Computational Materials Physics

Center for Molecular Modeling

Department of Materials Science and Engineering

basis set : intro

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http://molmod.ugent.be
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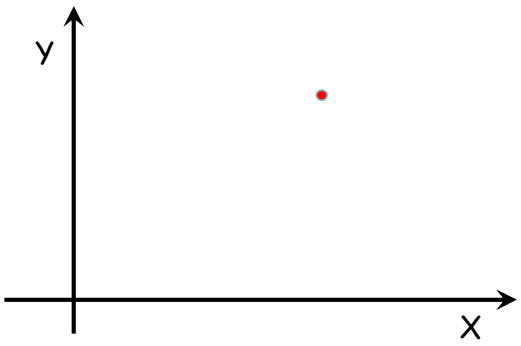
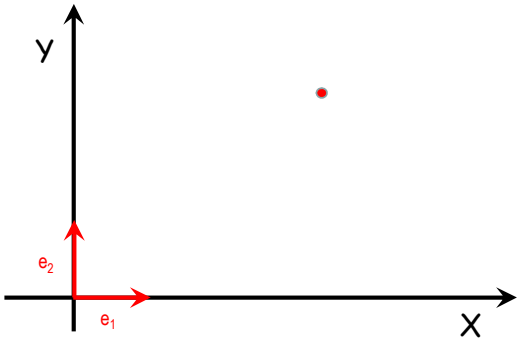
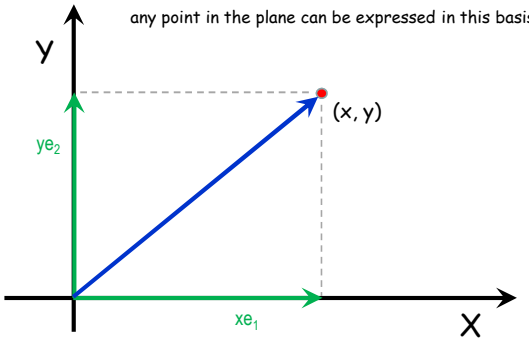


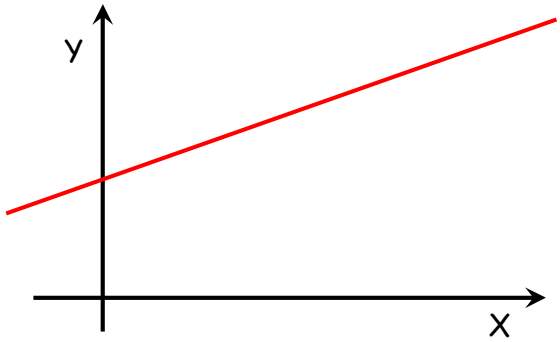
2-dimensional basis set : $\{e_1, e_2\}$

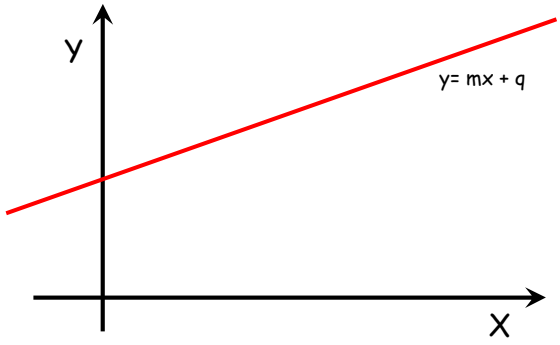


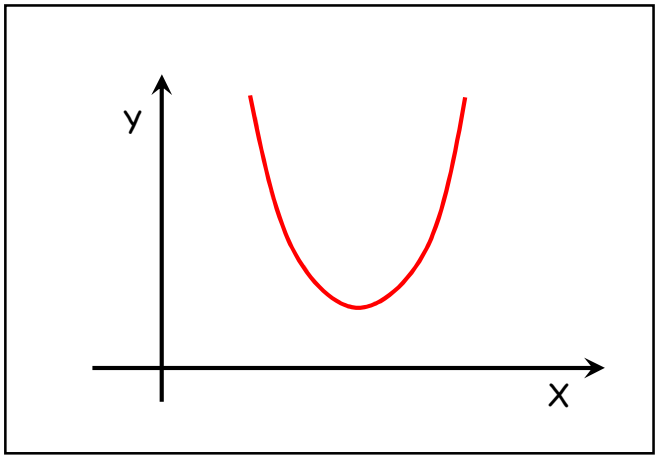
2-dimensional basis set : $\{e_1, e_2\}$

