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Technical University of Kenya

*Density Functional Theory:
Kohn Sham equations, exchange-correlation
functionals, and approximations*

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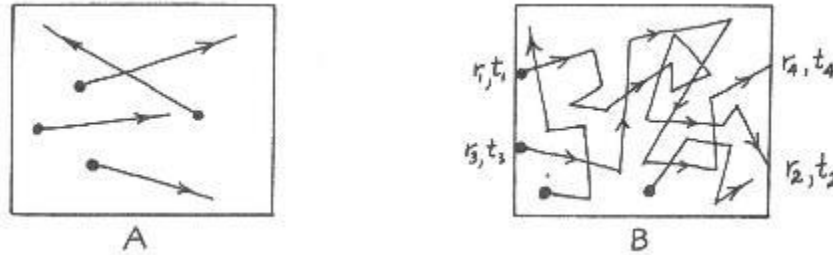
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Overview

- Properties of matter naturally fall into two main categories determined , respectively, by the *electronic ground state* and the *electronic excited states*
- Electronic ground state determines equilibrium properties such as: cohesive energy, equilibrium crystal structure, phase transitions between structures, elastic constants, charge density, magnetic order, static dielectric and magnetic susceptibilities, nuclear vibration and motion, etc.
- Electronic excited states determine properties such: low-energy excitations in metals, optical properties, transport, etc.
- In our overview of electronic structure methods we will focus mostly on the basic principles underlying the density functional theory, in particular, Kohn-Sham equations, exchange-correlation functional, approximations, plane-waves, and pseudo-potentials

The many-body problem

- *How do we solve for the electronic ground state?* Solve a many-body problem: the study of the effects of interaction between bodies, and the behavior of a many-body system
- The collection of nuclei and electrons in a piece of a material is a formidable many-body problem, because of the intricate motion of the particles in the many-body system:



- Electronic structure methods deal with solving this formidable problem starting from the fundamental equation for a system of electrons ($\{\mathbf{r}_i\}$) and nuclei ($\{\mathbf{R}_j\}$)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,l} \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$- \sum_i \frac{\hbar^2}{2M_l} \nabla_l^2 + \frac{1}{2} \sum_{l \neq j} \frac{e^2}{|\mathbf{R}_l - \mathbf{R}_j|}$$

The many-body problem

- Electronic terms:

$$-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,l} \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Nuclear terms:

$$-\sum_l \frac{\hbar^2}{2M_l} \nabla_l^2 + \frac{1}{2} \sum_{l \neq j} \frac{e^2}{|\mathbf{R}_l - \mathbf{R}_j|}$$

- Electrons are fast (small mass, 10^{-31} Kg) - nuclei are slow (heavy mass, 10^{-27} Kg) → natural separation of variables
- In the expression above we can ignore the kinetic energy of the nuclei, since it is a small term, given the inverse mass of the nuclei
- If we omit this term then the nuclei are just a fixed potential (sum of point charges potentials) acting on the electrons: this is called the **Born-Oppenheimer approximation**



Kohn and Sham ansatz

Kohn and Sham, Phys. Rev. 140, A1133 (1965)

- H-K theory is in principle exact (there are no approximations, only two elegant theorems) but impractical for any useful purposes

$$E[n] = T[n] + E_{\text{int}}[n] + \int d^3r V_{\text{ext}}(r)n(r)$$

- Kohn-Sham ansatz: replace a problem with another, that is the original many-body problem with an auxiliary independent-particle model
- Ansatz: K-S assume that the ground state density of the original interacting system is equal to that of some chosen non-interacting system that is exactly soluble, with all the difficult part (exchange and correlation) included in some approximate functional of the density.
- Key assumptions:
 - The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles. This is called “non-interacting-V-representability”;
 - The auxiliary Hamiltonian contains the usual kinetic energy term and a local effective potential acting on the electrons
- Actual calculations are performed on this auxiliary Hamiltonian

