The Plane-Wave Pseudopotential Method

*Eckhard Pehlke, Institut für Theoretische Physik und Astrophysik,
Christian-Albrechts-Universität zu Kiel, 24098 Kiel, 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

Treatment of electron-electron interaction

Hartree-Fock (HF)

Configuration-Interaction (CI)

Quantum Monte-Carlo (QMC)

Density-Functional Theory (DFT)

$$E_v[n] = T_0[n] + \int v(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}$$

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

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

$$(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{\mathrm{XC}}(\mathbf{r}))\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

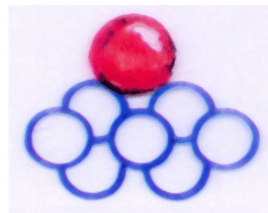
$$n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2 \,, \qquad v_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[n]}{\delta n(\mathbf{r})}$$

Problem: Approximation to XC functional.

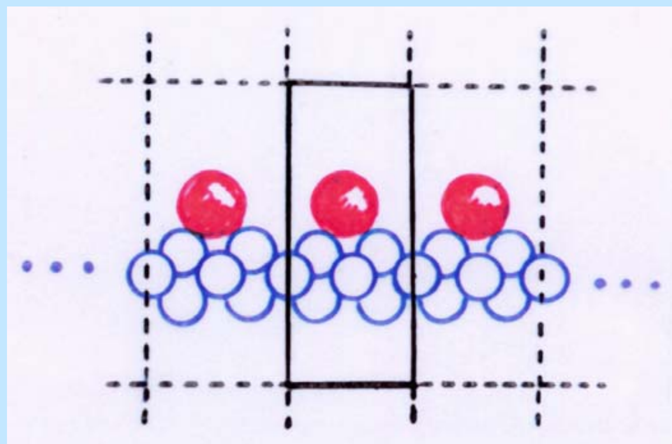
Simulation of Atomic Geometries

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

single molecule or cluster



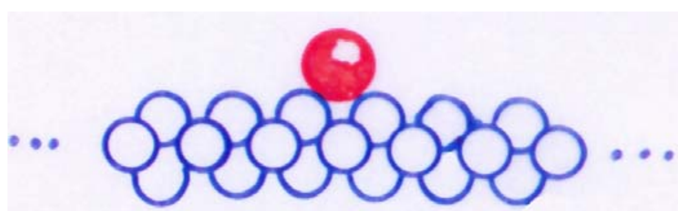
periodically repeated supercell, slab-geometry



Use Bloch theorem.

Efficient Brillouin zone integration schemes.

true half-space geometry, Green-function methods



Basis Set to Expand Wave-Functions

linear combination of atomic orbitals (LCAO)

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

$$\psi(\mathbf{k},\mathbf{r}) = \sum_{\mu,\tau} c_{\mu\tau}(\mathbf{k}) \; \phi_{\mu\tau}(\mathbf{k},\mathbf{r})$$

plane waves (PW)

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

simple, unbiased, independent of atomic positions

augmented plane waves (APW) . . .

and other basis functions

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 <-> fcc Mo, transformation energy 0.5 eV/atom