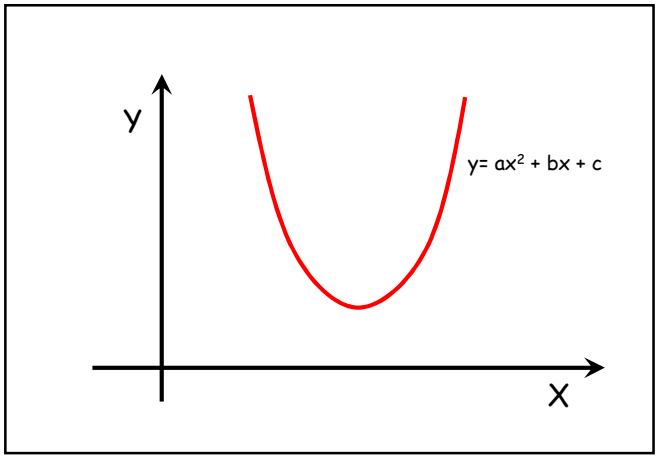
any point in the plane can be expressed in this basis









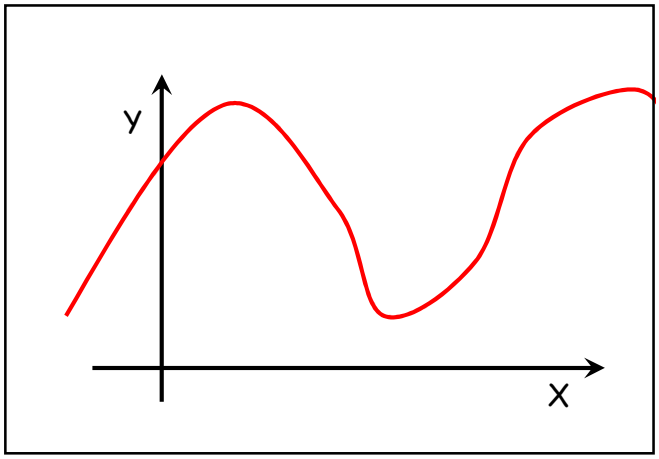


$$f(x) = c_0 + c_1x + c_2x^2 + c_3x^3 + \ldots$$

coefficient — basis function

∞-dimensional basis set : $\{1, x, x^2, x^3, \ldots\}$

There are functions, however, that need an even larger basis



CONTENT OVERVIEW

- o Basis sets: general idea
- ❶ o atomic orbital basis sets

→ introduction / recapitulation of week 6

- ❷ o plane wave basis sets
  - o Fourier transform
  - o reciprocal space
  - o plane waves
  - o reciprocal lattice
  - o properties of plane waves with reciprocal lattice vectors
  - o Wigner-Seitz cell and Brillouin zone
  - o Bloch's theorem
  - o plane waves as a basis set
  - o doing it all in reciprocal space
    - o example for density
    - o Brillouin zone sampling
  - o Basis set size
  - o Pseudopotentials
  - o Discussion

→ some overlap with comp. mat. phys.

- ❸ o 'Augmented' plane wave methods

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basis set for molecules/solids

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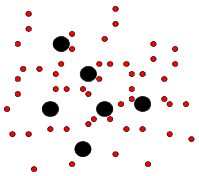
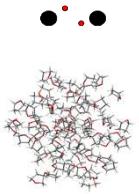
BASIS SET : GENERAL IDEA

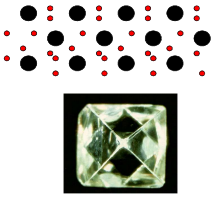
Our aim is to describe a quantum many-body system (=nuclei and electrons) :



This can be an atom or a molecule...



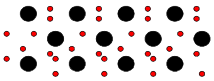
... or a (crystalline) solid



BASIS SET : GENERAL IDEA

The best possible antisymmetric independent particle approximation is given by a Slater determinant, in which the single-particle molecular orbitals are solutions of the HF equation:

$$\left|\Psi_0^{HF}\right\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(\vec{a}_1) & \Psi_1(\vec{a}_2) & \dots & \Psi_1(\vec{a}_N) \\ \Psi_2(\vec{a}_1) & \Psi_2(\vec{a}_2) & \dots & \Psi_2(\vec{a}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_N(\vec{a}_1) & \Psi_N(\vec{a}_2) & \dots & \Psi_N(\vec{a}_N) \end{vmatrix}$$



A fair mean-field approximation is given by DFT at the LDA/GGA-level, which provides a density that is constructed by crystal orbitals that are solutions of the Kohn-Sham equations:

$$\rho(\mathbf{r}) = \sum_{i=1} n_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r})$$

BASIS SET : GENERAL IDEA

We need therefore in both methods (HF/DFT) a way to express single-particle orbitals. In many practical methods, this is done by expressing them in a basis

$$\Psi_m = \sum_{i=1}^{\infty} c_i^m \phi_i$$

The space of single-particle functions Ψ_m has infinite dimensions, there are therefore an infinite number of basis functions ϕ_i needed. In practice, this infinite sum will be truncated once good accuracy is achieved.

