

Advanced DFT for solids

**Reminders about planewaves and Brillouin zone sampling.
Pseudopotentials, PAW and other basis sets**

Lecture 2

Alexander Kvashnin

30.03.2023

Plan of the lecture

- Wave function of electron in periodic potential
 - Bloch's theorem
 - Energy bands in solids
- Brillouin zone
 - Sampling
- The Orthogonalized Plane-Wave Method
- Pseudopotentials
- Projector-Augmented Waves
 - The idea
 - The math

Plan of the lecture

- **Wave function of electron in periodic potential**
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Wave function of electron in periodic potential

There is **no** mechanism in the model of free electron that takes into account the **interaction of electrons with the crystal lattice**

This model **cannot explain** why some compounds are **metals** and some are **semiconductors**

We need to move to a **more complex representation** describing the interaction of electrons with the lattice, which will affect the type of wave function, etc.

Wave function of electron in periodic potential

Let us introduce several simplifying definitions

1. In the motion of electrons, atomic nuclei are considered as **stationary sources** of the field acting on the electron
2. Ions are **located precisely** at the nodes of a **perfect crystal lattice** (no thermal vibrations)
3. **Interaction of electrons** with each other and with fields of atomic nuclei is replaced by an **effective field**: it is considered that there is a system of independent electrons moving in some given field (one-electron problem)

Wave function of electron in crystal

Let us denote the potential energy of the electron in the crystal field as $U(\vec{r})$

Then it should be a periodic function of the distance $U(\vec{r}) = U(\vec{r} + \vec{a}_n)$

where \vec{r} is the arbitrary radius vector, \vec{a}_n is the translation vector

The wave function and energy levels must satisfy the **Schrödinger equation**

$$\hat{H}\psi = \varepsilon\psi$$

where the energy operator (Hamiltonian) contains both potential and kinetic energy

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\vec{r})$$

The differential momentum operator in the three-dimensional case has the form

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{p}_y = -i\hbar \frac{\partial}{\partial y}$$

$$\hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

$$\hat{p} = -i\hbar \nabla$$

Wave function of electron in crystal

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U(\vec{r})\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

The dependence of the electron wave function on spin **is not taken into account** here

Physical meaning of the wave function? $|\psi(\vec{r})|^2 dV$

The probability of detecting an electron in a volume of space dV

If we take the integral over the entire space

$$\frac{1}{V} \int_V |\psi(\vec{r})|^2 dV = 1$$

Normalization condition of the wave function

Let's substitute the argument of the wave function in

$$\vec{r} \rightarrow \vec{r} + \vec{a}_n$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r} + \vec{a}_n) + U(\vec{r})\psi(\vec{r} + \vec{a}_n) = \varepsilon\psi(\vec{r} + \vec{a}_n)$$

Wave function of electron in crystal

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r} + \vec{a}_n) + U(\vec{r})\psi(\vec{r} + \vec{a}_n) = \varepsilon\psi(\vec{r} + \vec{a}_n)$$

Function $\psi(\vec{r} + \vec{a}_n)$ will satisfy the Schrödinger equation with the same energy value if

$$\psi(\vec{r} + \vec{a}_n) = C_n\psi(\vec{r})$$

The wave functions differ by some number

From the normalization condition of the wave function $|C_n|^2 = 1$ and $|\psi(\vec{r} + \vec{a}_n)|^2 = |\psi(\vec{r})|^2$

Means equal probability of detecting an electron both at a point with radius vector \vec{r} , and with $\vec{r} + \vec{a}_n$

The distribution of electrons has a spatial periodicity

Adding to the vector \vec{a}_n some vector $\vec{a}_{n'} = n'_1a_1 + n'_2a_2 + n'_3a_3$ will have

$$\psi(\vec{r} + \vec{a}_n + \vec{a}_{n'}) = C_nC_{n'}\psi(\vec{r})$$

In addition, it is obvious that $\vec{a}_n + \vec{a}_{n'} = \vec{a}_{n+n'}$ then

$$\psi(\vec{r} + \vec{a}_n + \vec{a}_{n'}) \equiv \psi(\vec{r} + \vec{a}_{n+n'}) = C_{n+n'}\psi(\vec{r})$$

Wave function of electron in crystal

Then $C_{n'}C_n = C_{n+n'}$

This relationship is satisfied by values of the form $C_n = \exp(i\vec{k}\vec{a}_n)$

Then we can rewrite the expression for the electron wave function

$$\psi(\vec{r} + \vec{a}_n) = \exp(i\vec{k}\vec{a}_n)\psi(\vec{r})$$

Multiply both parts by $\exp(-i\vec{k}(\vec{r} + \vec{a}_n))$

$$\exp(-i\vec{k}(\vec{r} + \vec{a}_n)) \cdot \psi(\vec{r} + \vec{a}_n) = \exp(i\vec{k}\vec{r})\psi(\vec{r})$$

Let's introduce the notation

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{a}_n) = \exp(-i\vec{k}(\vec{r} + \vec{a}_n)) \cdot \psi(\vec{r} + \vec{a}_n)$$

We obtain a very important relation - **Bloch's theorem**

$$\psi(\vec{r}) = \exp(i\vec{k}\vec{r})u_{\vec{k}}(\vec{r})$$

Wave function of electron in crystal

According to Bloch's theorem

The wave function of an electron moving in a periodic field of an intracrystalline potential is a modulated plane wave, so it is the product of the wave function of a free electron by the amplitude that varies periodically in the crystal

$$\psi(\vec{r}) = \exp(i\vec{k}\vec{r})u_{\vec{k}}(\vec{r})$$

If the electron is free, then $U(\vec{r}) = 0$, and $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = \varepsilon\psi(\vec{r})$



And the wave function will have the well-known form

$$\psi(\vec{r}) = \exp(i\vec{k}\vec{r}) \leftarrow \text{Plane wave}$$

\vec{k} is a wave vector, which is related to the momentum

$$\vec{p} = m\vec{v} = \hbar\vec{k}$$

Important

The de Broglie wave momentum characterizes the motion of a free electron when the system of electrons in the space is invariant with respect to a shift by any vector (all points in space are equivalent)

The quasi-wave vector characterizes the motion of an electron in a periodic field when the system of electrons in the space of the crystal is invariant with respect to the shift on the lattice vectors and

Analyzing this, we can conclude that the wave function of the electron must be invariant with respect to replacement

$$\vec{k} \rightarrow \vec{k} + \vec{G}$$

arbitrary vector of reciprocal space

The quasi-wave vector is defined with exactness to an arbitrary vector of the reciprocal lattice.

This allows one to restrict the change of vector components to a finite region that exhausts all physically non-equivalent values:

$$-\pi \leq k_1 a_1 \leq \pi$$

$$-\pi \leq k_2 a_2 \leq \pi$$

$$-\pi \leq k_3 a_3 \leq \pi$$

Define the volume of k-space, called as **first Brillouin zone**

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- **Brillouin zone**
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Brillouin zone

From Ewald construction, diffraction occurs when

$$\vec{k}' = \vec{k} + \vec{G}$$

If we square both sides of the equation:

$$\vec{k}' \cdot \vec{k}' = (\vec{k} + \vec{G})^2 \rightarrow \vec{k}'^2 = \vec{k}^2 + \vec{G}^2 + 2\vec{k} \cdot \vec{G}$$

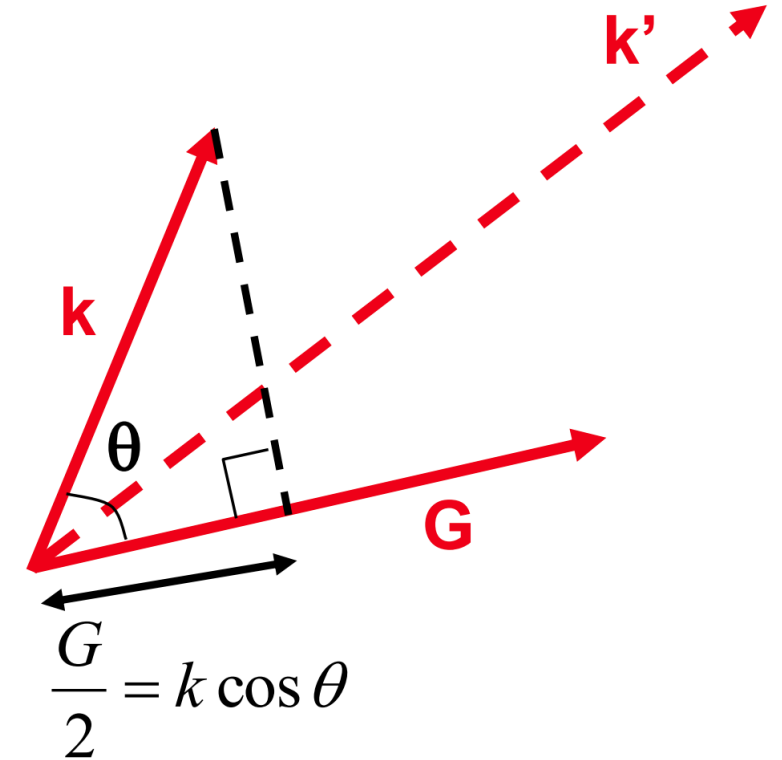
If scattering is inelastic, then $\vec{k}' \neq \vec{k}$