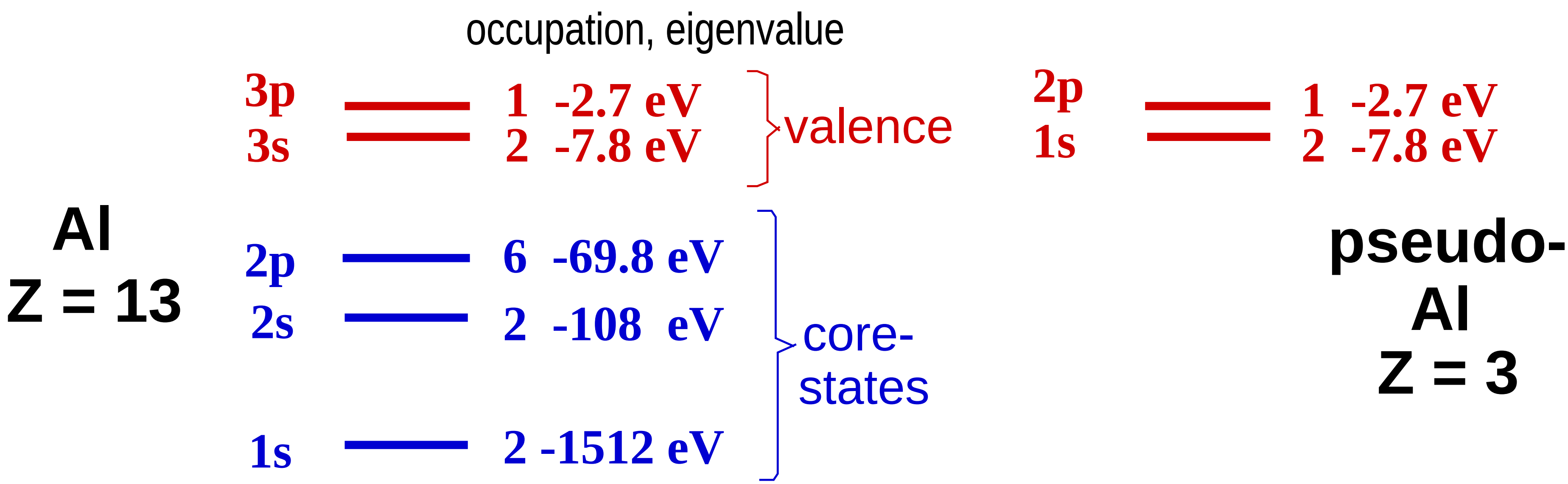
core kinetic energy change of 2.7 eV

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



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

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

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)

Al

3p	1	-2.7 eV	valence
3s	2	-7.8 eV	
2p	6	-69.8 eV	core-states
2s	2	-108 eV	
1s	2	-1512 eV	

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

pseudo-Al

2p	1	-2.7 eV
1s	2	-7.8 eV

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

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

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

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

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

Pseudopotentials and Pseudo-wavefunctions

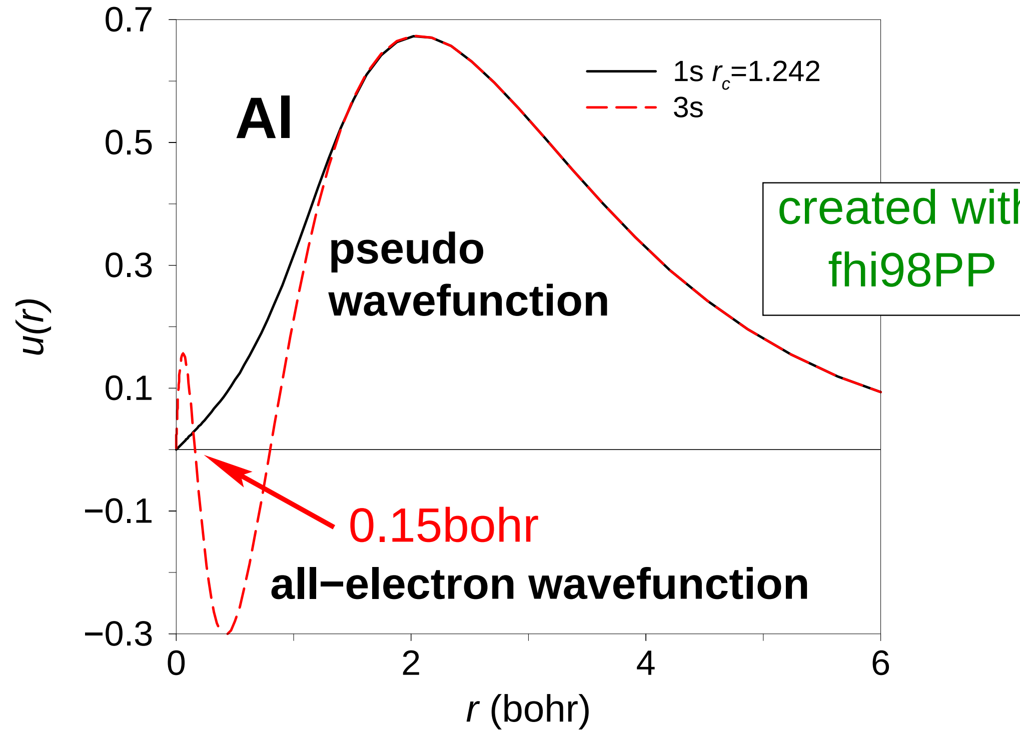
- Pseudopotentials are softer than all-electron potentials. (Pseudopotentials do not have core-eigenstates.)