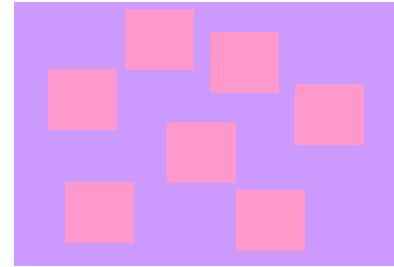
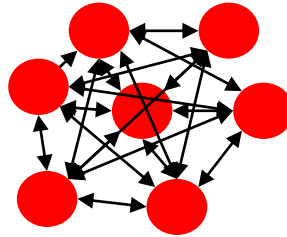
$$H_{\text{KS}}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\text{KS}}(\mathbf{r})$$

through the solution of the corresponding Schrödinger equation for N independent electrons (Kohn-Sham equations)

Kohn and Sham ansatz

Kohn and Sham, Phys. Rev. 140, A1133 (1965)

Interacting electrons
+ real potential



Non-interacting
auxiliary
particles in an
effective potential

- The density of this auxiliary system is then:

$$n(\mathbf{r}) = \sum_s \sum_{i=1, N} |\psi_i^s(\mathbf{r})|^2$$

- The kinetic energy is the one for the independent particle system:

$$T_s = -\frac{1}{2} \sum_s \sum_{i=1, N} \langle \psi_i^s(\mathbf{r}) | \nabla^2 | \psi_i^s(\mathbf{r}) \rangle = \frac{1}{2} \sum_s \sum_{i=1, N} |\nabla \psi_i^s(\mathbf{r})|^2$$

- We define the classic electronic Coulomb energy (Hartree energy) as usual:

$$E_{Hartree}[n] = \frac{1}{2} \iint d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Kohn and Sham equations

- Finally, we can rewrite the full H-K functional as

$$E_{KS}[n] = T_s[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n]$$

- All many body effects of exchange and correlation are included in E_{xc}

$$E_{xc}[n] = F_{HK}[n] - (T_s[n] + E_{Hartree}[n]) = \\ \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{int} \rangle - E_{Hartree}[n]$$

- So far the theory is still exact, provided we can find an “exact” expression for the exchange and correlation term
- If the universal functional $E_{xc}[n]$ were known, then the exact ground state energy and density of the many-body electron problem could be found by solving the Kohn-Sham equations for independent particles.
- To the extent that an approximate form for $E_{xc}[n]$ describes the true exchange-correlation energy, the Kohn-Sham method provides a feasible approach to calculating the ground state properties of the many-body electron system.

Kohn and Sham equations

- The solution of the Kohn-Sham auxiliary system for the ground state can be viewed as the problem of minimization with respect to the density $n(\mathbf{r})$ that can be done varying the wavefunctions and applying the chain rule to derive the variational equations:

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma*}(\mathbf{r})} = \frac{\delta T_s}{\delta \psi_i^{\sigma*}(\mathbf{r})} + \left[\frac{\delta E_{ext}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} \right] \frac{\delta n(\mathbf{r}, \sigma)}{\delta \psi_i^{\sigma*}(\mathbf{r})} = 0$$

subject to the orthonormalization constraint

$$\langle \psi_i^\sigma | \psi_j^{\sigma'} \rangle = \delta_{i,j} \delta_{\sigma,\sigma'}$$

- Since

$$\frac{\delta T_s}{\delta \psi_i^{\sigma*}(\mathbf{r})} = -\frac{1}{2} \nabla^2 \psi_i^\sigma(\mathbf{r}); \quad \frac{\delta n^\sigma(\mathbf{r})}{\delta \psi_i^{\sigma*}(\mathbf{r})} = \psi_i^\sigma(\mathbf{r})$$