Hence $\vec{G}^2 = -2\vec{k} \cdot \vec{G} = \underbrace{2\vec{k} \cdot \vec{G}}_{\text{red bracket}} = 2kG\cos\theta$

If \vec{G} is a lattice vector, then so is $-\vec{G}$!

$$k\cos\theta = \frac{G}{2}$$

i.e. diffraction condition is satisfied if \vec{k} lies in the plane that perpendicularly bisects \vec{G}



1st Brillouin zone

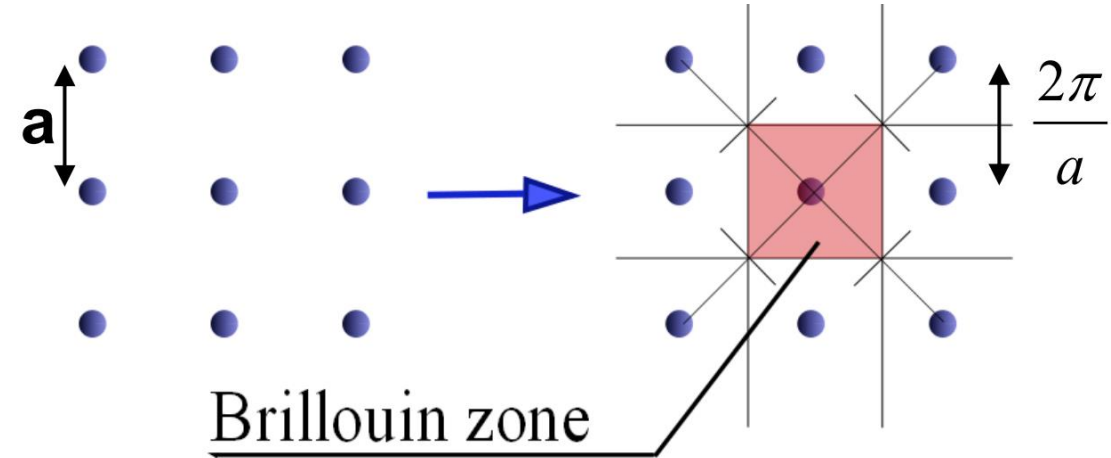
We define the “Brillouin Zone” as the boundary in the reciprocal lattice where scattering will occur

A Brillouin Zone is a primitive unit cell in reciprocal space (c.f. Wigner-Seitz cell in real space)

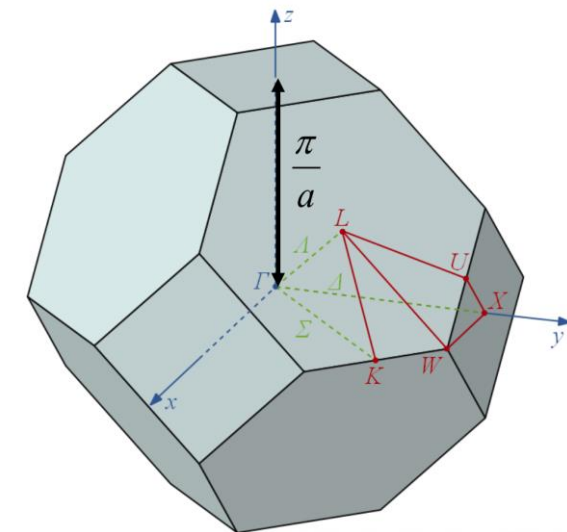
The Brillouin zone describes the behavior of the entire crystal, e.g. how electrons are influenced by the periodicity of the crystal (Bloch Waves) with implications for:

- electrical conduction
- light emission/absorption
- etc.

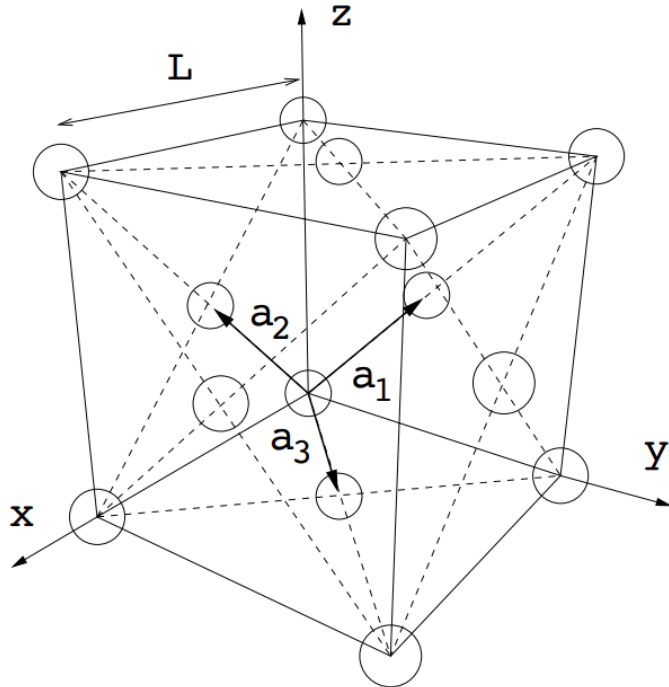
First Brillouin Zone for a square lattice



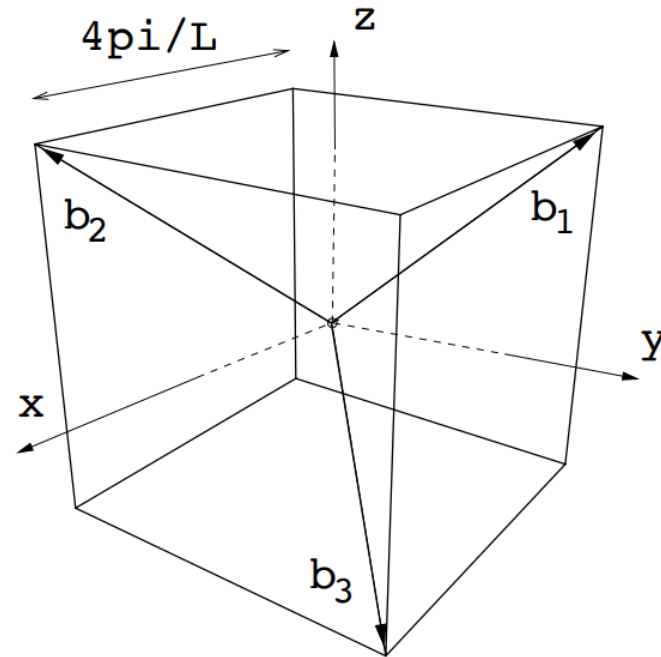
First Brillouin Zone for a fcc lattice in 3D



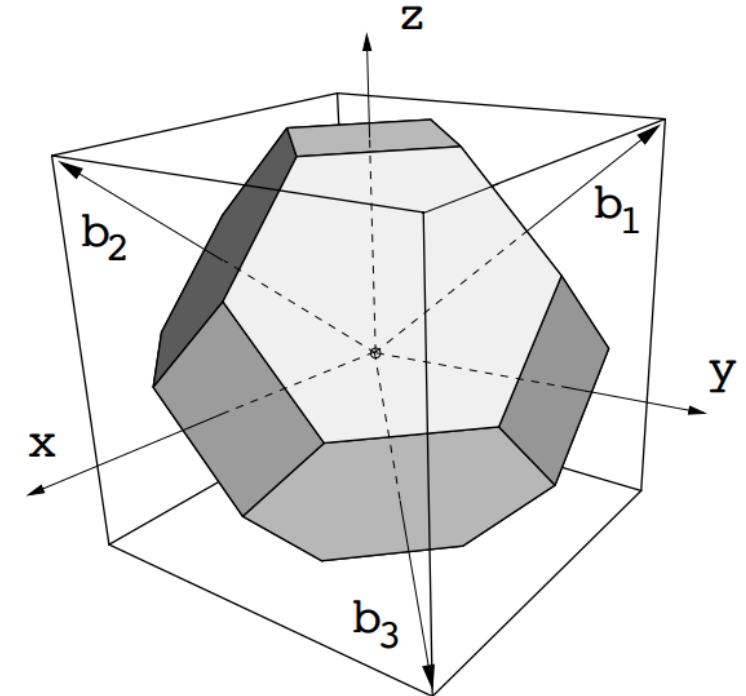
1st Brillouin zone



Real space



Reciprocal space



1st Brillouin zone
in reciprocal space

$$\mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{b}_2 = \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1 \quad \mathbf{b}_3 = \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2$$

$$\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \quad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

Sampling the 1st Brillouin zone

The evaluation of many key quantities involves an integral over the 1st BZ.