- **Cancellation Theorem:**

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

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

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_{total} = -2096 H	~ 10^5 H
pseudo-atom: (Z' = 4)	E_{total} = -3.8 H	~ 10^2 H
typical structural total-energy difference: (dimer buckling,...)		few 100 meV ~ 10^{-2} 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)

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

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

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

Electron density follows from sum over all occupied states:

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

(for semiconductors)

Kohn-Sham equation in reciprocal space:

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

Hohenberg-Kohn Functional in Momentum Space

Total-energy functional:

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

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

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

Define valence charge difference wrt. above Gaussian charge density:

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

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

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

Hohenberg-Kohn Functional in Momentum Space (continued)

- kinetic energy:

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

- 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:

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

- exchange-correlation energy:

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

- 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:

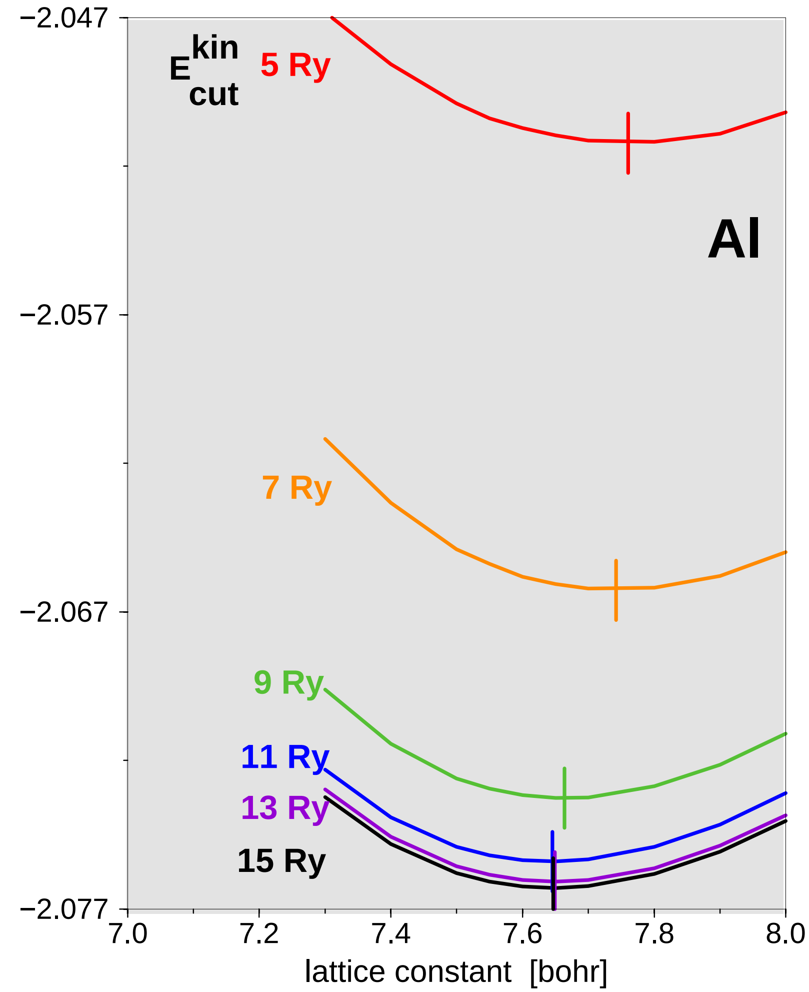
$$\psi_{j,\mathbf{k}}(\mathbf{G}) \longrightarrow (v_{\text{loc}}\ \psi_{j,\mathbf{k}})(\mathbf{G})$$

FFT ↓ $\qquad$ ↑ FFT^{-1}

$$\psi_{j,\mathbf{k}}(\mathbf{r}_n) \xrightarrow{\text{mult.}} v_{\text{loc}}(\mathbf{r}_n)\ \psi_{j,\mathbf{k}}(\mathbf{r}_n)$$

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:

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

(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 $\bar{f} = \int_{\Omega_{\mathrm{BZ}}} f(\mathbf{k}) \frac{d^3\mathbf{k}}{\Omega_{\mathrm{BZ}}}$ with

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

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

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

Choose special points k_i (i=1, ..., N) and weights w_i such that

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

for M as large as possible. The real-space vectors R_m are assumed to be ordered according to their length.