- One ends up with a set of Schrödinger-like equations

$$(H_{KS}^\sigma - \varepsilon_i^\sigma) \psi_i^\sigma(\mathbf{r}) = 0$$

where H_{KS} is the effective Hamiltonian

$$H_{KS}^\sigma(\mathbf{r}) = -\frac{1}{2} \nabla^2 + V_{KS}^\sigma(\mathbf{r})$$

with

$$\begin{aligned} V_{KS}^\sigma(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}^\sigma(\mathbf{r}). \end{aligned}$$

Kohn and Sham equations

- The previous result, trivial in the non-interacting case, raises interesting issues in the KS case
- Given the expression for the exchange and correlation energy, one can derive the expression for the exchange and correlation potential V_{xc}

$$E_{xc}[n] = \int dr n(r) \varepsilon_{xc}([n], r)$$

$$V_{xc}(r) = \frac{\partial E_{xc}[n]}{\partial n(r)} = \varepsilon_{xc}([n], r) + n(r) \frac{\delta \varepsilon_{xc}([n], r)}{\delta n(r)}$$

- It can be shown that the response part of the potential (the derivative of the energy wrt the density) can vary discontinuously between states giving rise to discontinuous jumps in the eigenvalues: “band-gap discontinuity”
- Critical problem of the gap in an insulator: the eigenvalues of the ground state Kohn-Sham potential should not be the correct gap, at least in principle.
- Indeed, it is well known that most known KS functionals underestimate the gap of insulators, however, this is an active field of research and new developments are always possible.

Approximations:

Local Density Approximation

- Although it might seem counterintuitive, solids can be often considered as close to the limit of the homogeneous electron gas = electron gas immersed in a uniformly positive charge background (true for metals, increasingly less true for very inhomogeneous charge distributions such as in nanostructures and isolated molecules)
- In this limit it is known that exchange and correlation (x-c) effects are **local in character and the x-c energy is simply the integral of the x-c energy density at each point in space assumed to be the same as a homogeneous electron gas with that density**
- Generalizing to the case of electrons with spin (spin-polarized or unrestricted), we can introduce the Local Spin Density Approximation (LSDA)

$$E_{xc}^{LSDA}[n^-, n^-] = \int d^3r n(\mathbf{r}) e_{xc}(n^-(\mathbf{r}), n^-(\mathbf{r}))$$

- Most general local expression for the exchange and correlation energy
- Ultimately, the validity of LDA or LSDA approximations lies in the remarkably good agreement with experimental values of the ground state properties for most materials
- Can be easily improved upon without losing much of the computational appeal of a local form
- Ignore corrections to the exchange-correlation energy at a point \mathbf{r} due to nearby inhomogeneities in the electron density

Local Density Approximation

- Problem of self-interactions: in the Hartree-Fock approximation the unphysical self term in the Hartree interaction (the interaction of an electron with itself) is exactly cancelled by the non-local exchange interaction.
- In the local approximation to exchange, the cancellation is only approximate and there remain spurious self-interaction terms that are negligible in the homogeneous gas but large in confined system such as atoms (need of Self-Interaction Corrections or SIC)
- A non exhaustive list of such drawbacks follows: the LDA tends to overbind (i.e. the computed cohesive energies are too large). The electrons are not localised enough in space; indeed, the LDA is a generalization of the HEG, which is appropriate for some s and p electrons, but not for d and f orbitals.
- However, in most known cases LSDA works remarkably well, due to the lucky occurrence that the exchange and correlation hole, although approximate, still satisfies all the sum rules.

Generalized Gradient Approximations

- The first step beyond the L(S)DA approximation is a functional that depends both on the magnitude of the density $n(\mathbf{r})$ and of its gradient $|\nabla n(\mathbf{r})|$: Generalized Gradient Approximations (GGA's) where higher order gradients are used in the expansion:

$$\begin{aligned} E_{xc}^{GGA}[n^\uparrow, n^\downarrow] &= \int d^3r n(\mathbf{r}) \epsilon_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|, \dots) \\ &\equiv \int d^3r n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xc}(n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|, \dots) \end{aligned}$$

where F_{xc} is a dimensionless function and ϵ_x^{hom} is the exchange energy of the uniform electron gas.