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exercises:
basis set size (ENCUT)

BASIS SET : GENERAL IDEA

Thanks to this basis set formulation, we can transform the task of searching the eigenvalues and eigenfunctions into matrix algebra.

Indeed, take any single-particle hamiltonian H_{sp}, with eigenfunctions Ψ_m and eigenvalues ε_m. It is straightforward to show that

$$\hat{H}_{sp} \left| \Psi_m \right\rangle = \epsilon_m \left| \Psi_m \right\rangle$$

leads to this matrix expression

$$\begin{bmatrix} \cdots & \cdots & \cdots \\ \vdots & \left\langle \phi_i^b \middle| \hat{H}_{sp} \middle| \phi_j^b \right\rangle - \epsilon_m \left\langle \phi_i^b \middle| \phi_j^b \right\rangle & \vdots \\ \cdots & \cdots & \cdots \end{bmatrix} \begin{bmatrix} c_1^m \\ \vdots \\ c_P^m \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}$$

where the dimension of the matrix is determined by the number of basis functions (you can find this by filling out the expression for Ψ_m into H_{sp} $\Psi_m = \varepsilon_m \Psi_m$, and then left-multiply it with each basis function)

BASIS SET : GENERAL IDEA

This is a generalized eigenvalue problem, where the matrix equation

HC=SCE

has to be solved (diagonalized). The problem is somewhat simpler for orthogonal basis functions, where the overlap matrix S is diagonal.

➔ Matrix diagonalization will be a major ingredient of most codes.
It is responsible for most of the time consumption.

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→ Matrix diagonalization will be a major ingredient of most codes.
It is responsible for most of the time consumption.

exercises:
total energy depends on these

BASIS SET : GENERAL IDEA

There are 3 major choices that can be made for the basis set functions :

1. **Atomic Orbitals (AO)**
   The basis functions are similar to free atom orbitals
2. **Plane waves (PW)**
   The basis functions are simple plane waves (in 3 dimensions)
3. **'Augmented' plane waves**
   This name indicates various methods where the basis functions are plane waves that are in one way or another modified/improved.

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- o Basis sets: general idea
- ❶ o atomic orbital basis sets (see before)
- ❷ o plane wave basis sets
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  - o reciprocal space
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  - o Wigner-Seitz cell and Brillouin zone
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atomic orbital basis sets

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ATOMIC ORBITAL BASIS SET (AO)

Philosophy : Molecules are assemblies of slightly distorted atoms

$$\varphi_\alpha(\mathbf{r}) = \varphi_\alpha(r) Y_{lm}(\Theta, \phi)$$

$$\varphi_\alpha(r) = \begin{cases} \exp[-\alpha r^2] & \text{Gaussian} \quad \text{(GTO)} \\ \exp[-\alpha r] & \text{Slater} \quad \text{(STO)} \end{cases}$$

$\varphi_\alpha(\mathbf{r}; \mathbf{R}_I)$: basis functions are attached to nuclear positions

Implemented in Gaussian09
www.gaussian.com
and others

Implemented in ADF
www.scm.com
and others

The solid state code SIESTA uses numerical atomic orbitals (www.icmab.es/siesta)

ATOMIC ORBITAL BASIS SET (AO)

Philosophy : Molecules are assemblies of slightly distorted atoms

Advantages / Disadvantages AO Basis Sets

+ according to chemical insight

+ small basis sets give already good results

– non-orthogonal $\langle \phi_i | \phi_j \rangle \neq \delta_{ij}$

– depend on atomic position

– can suffer from basis set superposition error (BSSE)

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plane wave basis sets : technical preliminaries

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PLANE WAVE BASIS SETS (PW)

Philosophy : Assemblies of atoms are slight distortions to free electrons

Explaining a plane wave basis set requires to introduce/remember a few concepts:

- Fourier transform
- reciprocal space
- plane waves
- reciprocal lattice
- properties of plane waves with reciprocal lattice vectors
- Wigner-Seitz cell and Brillouin zone
- Bloch's theorem

⇩

- plane waves as a basis set

PLANE WAVE BASIS SETS (PW)

Fourier Transform

A Fourier transform transforms a (real or complex) function of time into a (real or complex) function of frequency, without information loss. The inverse Fourier transform does the opposite :

$$F(\omega) = \mathcal{F}\{f\} = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$

$$f(t) = \mathcal{F}^{-1}\{F\} = \frac{-1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} d\omega$$

PLANE WAVE BASIS SETS (PW)

Reciprocal space

The collection of all position vectors $\vec{r}$ is called '**real space**'. It is a continuous space, and the dimension of a position vector is length.