For instance, the charge density:

$$\rho(\vec{r}) = \frac{1}{\Omega_{BZ}} \sum_n \int_{BZ} f_{n,\vec{k}} |\Psi_{n,\vec{k}}(\vec{r})|^2 d\vec{k}$$

is the occupation of the state \vec{k} in the band n

We exploit the fact that the orbitals at Bloch vectors \vec{k} that are close together are almost identical and approximate the integral over the 1st BZ by a weighted sum over a discrete set of k-points:

$$\rho(\vec{r}) = \sum_n \omega_{\vec{k}} f_{n,\vec{k}} |\Psi_{n,\vec{k}}(\vec{r})|^2$$

The intractable task of determining $\Psi(\vec{r}_1 \dots \vec{r}_N)$ with $N = 10^{23}$ has been reduced to calculating $\Psi_{n,\vec{k}}$ at a discrete set of k-points in the 1st Brillouin zone, for a number of bands that is of the order of the number of electrons in the unit cell

Clearly, as the number of k-points increases, the sum approximates the "true" value of the above integral to a greater accuracy.

Sampling the 1st Brillouin zone

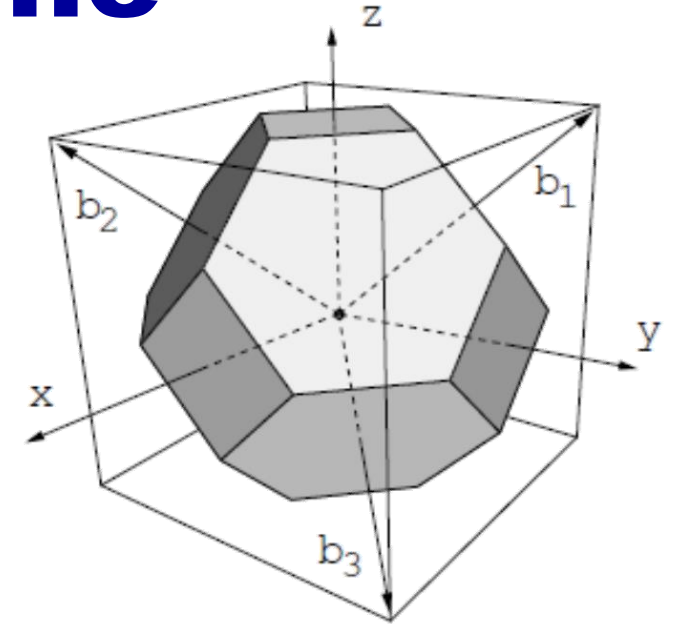
Good idea is the mesh with equally spaced points in the 1st BZ

$$\vec{k}_{prs} = u_p \vec{b}_1 + u_r \vec{b}_2 + u_s \vec{b}_3$$

Reciprocal lattice vectors

$$u_r = \frac{2r - q_r - 1}{2q_r} \quad r = 1, 2, \dots, q_r$$

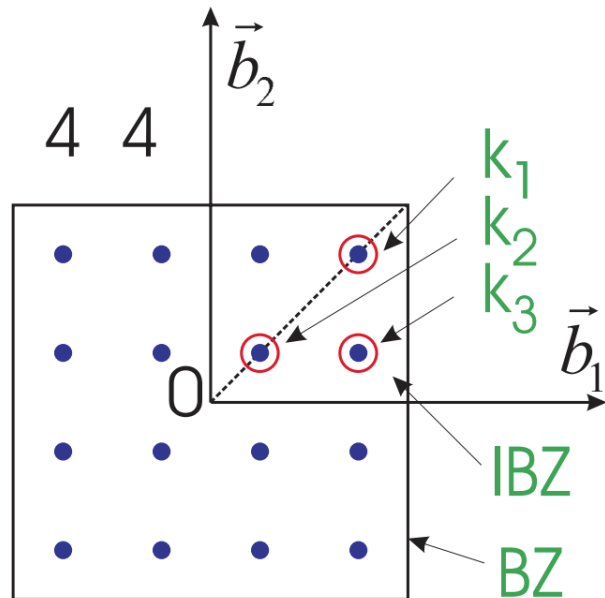
determines number of k-points in r-direction



Example: a quadratic 2D lattice

$q_1 = q_2 = 4$, i.e. 16 points in total

Only 3 symmetry inequivalent points:



$$4 \times \vec{k}_1 = \left(\frac{1}{8}, \frac{1}{8} \right) \Rightarrow \omega_1 = \frac{1}{4}$$

$$4 \times \vec{k}_2 = \left(\frac{3}{8}, \frac{3}{8} \right) \Rightarrow \omega_1 = \frac{1}{4}$$

$$4 \times \vec{k}_3 = \left(\frac{3}{8}, \frac{1}{8} \right) \Rightarrow \omega_1 = \frac{1}{2}$$

$$\begin{aligned} \frac{1}{\Omega_{BZ}} \int_{BZ} F(\vec{k}) d\vec{k} &= \\ &= \frac{1}{4} F(\vec{k}_1) + \frac{1}{4} F(\vec{k}_2) + \frac{1}{2} F(\vec{k}_3) \end{aligned}$$

Sampling the 1st Brillouin zone

Algorithm

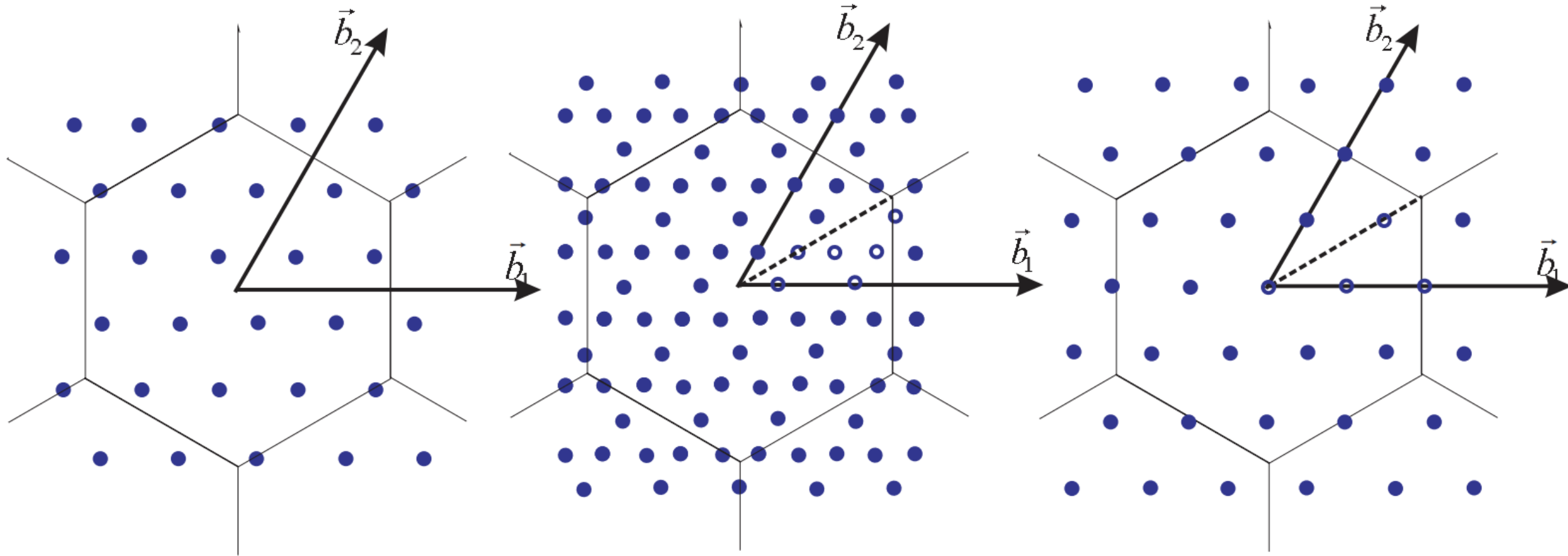
Calculate equally spaced mesh.