- Gradients are difficult to work with and often can lead to worse results. There are however consistent ways to improve upon L(S)DA using gradient expansions
- Most common forms differ by the choice of the F function:
PW91, PBE, BLYP,...

Beyond GGA

- Non-local density functionals: functionals that depend on the value of the density around the point \mathbf{r} (Average Density and Weighted Density Approximations)

where

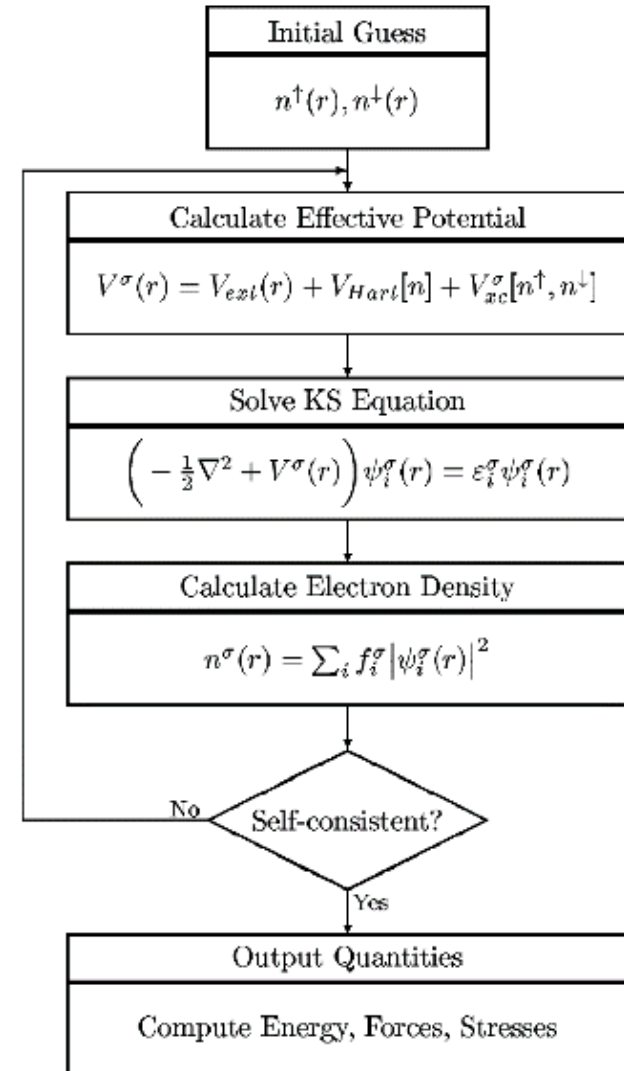
$$E_{xc}^{ADA}[n^\uparrow, n^\downarrow] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{hom}(\bar{n}^\uparrow(\mathbf{r}), \bar{n}^\downarrow(\mathbf{r}))$$

$$\bar{n}(\mathbf{r}) = \int d^3r' w(\bar{n}(\mathbf{r}); |\mathbf{r} - \mathbf{r}'|) n(\mathbf{r}')$$

- Orbital dependent functionals: mostly useful for systems where electrons tend to be localized and strongly interacting
 - SIC - self-interaction corrected functionals
 - LDA+U - local functional + orbital-dependent interaction for highly localized atomic orbitals (Hubbard U)
 - EXX (exact exchange) - functionals that include explicitly the exact exchange integral of Hartree-Fock
 - Hybrid functionals (B3LYP) - combination of orbital-dependent Hartree-Fock and explicit DFT. Most accurate functional on the market - most preferred for chemistry calculations