The collection of all vectors $\vec{g}$ defined as: $\vec{g} = \frac{1}{x}\vec{i}^* + \frac{1}{y}\vec{j}^* + \frac{1}{z}\vec{k}^*$ $\quad \vec{i}^* = 2\pi\vec{i}$, $\vec{j}^* = 2\pi\vec{j}$, $\vec{k}^* = 2\pi\vec{k}$

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PLANE WAVE BASIS SETS (PW)

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is called '**reciprocal space**'. It is a continuous space, and the dimension of each reciprocal space vector is inverse length.

A procedure very similar to the common time/frequency Fourier transform can be used to convert functions that are defined on real space to functions defined on reciprocal space:

$$F(\vec{g}) = \mathcal{F}\{f\} = \int f(\vec{r})\, e^{-i\vec{g}\cdot\vec{r}}\, d^3\vec{r}$$

$$f(\vec{r}) = \mathcal{F}^{-1}\{F\} = \frac{-1}{2\pi} \int F(\vec{g})\, e^{i\vec{g}\cdot\vec{r}}\, d^3\vec{g}$$

PLANE WAVE BASIS SETS (PW)

plane waves

Plane waves are a particular kind of function defined on real space:

$$f(\vec{r}) \;=\; A\, e^{i\vec{g}_0\cdot\vec{r}}$$

(Interpretation: periodic function in 3D, reaches the same value at planes that are separated by $2\pi/g_0$ (the period) and that are orthogonal to $\vec{g}_0$ (the wave vector)).

A is a constant, and $\vec{g}_0$ is any reciprocal space vector.

The Fourier transform of a plane wave is nonzero at a single point in reciprocal space only, namely at the point given by the vector $\vec{g}_0$:

$$\begin{aligned} F(\vec{g}) \;&=\; \int e^{i(\vec{g}_0-\vec{g})}\, d^3\vec{r} \\ &=\; \delta(\vec{g}_0-\vec{g}) \end{aligned}$$

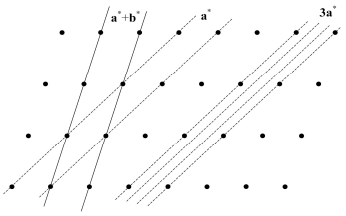
PLANE WAVE BASIS SETS (PW)

Reciprocal lattice

All reciprocal space vectors that lead to a plane wave

$$f(\vec{r}) \;=\; A\, e^{i\vec{K}\cdot\vec{r}}$$

that is commensurate with the Bravais lattice in real space (= if the plane wave has a particular value α in the point $\vec{r}_0$, then it has the same value α in all points $\vec{r}_0 + \ell\,\vec{a} + m\,\vec{b} + n\,\vec{c}$, form together the **reciprocal lattice** of that Bravais lattice.



The factor A is by convention and for convenience chosen as

$$A \;=\; \frac{1}{\sqrt{\Omega}}$$

with Ω the volume of the unit cell of the Bravais lattice. Such a plane wave, we write as $\phi_{\vec{K}}$

PLANE WAVE BASIS SETS (PW)

Mind the difference !

reciprocal *space* :

- defined once and for all (just as real space)
- continuous
- symbol : $\vec{g}$

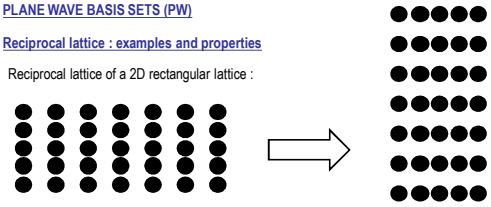
reciprocal *lattice* :

- a discrete set of points in reciprocal space
- defined with respect to a Bravais lattice in real space.
- symbol : $\vec{K}$ (or in other texts: $\vec{G}$)

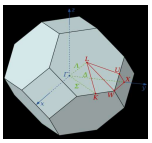
PLANE WAVE BASIS SETS (PW)

Reciprocal lattice : examples and properties

Reciprocal lattice of a 2D rectangular lattice :



Reciprocal lattice of a 3D body centered cubic lattice is a face-centered cubic lattice. The latter has this Wigner-Seitz cell :



Property: the larger the volume of the unit cell in real space,
the smaller the volume of the unit cell in reciprocal space.

