oppenheimer approximation
- (2) apply density-functional theory (DFT) to calculate the electronic structure;
 - approximation for the exchange-correlation energy-functional (LDA, GGA, ...)
 - approximate treatment of spin effects (LSDA, ...)
- (3) construct **pseudopotentials**: get rid of core electrons
 - frozen-core approximation
 - non-linear core-valence exchange-correlation
 - transferability of the pseudopotential
- (4) specify atomic geometry, e.g. slab and periodically repeated **supercells**
 - convergence with cell size (cluster size)
- (5) **plane-wave basis-set**: unbiased, no basis-set corrections to the forces, switch between real space and reciprocal space via FFT
 - convergence of total-energy differences with kinetic-energy cut-off
- (6) Brillouin-zone integrals approximated by sums over **special k-points**
 - check the convergence with number of k-points and Fermi-surface smearing (different for semiconductors/insulators and metals!)