- Shift the mesh if desired.
- Apply all symmetry operations of the Bravais lattice to all k-points.
- Extract the irreducible k-points (IBZ).
- Calculate the proper weighting.

Common meshes

- Centered on Γ
- Centered around Γ (can break the symmetry!)

Sampling the 1st Brillouin zone



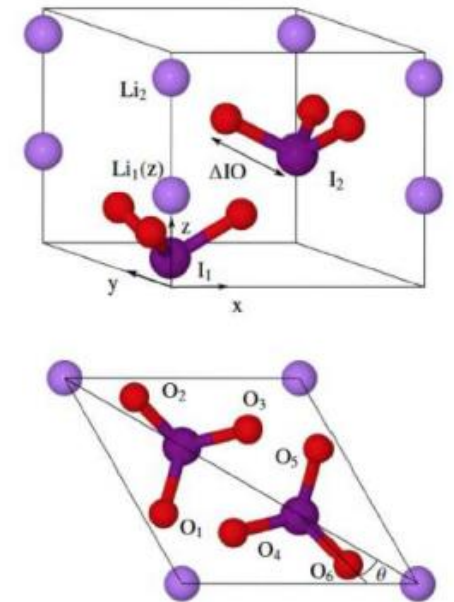
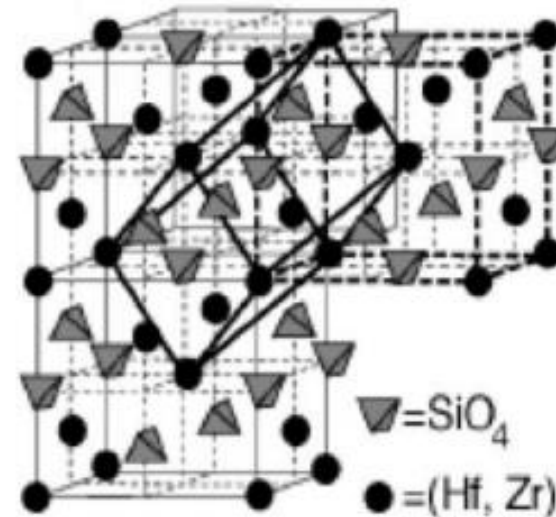
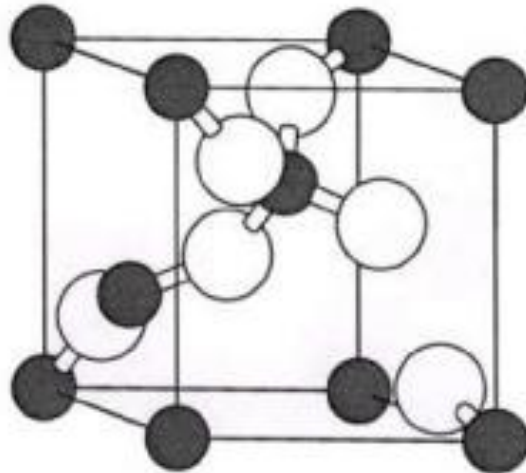
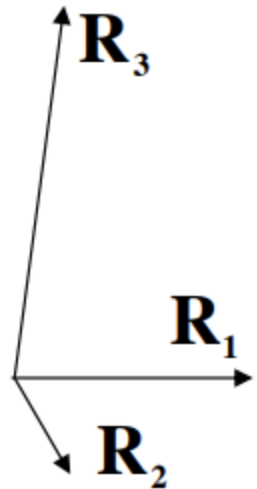
In certain cell geometries (e.g. hexagonal cells) even meshes break the symmetry.

- Symmetrization results in non-uniform distributions of k-points.
- Γ -point centered meshes preserve the symmetry

Materials : infinite extent, periodicity

Periodicity is very important, otherwise it will be not possible to consider infinite number of atoms

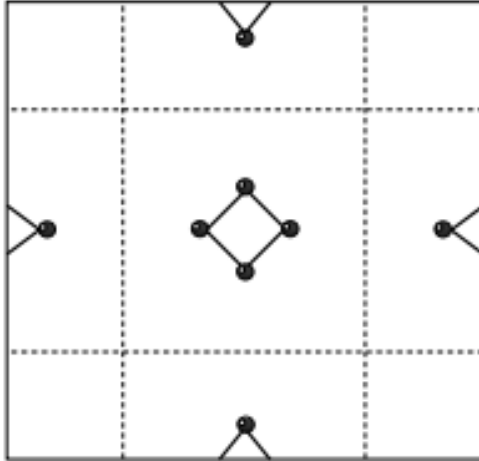
For this purpose, the **primitive vectors** and **periodic boundary conditions** are defined



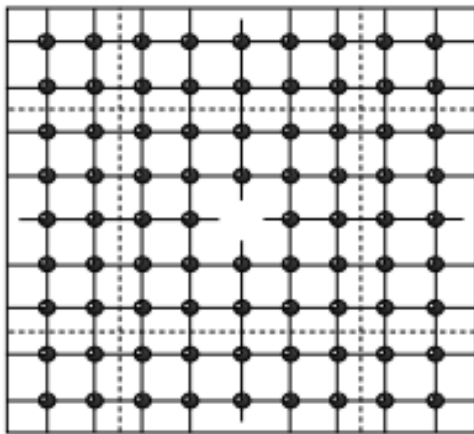
OK for crystalline solids

But: finite systems, surfaces, defects, polymers, nanosystems ... ?

Solution : the supercell technique

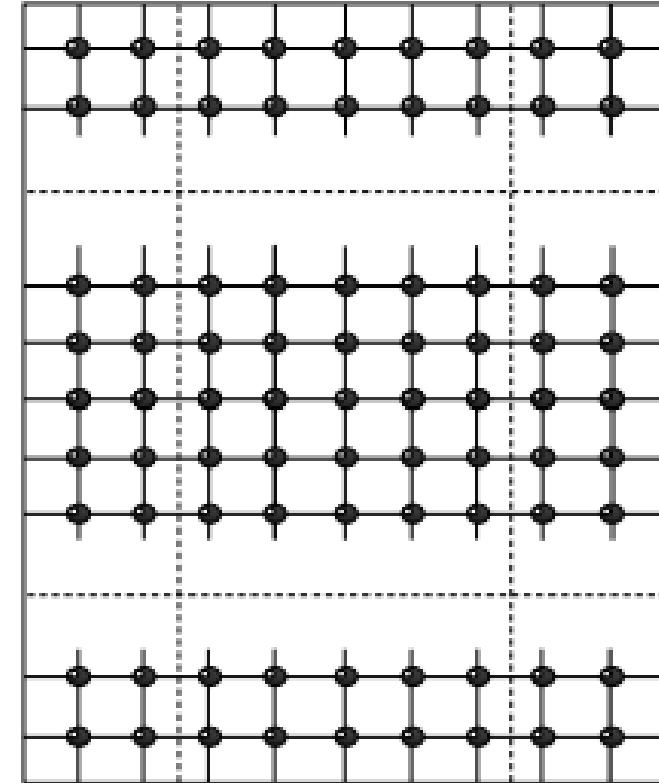


Atom,
molecule,
cluster



Point defect in
a bulk solid

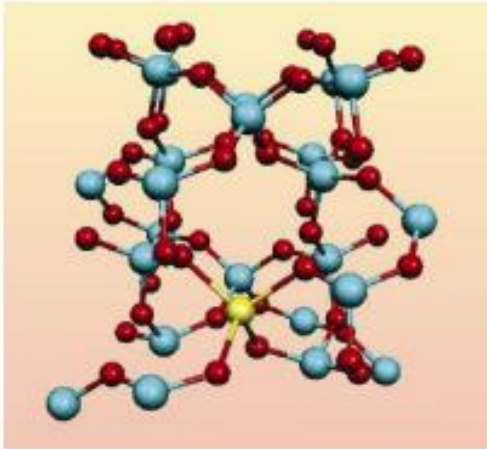
Surface:
treatment of a
slab interface



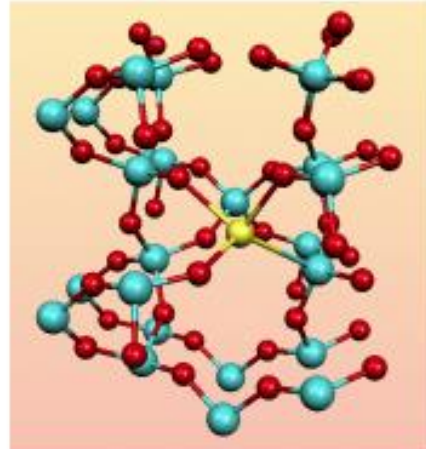
The supercell must be sufficiently big : convergence study