PLANE WAVE BASIS SETS (PW)

Properties of plane waves with reciprocal lattice vectors

❶ The $\phi_{\vec{K}}$ are commensurate with the lattice (see previous slide)

❷ The $\phi_{\vec{K}}$ are orthonormal:

$$\left\langle \phi_{\vec{K}_i} \middle| \phi_{\vec{K}_j} \right\rangle = \frac{1}{\Omega} \int_{\Omega} e^{i(\vec{K}_j - \vec{K}_i)\cdot\vec{r}}\, d\vec{r} = \delta_{ij}$$

❸ The (infinite set) of $\phi_{\vec{K}}$ forms a basis for any function $f_p(\vec{r})$ that has the periodicity of the lattice:

$$f_p(\vec{r}) = f(\vec{r} + \vec{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{K}}^{\infty} F_p(\vec{K})\, e^{i\vec{K}\cdot\vec{r}}$$

(This is a discrete version of the Fourier transform, valid for such periodic functions only. The inverse of this expression defines $F_p(\vec{K})$ which is the fourier transform of the original function, or "the original function in reciprocal space". The latter is non-zero on reciprocal lattice points only.)

Wave functions do not need to have the periodicity of the lattice, only the density has to.

Therefore, one more step is needed
until we can use plane waves as a basis… :

PLANE WAVE BASIS SETS (PW)

Bloch's theorem

Bloch's theorem – which states that a single-particle wave function can be written as the product of a plane wave with a wave vector k inside the first Brillouin zone and a function u that has the periodicity of the direct lattice:

$$\Psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}^{n}(\vec{r})$$

…implies that this vector k and a natural number n (the band index) can serve as quantum numbers for this single-particle wave function:

$$\Psi(\vec{r}) \longrightarrow \Psi_{\vec{k}}^{n}(\vec{r})$$

Because the function u is periodic in space, it can be written as a sum over plane waves. Therefore, the single particle wave function can be written as a sum over plane waves as well:

$$\psi_{\vec{k}}^{n}(\vec{r}) = \sum_{\vec{K}} c_{\vec{K}}^{n,\vec{k}}\, e^{i(\vec{k}+\vec{K})\cdot\vec{r}}$$ **QED**

- There is an infinite amount of basis functions needed.
- An alternative notation for $c_{\vec{K}}^{n,\vec{k}}$ is $\Psi_n(\vec{k}+\vec{K})$ ("the eigenfunction in reciprocal space").

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plane wave basis sets : working in reciprocal space

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PLANE WAVE BASIS SETS (PW)

doing it all in reciprocal space

Electronic structure calculations for crystals are often simplified when they are transformed to reciprocal space (remember: fourier transform, no information loss).

Examples:

http://portellen.phycmt.dur.ac.uk/sjc/thesis_mcg/node21.html
http://portellen.phycmt.dur.ac.uk/sjc/thesis_mcg/node22.html

PLANE WAVE BASIS SETS (PW)

doing it all in reciprocal space

Transforming the electron density into reciprocal space

The density in an infinite periodic system can be expressed by a sum over the occupied Kohn-Sham orbitals :

$$\rho(\mathbf{r}) = \sum_{i=1}^{\max} n_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r})$$

n_i are occupation numbers of the Kohn-Sham orbitals : $0 \leq n_i \leq 1$ and $N = \sum_i n_i$

For an infinite periodic system, the sum over i runs over the discrete band index n and the continuous 1st Brillouin zone points $\mathbf{k}$. It should be written as a sum and an integral:

$$\rho(\vec{r}) = \frac{1}{V_{BZ}} \int_{BZ} \left(\sum_{i=1}^{n_{max}} n_{\vec{k}}^i \left| \Psi_{\vec{k}}^i(\vec{r}) \right|^2 \right) d\vec{k}$$

$V_{BZ} = \frac{(2\pi)^3}{\Omega}$ is the volume of the first Brillouin zone

$\int_{BZ} d\vec{k}$ is the integration over the first Brillouin zone

PLANE WAVE BASIS SETS (PW)

doing it all in reciprocal space

Transforming the electron density into reciprocal space

As we know how $\Psi_{\vec{k}}^i(\vec{r})$ can be written in reciprocal space, it is straightforward to transform

$$\rho(\vec{r}) = \frac{1}{V_{BZ}} \int_{BZ} \left(\sum_{i=1}^{n_{max}} n_{\vec{k}}^i \left| \Psi_{\vec{k}}^i(\vec{r}) \right|^2 \right) d\vec{k}$$

into an expression containing only reciprocal space quantities.