Then:

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

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
$(\frac{1}{20}\ \frac{3}{20})\ (\frac{3}{20}\ \frac{9}{20})\ (\frac{5}{20}\ \frac{5}{20})$ $(\frac{7}{20}\ \frac{1}{20})\ (\frac{9}{20}\ \frac{7}{20})$	$\frac{1}{5}\ \frac{1}{5}\ \frac{1}{5}\ \frac{1}{5}\ \frac{1}{5}$	5	16

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

Monkhorst-Pack Special k-Points

Equally spaced k-point mesh in reciprocal space:

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

and

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

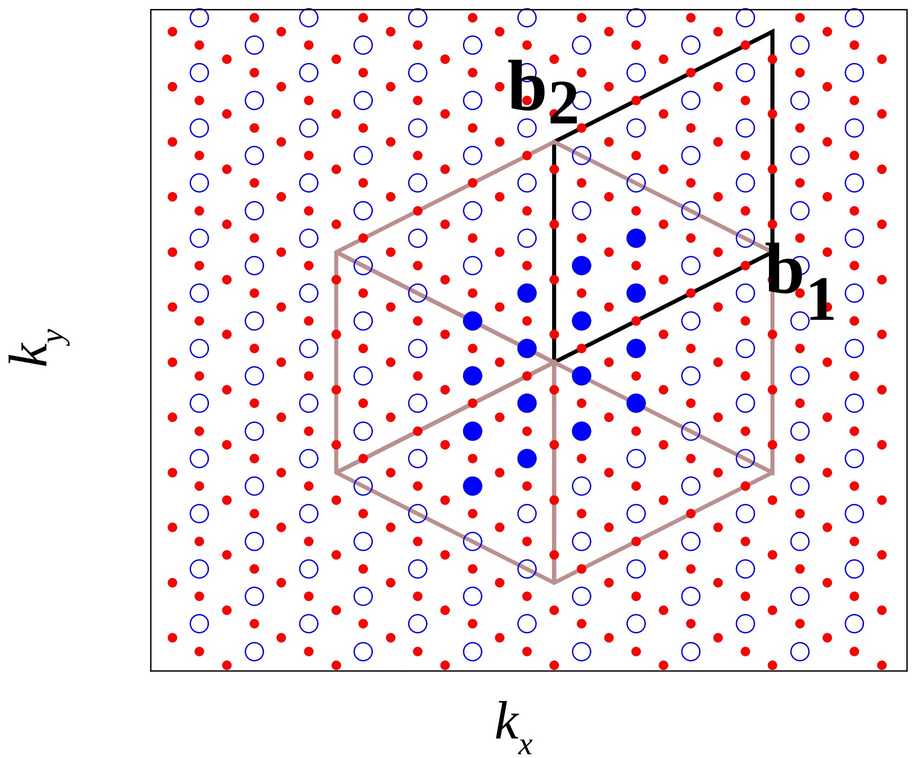
Restrict k-point set to points in the irreducible part of the Brillouin zone.
Weight of each point ~ number of points in the star of the respective wave vector:

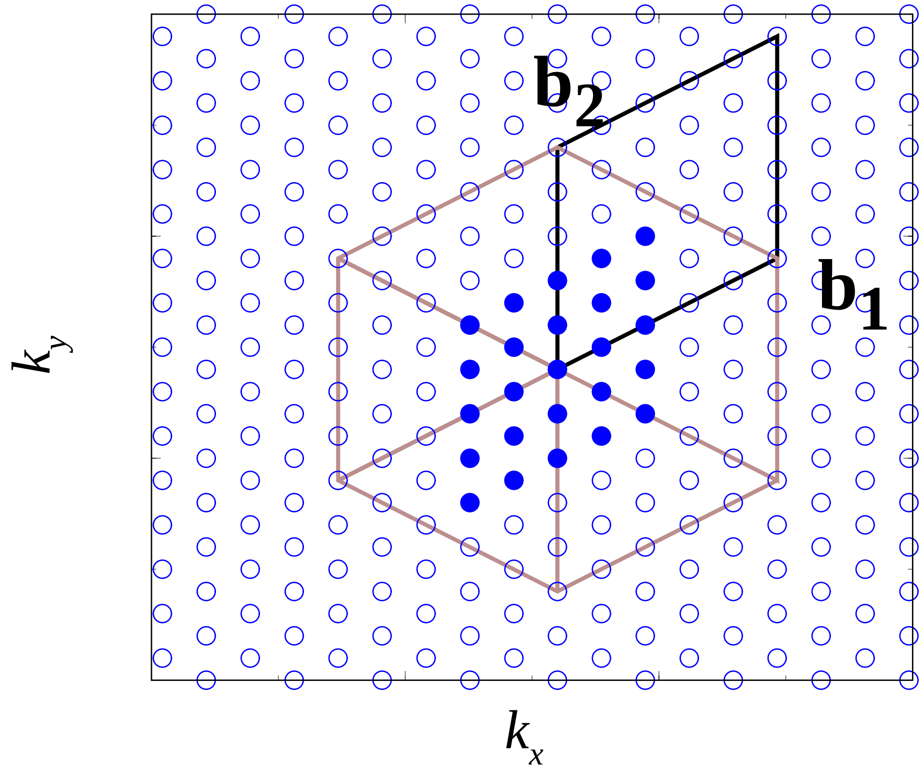
Weights:

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

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

Special k-Points for 2D Hexagonal Lattice





attention: even q (q=4)

incomplete k-point mesh

q=5 (MP)

J.D. Pack, H.J. Monkhorst, PRB 16, 1748 (1977).

Why Few k-Points Already Work Fine for Semiconductors

Semiconductors and insulators: always integrate over complete bands!

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

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

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.

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

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

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

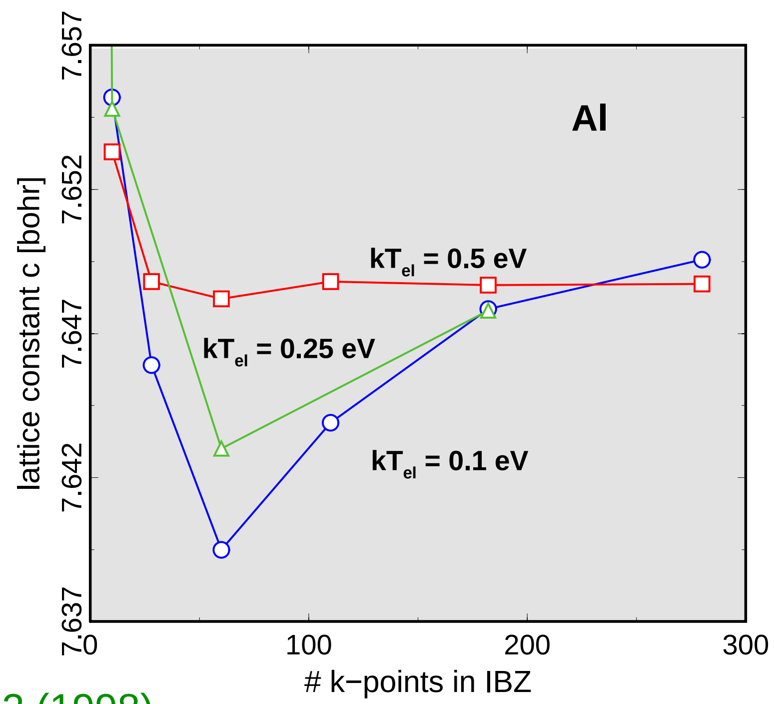
$$n(\mathbf{r}) = \sum_j \int_{\Omega_{\rm BZ}} f_{\rm F}\left(\frac{\varepsilon_j(\mathbf{k}) - \mu}{k_{\rm B}T}\right) \; |\psi_j(\mathbf{k},\mathbf{r})|^2 \, \frac{d^3\mathbf{k}}{\Omega_{\rm BZ}}$$

"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:

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

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



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!)