Examples of defects SiO₂-quartz

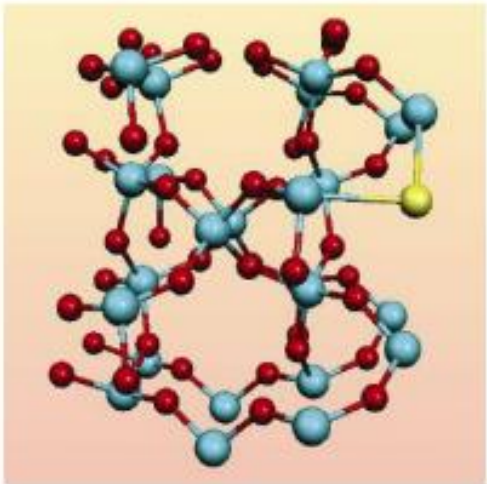
72-atom supercell of quartz



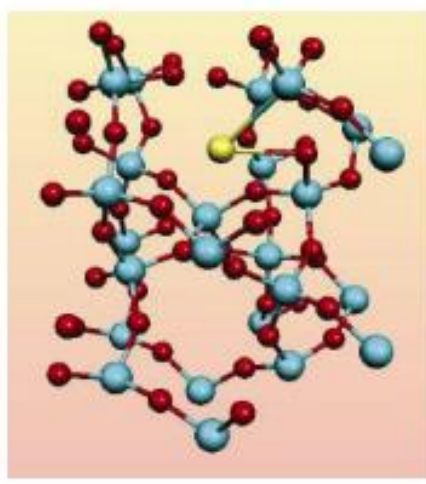
Pb^{Si}



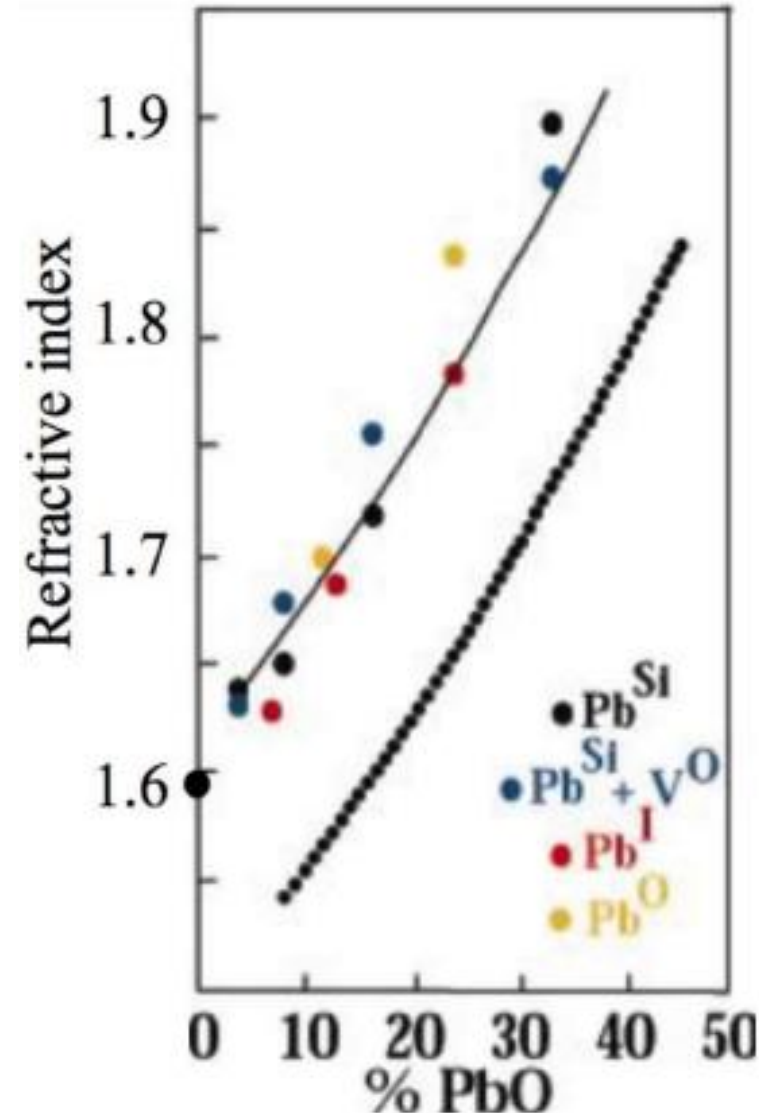
Pb^{Si} + V^O



Pb^O



Pb^I



Comparison with
amorphous SiO₂

Periodic system : wavevectors

For a periodic Hamiltonian : wavefunctions characterized by a wavevector k (crystal momentum) in Brillouin Zone

Bloch theorem in another form $\Psi_{n,\vec{k}}(\vec{r} + \vec{R}_j) = e^{i\vec{k}\vec{R}_j} \Psi_{n,\vec{k}}(\vec{r})$

$$\Psi_{m,\vec{k}}(\vec{r}) = (N\Omega_0)^{-\frac{1}{2}} e^{i\vec{k}\vec{r}} u_{m,\vec{k}}(\vec{r}) \qquad u_{m,\vec{k}}(\vec{r} + \vec{R}_j) = u_{m,\vec{k}}(\vec{r})$$

Bloch wavefunction is periodic function w.r.t. lattice vectors

In this case the Plane waves $e^{i\vec{k}\vec{R}_j}$ are particularly simple and efficient (when used with pseudopotentials), infinite spatial extent

Planewave basis set

Reciprocal lattice : set of \vec{G} vectors such that $e^{i\vec{G} \cdot \vec{R}_j} = 1$ Reciprocal lattice vector
 $e^{i\vec{G} \cdot \vec{r}}$ has the periodicity of the real lattice Compatible with pbc

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{k}}(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

Rebuild the full Bloch wavefunction as

$$\Psi_{\vec{k}}(\vec{r}) = (N\Omega_0)^{-\frac{1}{2}} \sum_{\vec{G}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} u_{\vec{k}}(\vec{G})$$

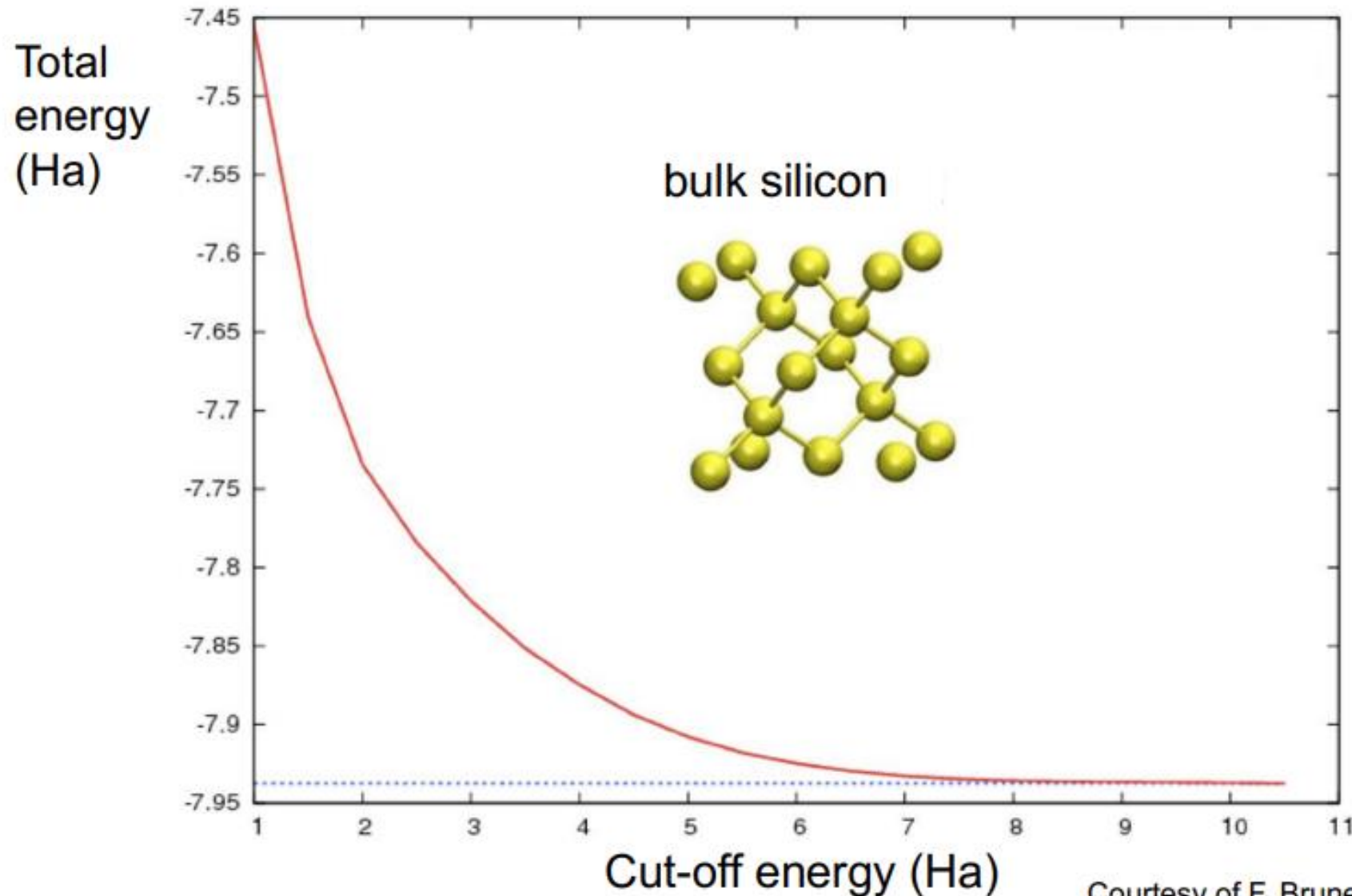
$$u_{\vec{k}}(\vec{G}) = \frac{1}{\Omega_0} \int_{\Omega_0} e^{-i\vec{G} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) d\vec{r} \quad \text{Inverse Fourier transform}$$