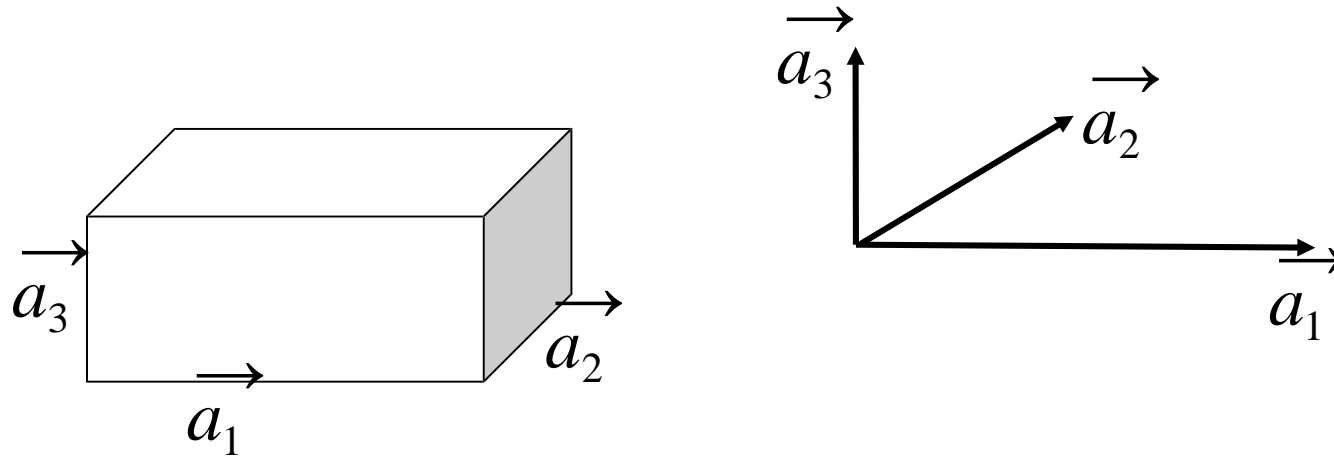
DFT in Practice

- Finally, the set of K-S equations with LDA for exchange and correlation give us a formidable theoretical tool to study ground state properties of electronic systems
- Set of *self-consistent* equations that have to be solved simultaneously until convergence is achieved
- Note: K-S eigenvalues and energies are interpreted as true electronic wavefunction and electronic energies (electronic states in molecules or bands in solids)
- Note: K-S theory is a ground-state theory and as such is supposed to work well for ground state properties or small perturbations upon them
- Extremely successful in predicting materials properties - golden standard in research and industry



Plane-Wave: Basis Sets

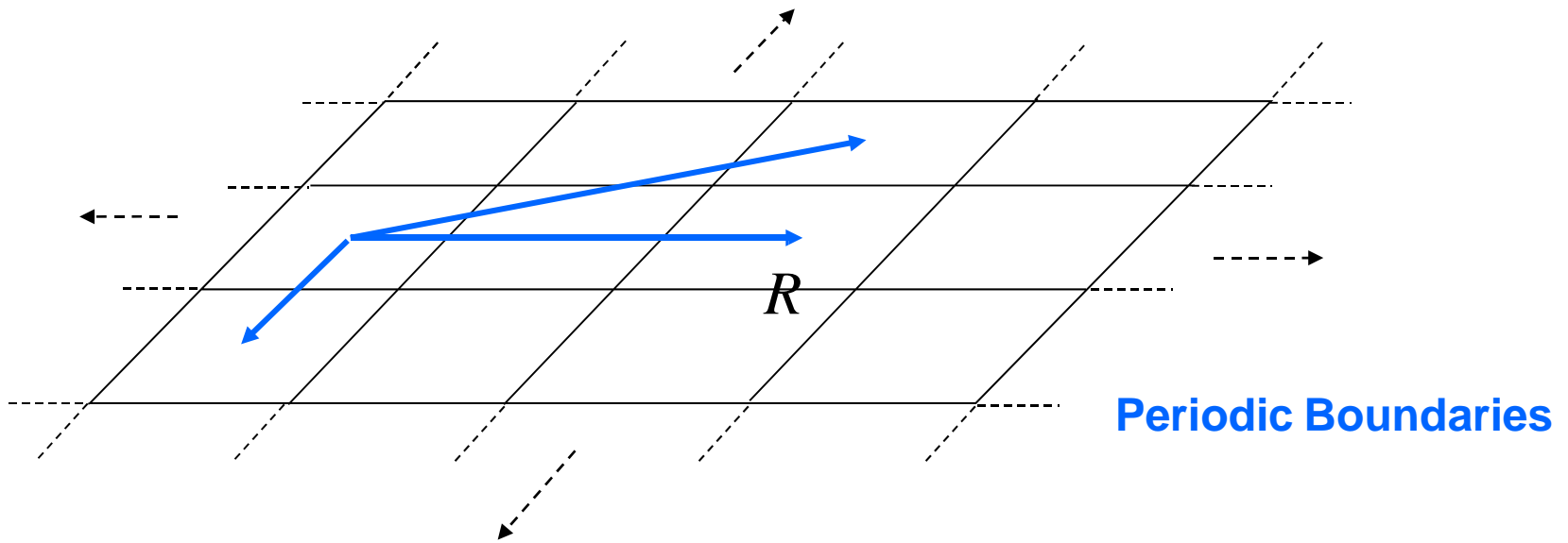
System is assumed to be placed inside a unit cell defined by the unit vectors