PLANE WAVE BASIS SETS (PW)

Brillouin zone sampling

Calculation of the density requires a calculation at every **k** of the Brillouin zone.
It requires an infinite number of calculations.
In practical calculations the integral over the first Brillouin zone is approximated by quadrature with **a finite number of Brillouin zone sampling points**. Each sampling point has a weighting factor w_k. Then the density can be written as:

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} w_k \sum_i n_{ik} |\psi_{ik}(\mathbf{r})|^2$$

There are situations where it is sufficient to use only one sampling point: $\mathbf{k} = (0,0,0)$
This is the origin of the reciprocal lattice, and this point is conventionally labelled by Γ.
Such a calculation is called a **Γ point calculation**
There are situations where this is a very good approximation (large unit cells, semiconductors, single atoms or molecules,...)

The density can then be written as : $\rho(\mathbf{r}) = \sum_i n_{ik} |\psi_{ik}(\mathbf{r})|^2$

Explicit expression in reciprocal space for a **Γ point calculation** : $\rho(\mathbf{r}) = \sum_i n_i \sum_{\mathbf{K},\mathbf{K}'} e^{i(\mathbf{K}-\mathbf{K}').\mathbf{r}} \psi_i(\mathbf{K}) \psi_i^*(\mathbf{K}')$

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There are situations where this is a very good approximation (large unit cells, semiconductors, single atoms or molecules,...)

The density can then be written as : $\rho(\mathbf{r}) = \sum_i n_{ik} |\psi_{ik}(\mathbf{r})|^2$

exercises:
k-point sampling
- What to expect with more sampling points ?

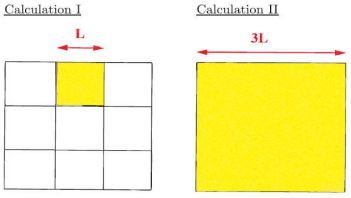
Explicit expression in reciprocal space for a **Γ point calculation** : $\rho(\mathbf{r}) = \sum_i n_i \sum_{\mathbf{K},\mathbf{K}'} e^{i(\mathbf{K}-\mathbf{K}').\mathbf{r}} \psi_i(\mathbf{K}) \psi_i^*(\mathbf{K}')$

PLANE WAVE BASIS SETS (PW)

Brillouin zone sampling

Γ-sampling may be accurate enough if large simulation cells are used.

Illustration with two-dimensional example



Simulation cells in real space

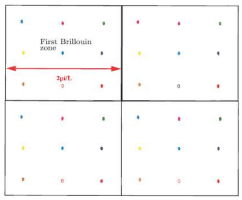
Calculation I:
a two dimensional cubic simulation cell LxL with Brillouin zone sampling points (0,0), (2/3,0), (-2/3,0), (-2/3,0), (0,2/3), (2/3,2/3), (-2/3,2/3), (2/3,-2/3), (-2/3,-2/3).

Calculation II:
a two dimensional cubic simulation cell 3Lx3L in a Γ-point calculation.

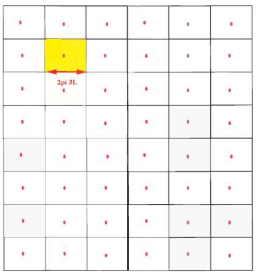
PLANE WAVE BASIS SETS (PW)

Brillouin zone sampling

Brillouin zones for both calculations
Same plane waves are used in both calculations but in Calculation II, the atoms have more freedom within the larger real space cell.



Calculation I



Calculation II

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} \psi_i(\mathbf{K}+\mathbf{k})$$

CONTENT OVERVIEW

- o Basis sets: general idea
- ❶ o atomic orbital basis sets
- ❷ o plane wave basis sets
  - o Fourier transform
  - o reciprocal space
  - o plane waves
  - o reciprocal lattice
  - o properties of plane waves with reciprocal lattice vectors
  - o Wigner-Seitz cell and Brillouin zone
  - o Bloch's theorem
  - o plane waves as a basis set
  - o doing it all in reciprocal space
    - o example for density
    - o Brillouin zone sampling
  - o Basis set size
  - o Pseudopotentials
  - o Discussion
- ❸ o 'Augmented' plane wave methods

Center for Molecular Modeling

Computational Materials Physics

Department of Materials Science and Engineering

plane wave basis sets : the need for pseudopotentials

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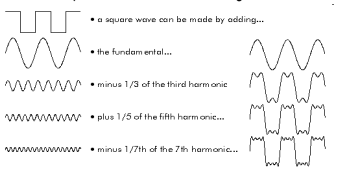
http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

PLANE WAVE BASIS SETS (PW)

Basis set size

What makes a plane wave basis set to be large?



The steeper the feature you want to describe, the more basis functions (plane waves) are needed.

PLANE WAVE BASIS SETS (PW)

Basis set size

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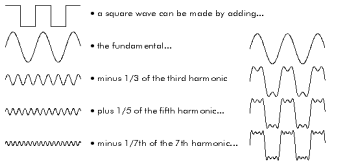

The steeper the feature you want to describe, the more basis functions (plane waves) are needed.