Kinetic energy of a plane wave $-\frac{\Delta^2}{2} \rightarrow \frac{(\vec{k} + \vec{G})^2}{2}$

Allows us to perform the finite summation and select the coefficients $u_{\vec{k}}(\vec{G})$ for the lowest eigenvectors decrease exponentially with the kinetic energy

Thus, we select the plane waves with cut-off energy E_{cut} $\frac{(\vec{k} + \vec{G})^2}{2} < E_{cut}$

Convergence w.r.t. to kinetic energy cutoff



Courtesy of F. Bruneval

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The Orthogonalized Plane-Wave Method (OPW)

JUNE 15, 1940

PHYSICAL REVIEW

VOLUME 57

A New Method for Calculating Wave Functions in Crystals

CONYERS HERRING*

Massachusetts Institute of Technology, Cambridge, Massachusetts

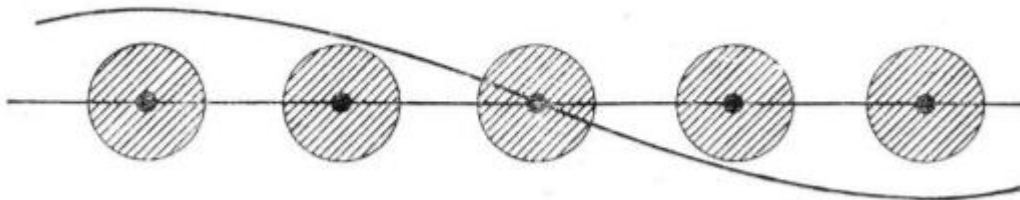
(Received April 8, 1940)

For many problems in the electron theory of metals none of the methods hitherto used to calculate the eigenfunctions and energy values of an electron in a crystal lattice is satisfactory. It is here proposed that these wave functions and energies be calculated by solving a secular equation with wave functions χ_k which are simply plane waves made orthogonal to the core eigenfunctions. The rapidity of convergence to be expected for such a procedure is discussed. Some methods for practical computation are suggested, and expressions are given for the matrix elements occurring in the secular equation.

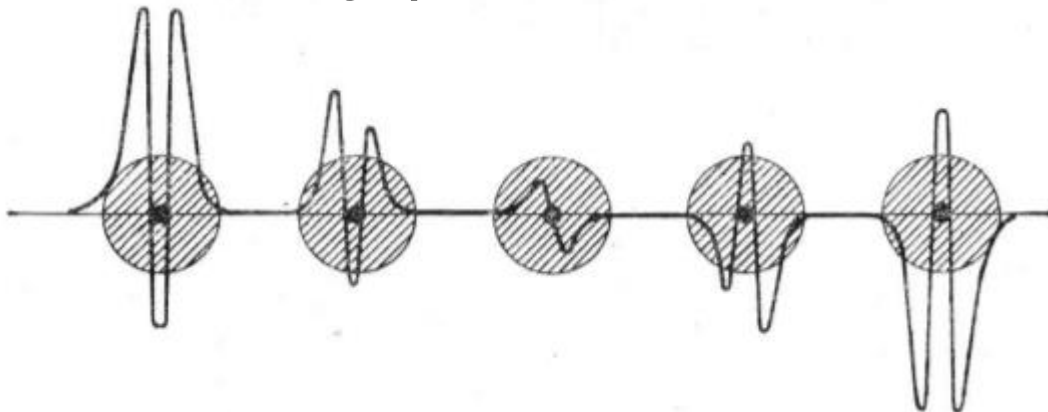
The accuracy and simplicity of calculating the electronic structure of solids depends on the choice of the electron wave function

It is known that near the nucleus the wave function of the electron must oscillate strongly, while away from the nucleus it must take the form of a plane wave with periodic boundary conditions.

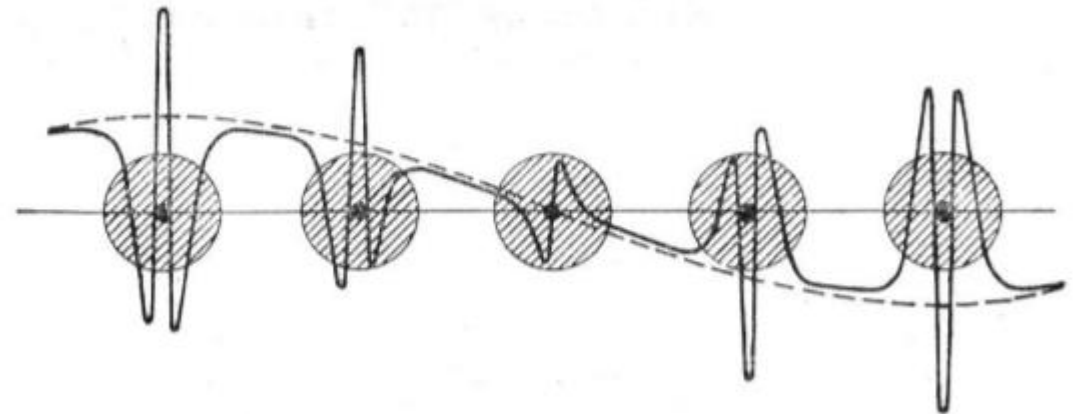
Plane wave



Highly localized states



Orthogonalized plane wave, i.e. a plane wave minus the wave function of a highly localized state



It makes no sense to approximate the wave function of the valence level in all space with a few plane waves, as was done in the method of almost free electrons

This approach does not allow for fast oscillatory behavior in ionic core regions

Herring noted that to account for this behavior, one can use not simple plane waves, but ones that are orthogonal to the wave functions of the ion from the beginning

The $\phi_{\vec{k}}$ orthogonalized wave has the form:

$$\phi_{\vec{k}} = \exp(i\vec{k} \cdot \vec{r}) + \sum_c b_c \psi_{\vec{k}}^c(\vec{r})$$

The indices **c** or **v** will stand for the wave functions referring to the levels of the ions or the valence electrons

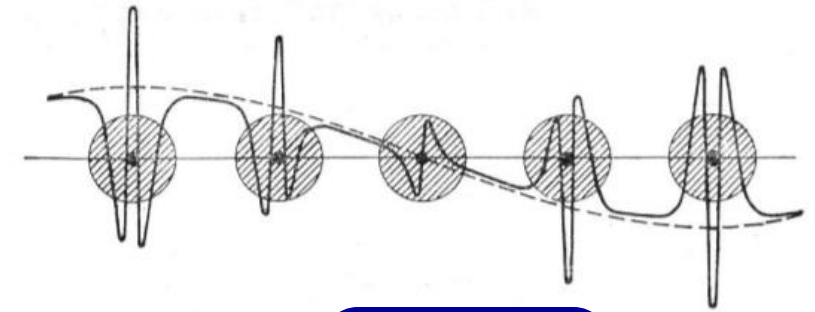


The summation is carried out for **all** levels of the frame with the Bloch wave vector \vec{k}

The wave functions of the ion are usually considered to be known, which can be obtained using the tight-binding method