Back-of-the-envelop estimate for Ca-3s: 10^8 plane waves. Diagonalize 10^8x10^8 matrices...?

The steepest features appear near to the nuclei:

➔ get rid of them by PP (see soon)

➔ use basis functions that have such steep features built-in (next week)

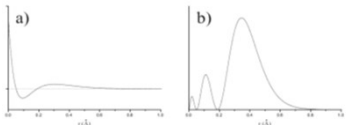

Figure 2.1: Radial part of wave function (a) and radial probability distribution (b) of a 3s electron in Ca (Y-axis has arbitrary units).

PLANE WAVE BASIS SETS (PW)

Basis set size

Formulate this idea in a more technical way:

Even in the case of Γ-sampling, the expansion still has an infinite number of plane waves

$$\Psi_{\vec{k}}^{n}(\vec{r}) \;=\; \sum_{\vec{K}} \Psi_n(\vec{K})\, e^{i\vec{K}\cdot\vec{r}} \qquad \mathbf{K} = n_1\mathbf{a}^* + n_2\mathbf{b}^* + n_3\mathbf{c}^*$$

The most rapid fluctuations of the orbitals are obtained by the largest values of K.

For practical purposes the expansion is truncated to get a finite basis set.

The maximum kinetic energy determines the cut-off.

$$\frac{1}{2}(\mathbf{K})^2 \le E_{max}$$

(just another way to express the maximal reciprocal lattice vector)

$$n_1^2 + n_2^2 + n_3^2 \;\le\; \frac{E_{max} L^2}{(2\pi)^2}$$

(cfr. particle-in-a-box derivation in many textbooks)

The most rapid variations are found in the core region, resulting from the hard nuclear potential

PLANE WAVE BASIS SETS (PW)

Basis set size

Formulate this idea in a more technical way:

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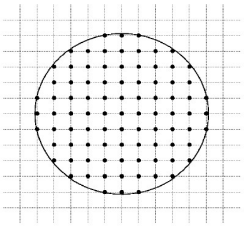
exercises:
ENCUT (= basis set size)
- What to expect with more basis functions ?

The most rapid variations are found in the core region, resulting from the hard nuclear potential

PLANE WAVE BASIS SETS (PW)

Basis set size

Schematic representation of the plane waves that are taken into the basis set :



$$\frac{1}{2}(\mathbf{K})^2 \leq E_{max}$$

$$n_1^2 + n_2^2 + n_3^2 \leq \frac{E_{max} L^2}{(2\pi)^2}$$

The basis set size depends only on the volume of the box and the cut-off

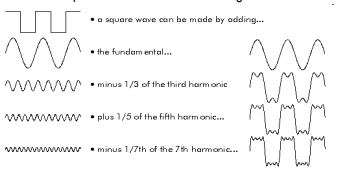
For a given E_{max}, you need more plane waves to describe a larger cell

The larger you take E_{max}, the larger your basis, the more accurate your calculation, and the more expensive your calculation.

PLANE WAVE BASIS SETS (PW)

Basis set size

What makes a plane wave basis set to be large?



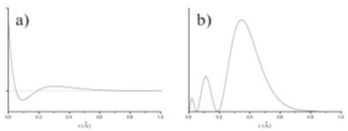


Figure 2.1: *Radial part of wave function (a) and radial probability distribution (b) of a 3s electron in Ca (Y-axis has arbitrary units).*

The steeper the feature you want to describe, the more basis functions (plane waves) are needed.

Back-of-the-envelop estimate for Ca-3s: 10^6 plane waves. Diagonalize 10^6x10^6 matrices...?

The steepest features appear near to the nuclei:
- → **get rid of them by PP**
- → use basis functions that have such steep features built-in (next week)

PLANE WAVE BASIS SETS (PW)

Pseudopotentials

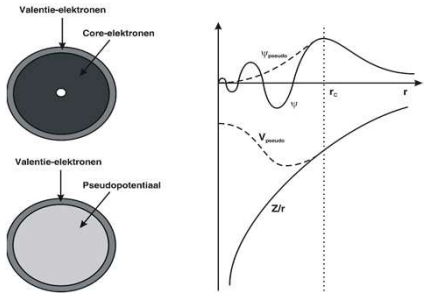
Not all electrons are the same ... :

Core electrons
- Deeply bound
- Localized around core region
- Are subject to the attractive Coulomb potential with respect to the positive nucleus and interaction mainly with other core electrons
- Orbitals do not change substantially when placed in various molecular environments