An orthogonalized plane wave $\phi_{\vec{k}}$ has the following properties that are characteristic of wave functions of valence electrons

1. In its construction, it is orthogonal to all levels of the ions, so it also has the required fast oscillations in the ionic core regions
2. Due to the fact that the levels of the core are localized near the nodes of the lattice, the second term in the expression for OPW is small in the area between the nodes, and there the function is close to a plane wave



$$\phi_{\vec{k}} = \exp(i\vec{k} \cdot \vec{r}) + \boxed{\sum_c b_c \psi_{\vec{k}}^c(\vec{r})} \ll 1$$

Since $\exp(i\vec{k} \cdot \vec{r})$ and $\psi_{\vec{k}}^c(\vec{r})$ satisfy Bloch condition, so $\phi_{\vec{k}}$ does

Therefore, we are looking for a decomposition of real eigenstates for the Schrödinger equation as a superposition of OPW

$$\psi_{\vec{k}} = \sum_{\vec{K}} c_{\vec{K}} \phi_{\vec{k}+\vec{K}}$$

OPW method

The solution of the Schrödinger equation for the Bloch wave functions corresponds to the extremum of this functional

The coefficients $c_{\vec{K}}$ and energies $\varepsilon(\vec{k})$ can be determined by substituting the expansion into the functional

$$E[\psi] = \frac{\int \left(\frac{\hbar^2}{2m} |\nabla \psi(\vec{r})|^2 + U(\vec{r}) |\psi(\vec{r})|^2 \right) d\vec{r}}{\int |\psi(\vec{r})|^2 d\vec{r}}$$

Formula (11.17), page.
205, 1 volume,
Ashcroft, condensed
matter physics

and assuming that all derivatives of this expression are zero for all $c_{\vec{K}}$

The crystal potential enters the resulting eigenvalue problem through its matrix elements by orthogonalized plane waves

$$\int \phi_{\vec{k}+\vec{K}}^{c*}(\vec{r}) U(\vec{r}) \phi_{\vec{k}+\vec{K}'}(\vec{r}) d\vec{r}$$

The efficiency of this method is due to the fact that the matrix elements of the potential U by OPW **are small, while its matrix elements by plane waves are large**

Because of this, the OPW decomposition **converges very quickly**, and it is almost impossible to achieve **convergence over plane waves**

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Pseudopotential (PP)

is a generalization of the OPW method and explains why the calculations by the method of weakly coupled electrons can give a good agreement with the real band structures of some metals

Assume that the exact wave function for the valence level is written as a linear combination of orthogonalized plane waves, similar to the expression

$$\psi_{\vec{k}} = \sum_{\vec{K}} c_{\vec{K}} \phi_{\vec{k}+\vec{K}}$$

Let $\phi_{\vec{k}}^v(\vec{r})$ be a part of this decomposition that includes only plane waves

$$\psi_{\vec{k}}^v(\vec{r}) = \sum_{\vec{K}} c_{\vec{K}} \exp(i(\vec{k} + \vec{K}) \cdot \vec{r})$$

Then the decomposition of the wave function from the OPW method can be rewritten as follows

$$\psi_{\vec{k}}^v(\vec{r}) = \phi_{\vec{k}}(\vec{r}) - \sum_c \left(\int d\vec{r}' \psi_{\vec{k}}^{c*}(\vec{r}') \phi_{\vec{k}}^v(\vec{r}') \right) \psi_{\vec{k}}^c(\vec{r})$$

The analogue of the overlap integral in the tight-binding method

Pseudopotential (PP)

Since $\psi_{\vec{k}}^v(\vec{r})$ represents the exact wave function of the valence level, it satisfies the Schrödinger equation of the following form

$$H\psi_{\vec{k}}^v = \varepsilon_{\vec{k}}^v \psi_{\vec{k}}^v$$

Substituting $\psi_{\vec{k}}^v(\vec{r})$ into the Schrödinger equation we have

$$H\phi_{\vec{k}}^v - \sum_c \left(\int d\vec{r}' \psi_{\vec{k}}^{c*} \phi_{\vec{k}}^v \right) H\psi_{\vec{k}}^c = \varepsilon_{\vec{k}}^v \left(\phi_{\vec{k}}^v - \sum_c \left(\int d\vec{r}' \psi_{\vec{k}}^{c*} \phi_{\vec{k}}^v \right) \psi_{\vec{k}}^c \right)$$

Taking into account that $H\psi_{\vec{k}}^c = \varepsilon_{\vec{k}}^c \psi_{\vec{k}}^c$ for the exact levels of the ionic core, we can write

$$(H + V^R)\phi_{\vec{k}}^v = \varepsilon_{\vec{k}}^v \phi_{\vec{k}}^v$$

where bulky summaries are entered in V^R

$$V^R = \sum_c (\varepsilon_{\vec{k}}^v - \varepsilon_c) \left(\int d\vec{r}' \psi_{\vec{k}}^{c*} \psi \right) \psi_{\vec{k}}^c$$

Pseudopotential (PP)

The result is an effective Schrödinger equation $(H + V^R)\phi_k^v = \varepsilon_k^v \phi_k^v$

which is satisfied by the smooth component of the Bloch wave function ϕ_k^v and can be approximated as a decomposition of a small number of plane waves

Therefore, to solve the Schrödinger equation we can apply the method of weakly bound electrons

The pseudopotential is defined as the sum of the real periodic potential U and the value V^R

$$H + V^R = -\frac{\hbar^2}{2m} \nabla^2 + V^{pseudo}$$

We hope that the pseudopotential will be small enough in the region of valence levels.

The real periodic potential of the ions has an attractive character, so the matrix element

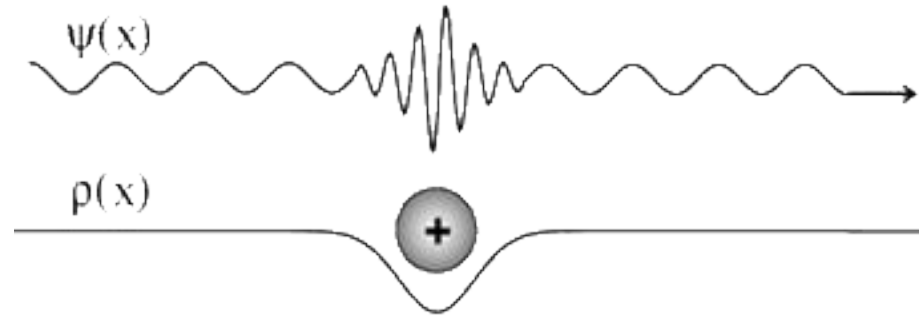
$\langle \psi | U | \psi \rangle = \int d\vec{r} \psi^*(\vec{r}) U(\vec{r}) \psi(\vec{r})$ will be negative

$\langle \psi | V^R | \psi \rangle = \sum_c (\varepsilon_k^v - \varepsilon_c) \left| \int d\vec{r} \psi_k^{c*} \psi \right|^2$ is positive

The energies of the valence levels are always higher than the energies of the core levels

Pseudopotential. Summary

The essence of the pseudopotential theory is to reduce the degree of oscillations of the calculated valence wave functions near the atomic nucleus by some procedure.



Only the valence electrons are calculated, since it is known that most of the physical properties of the system depend on the behavior of the valence electrons

The inner electrons, on the other hand, are assumed to be unchanged, i.e., it is assumed that the behavior of the wave functions of the inner electrons does not change with changes in the external chemical environment of the atom. These electrons will only lead to a change in the effective charge of the ion.

This procedure is equivalent **to replacing the strong electron-ion potential with a weaker pseudopotential**, which determines all explicit properties of valence electrons, including relativistic effects.