Valence electrons
- Single particle energies are situated near the Fermi-level
- Charge density is concentrated in region further from the nucleus
- The valence electrons feel a screened Coulomb potential due to the other core electrons
- Valence wavefunctions are subject to strong oscillations in core region, as they are orthonormal to the core wavefunctions
- These valence wavefunctions undergo drastic changes depending on the molecular environment in which they are placed

PLANE WAVE BASIS SETS (PW)

Pseudopotentials

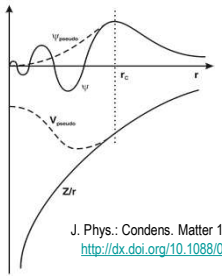


PLANE WAVE BASIS SETS (PW)

Pseudopotentials

Advantages of the PSP method

- Number of electrons to be treated is reduced
- The number of basis functions needed to expand the atomic orbitals can be drastically reduced as the valence wavefunctions do not exhibit the large fluctuations anymore in the core.



Accessible review:

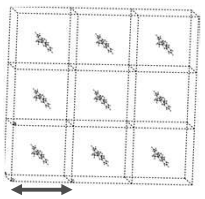
Segall et al.,
J. Phys.: Condens. Matter 14 (2002) 2717–2744
http://dx.doi.org/10.1088/0953-8984/14/11/301

Available on Minerva. Deals with DFT and related basic machinery as well

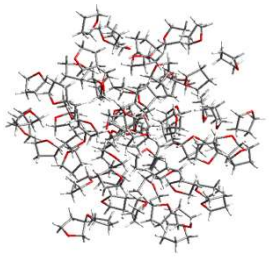
PLANE WAVE BASIS SETS (PW)

Discussion

- Plane waves are ideally suited for simulations of periodic systems (crystalline materials, solvents)
- For the simulations of isolated molecules a large portion of vacuum needs to be placed around the molecule



35 Angstrom



PLANE WAVE BASIS SETS (PW)

Discussion

Philosophy : Assemblies of atoms are slight distortions to free electrons

\+ orthogonal

\+ independent of atomic positions

\+ no BSSE

± naturally periodic

− many functions needed because unlike STO and GTO's, plane wave do not look like atomic orbitals

\+ the same basis set can be used for all atomic species (⇔ STO, GTO)

\+ convergence toward completeness can easily be tested

-- introducing a pseudopotential might produce unphysical artifacts, and not always in properties where you would have expected this.

(example on next slide)

Computational Materials Science 52 (2012) 2–6

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Pseudopotential errors in titanium

See Minerva – interesting to read.

Bengt E. Tegner*, Graeme J. Ackland

ICMCS and SUPA, School of Physics and Astronomy, The University of Edinburgh, James Clerk Maxwell Building, The King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK

A B S T R A C T

We present a study of the effect of using different pseudopotentials to represent titanium. We show that apparently arbitrary choices in the reference configuration can lead to significant differences in the calculated quantities. These differences are most striking in the Kohn–Sham "electron" state energies: in structural properties of the solid there is a considerable cancellation of errors. However, 4-electron pseudopotentials with apparently reasonable atomic and scattering properties can give different ground state crystal structures and predict volumes varying by several percent.

Important issue: validation of pseudopotentials

see for instance :

K. Garrity et al. (2014) [next slide]

K. Lejaeghere et al. (2014) [open access, http://dx.doi.org/10.1080/10408436.2013.772503]

Recent pseudopotential library:

http://www.physics.rutgers.edu/gbrv/

Computational Materials Science 81 (2014) 446–452

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Pseudopotentials for high-throughput DFT calculations

Kevin F. Garrity *, Joseph W. Bennett, Karin M. Rabe, David Vanderbilt

Department of Physics & Astronomy, Rutgers University, Piscataway, NJ 08854-8019, USA

A B S T R A C T

The increasing use of high-throughput density-functional theory (DFT) calculations in the computational design and optimization of materials requires the availability of a comprehensive set of soft and transferable pseudopotentials. Here we present design criteria and testing results for a new open-source "GBRV" ultrasoft pseudopotential library that has been optimized for use in high-throughput DFT calculations. We benchmark the GBRV potentials, as well as two other pseudopotential sets available in the literature, to all-electron calculations in order to validate their accuracy. The results allow us to draw conclusions about the accuracy of modern pseudopotentials in a variety of chemical environments.

PW+PP codes

VASP
http://cms.mpi.univie.ac.at/vasp/

review paper
Computer Physics Communications 177 (2007) 6-13

ABINIT
http://www.abinit.org/

review paper
Computer Physics Communications 180 (2009) 2582-2615

Quantum-Espresso (f.k.a. PWscf)
http://www.quantum-espresso.org/index.php

review paper
Journal of Physics: Condensed Matter **21** (2009) 395502

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  (next week)