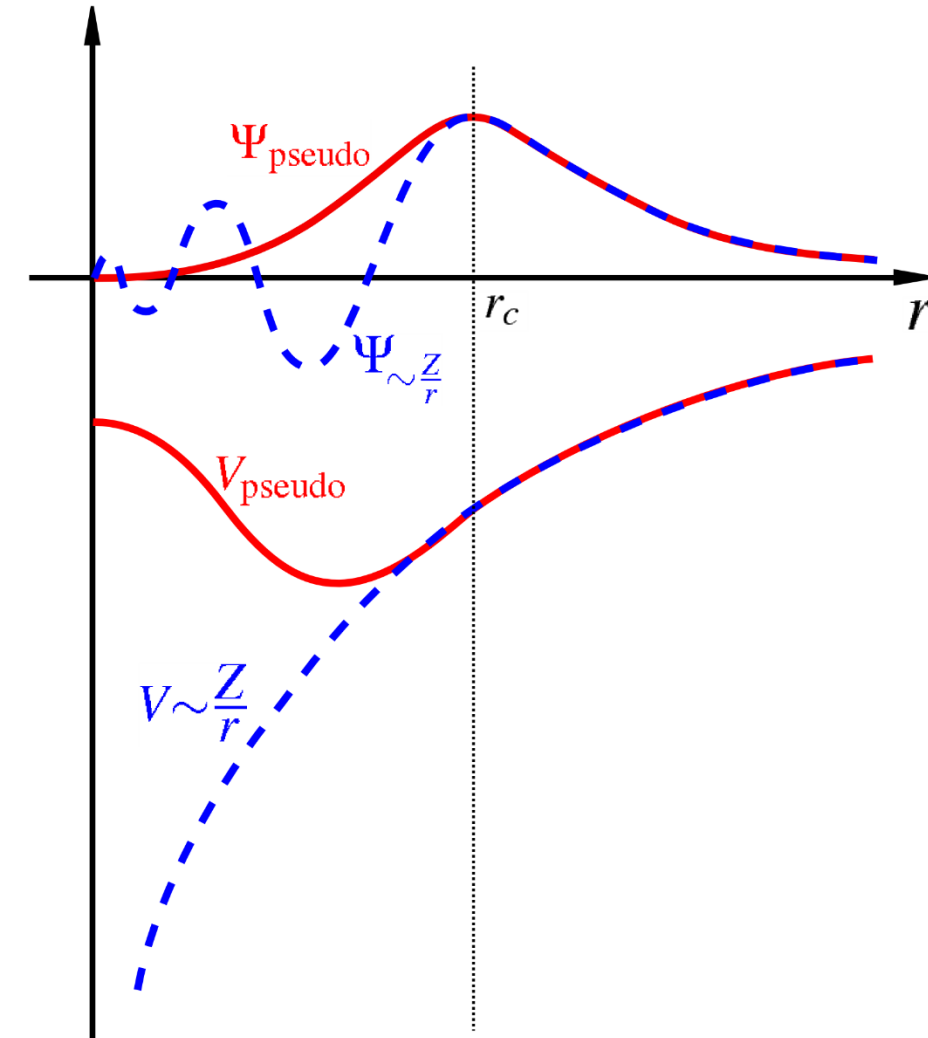
Pseudopotential. Summary

Thus, the studied system is replaced by a system consisting of pseudovalence electrons and pseudo-ions.

The properties of the pseudo-ion are such that its potential outside a certain cutoff radius r_c coincides with the potential of the true ion, but inside this sphere it is much weaker.

Just the weakness of the internal potential is the main thing in the theory of the pseudopotential.

The Schrödinger equation in this case is solved inside a sphere of radius r_c much easier, since the desired wave function is decomposed by a much smaller number of basis functions.



Plan of the lecture

- Wave function of electron in periodic potential
 - Bloch's theorem
 - Energy bands in solids
- Brillouin zone
 - Sampling
- The Orthogonalized Plane-Wave Method
- Pseudopotentials
- **Projector-Augmented Waves**
 - The idea
 - The math

Projector-Augmented Waves: the idea

Idea **P. Blöchl Phys. Rev. B 50, 17953 (1994)**

The true wavefunction and a well-behaving pseudo-wavefunction are linked by a linear transformation

The diagram shows the equation $\Psi = \hat{T} \tilde{\Psi}$. The symbol Ψ is circled in red, with a red arrow pointing to the text "True wavefunction (all electrons)" below it. Above the Ψ is the red text "Strong oscillations near the nucleus". The symbol $\tilde{\Psi}$ is also circled in red, with a red arrow pointing to the text "Auxiliary wavefunction (soft pseudofunction)" below it. Above the $\tilde{\Psi}$ is the red text "No oscillations near the nucleus".

Strong oscillations near the nucleus

$\Psi = \hat{T} \tilde{\Psi}$

No oscillations near the nucleus

True wavefunction (all electrons)

Auxiliary wavefunction (soft pseudofunction)

Projector-Augmented Waves: the math

True wavefunction

$$\Psi$$

Well-behaving pseudo-wavefunction

$$\tilde{\Psi}$$

Linked by a linear transformation

$$\Psi = \hat{T} \tilde{\Psi}$$

i.e. kinetic energy, local part of the energy, angular momentum etc.

Physical quantities can be calculated as

$$\langle \Psi | \hat{A} | \Psi \rangle$$

original operator is replaced by pseudo operator thank to this

Computed in the pseudo representation

$$\langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi} \rangle$$

with

$$\tilde{A} = T^+ \hat{A} T$$

Similarly, variational principle for total energy gives

$$\frac{\partial E[\hat{T}|\tilde{\Psi}]}{\partial \langle \tilde{\Psi} |} = \varepsilon \hat{T}^+ \hat{T} |\tilde{\Psi}\rangle$$

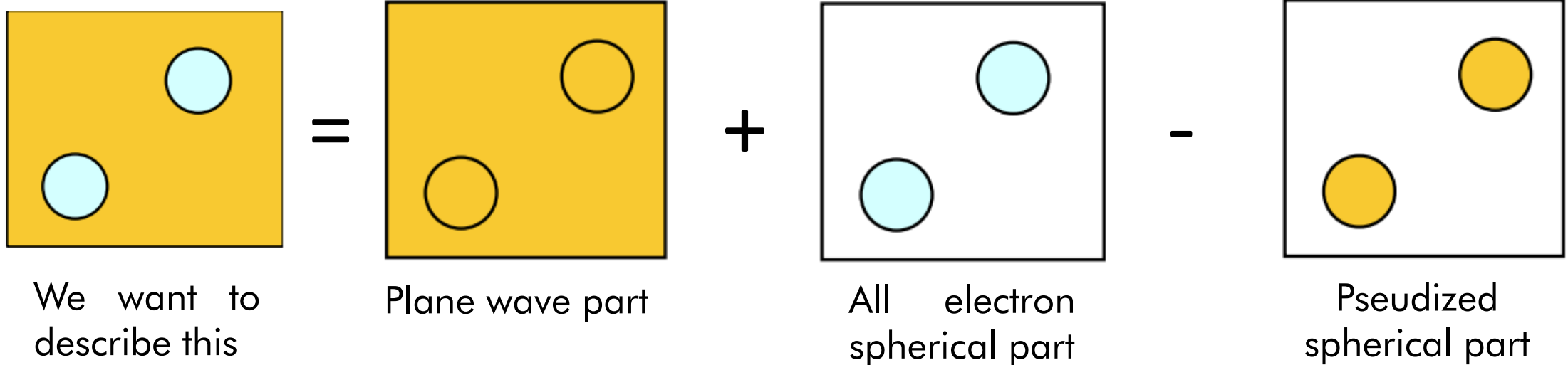
Equivalent to Kohn-Sham eq., for pseudo-wavefunctions.
Search for ground state done in the pseudo space.

Transformation operator

Operator T has to modify the smooth pseudo wavefunction in each atomic region, to give it the correct nodal structure.

$$\Psi = \hat{T} \tilde{\Psi} \quad \text{with} \quad \hat{T} = 1 + \sum_R \hat{S}_R$$

atomic site label



smth in the interstitial is smooth, but in the nuclei, it is hard to describe with PW

This is the role of the operator S_R
(Change all electron spherical part by pseudized spherical part)

Transformation operator

Operator T has to modify the smooth pseudo wavefunction in each atomic region, to give it the correct nodal structure.

$$\Psi = \hat{T}\tilde{\Psi} \quad \text{with} \quad \hat{T} = 1 + \sum_R \hat{S}_R$$

atomic site label

Choose:

Partial waves $|\phi_i\rangle$ = basis set, solutions of the Schrödinger Eq. for the isolated atoms within some cut-off radius $r_{c,R}$

Pseudo partial waves $|\tilde{\phi}_i\rangle$ = identical to the partial waves beyond the cut-off radius, but smoother inside

Define S such as:

$$|\phi_i\rangle = (1 + \hat{S}_R)|\tilde{\phi}_i\rangle \quad \text{So} \quad \hat{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle\tilde{p}_i|$$

Projector

Explicitly

$$\Psi = \tilde{\Psi} + \sum_R (|\Psi_R^1\rangle - |\tilde{\Psi}_R^1\rangle) \quad \text{where} \quad |\Psi_R^1\rangle = \sum_{i \in R} |\phi_i\rangle \langle\tilde{p}_i|\tilde{\Psi}\rangle \quad |\tilde{\Psi}_R^1\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle\tilde{p}_i|\tilde{\Psi}\rangle$$

Thx!