The volume of the unit cell is

$$\Omega = [\vec{a}_1, \vec{a}_2, \vec{a}_3] = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

Plane-Wave: Basis Sets



$$\vec{r} \rightarrow \vec{r} + \vec{R}$$

where

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3,$$

$n_1, n_2, n_3 = \text{integers}$

Plane-Wave: Basis Sets

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\psi}_n(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Plane-wave Expansion

Since the system is periodic, our plane-wave expansion must consist of only the plane-waves $e^{i\vec{G}\cdot\vec{r}}$ that have the periodicity of the lattice,

We can determine these plane-waves from the following constraint

$$e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}$$

Plane-Wave: Basis Sets

It is easy to show from the periodicity constraint that the wave-vectors can be defined in terms of the following reciprocal lattice vectors

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

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

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

Reciprocal lattice vectors

Wave-vectors that satisfy the periodicity of the lattice

$$\vec{G}_{i_1 i_2 i_3} = \left(i_1 - \frac{N_1}{2} \right) \vec{b}_1 + \left(i_2 - \frac{N_2}{2} \right) \vec{b}_2 + \left(i_3 - \frac{N_3}{2} \right) \vec{b}_3$$

Plane-Wave: Basis Sets

The exact form of the plane-wave expansion used in plane-wave code is

$$u_n(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{i_1=1}^{N_1} \sum_{i_2=1}^{N_2} \sum_{i_3=1}^{N_3} \tilde{u}_n(\vec{G}_{i_1 i_2 i_3}) e^{i\vec{G}_{i_1 i_2 i_3} \cdot \vec{r}}$$

The upper-limits of the summation (N_1, N_2, N_3) control the spacing of the real-space grid

$$\vec{r}_{i_1 i_2 i_3} = \left(\frac{i_1}{N_1} - \frac{1}{2} \right) \vec{a}_1 + \left(\frac{i_2}{N_2} - \frac{1}{2} \right) \vec{a}_2 + \left(\frac{i_3}{N_3} - \frac{1}{2} \right) \vec{a}_3$$

Plane-Wave: Basis Sets

There is a further truncation of plane wave expansion in plane-wave calculations. Namely, only the reciprocal lattice vectors whose kinetic energy lower than a predefined maximum cutoff energy,

$$\frac{1}{2}|\vec{G}|^2 < E_{cut}$$

Wavefunction Cutoff Energy

are kept in the expansion, while the rest of the coefficients are set to zero. Besides reducing the computational load, this truncation strategy limits the effects of unit cell orientation on the outcome of the calculation.

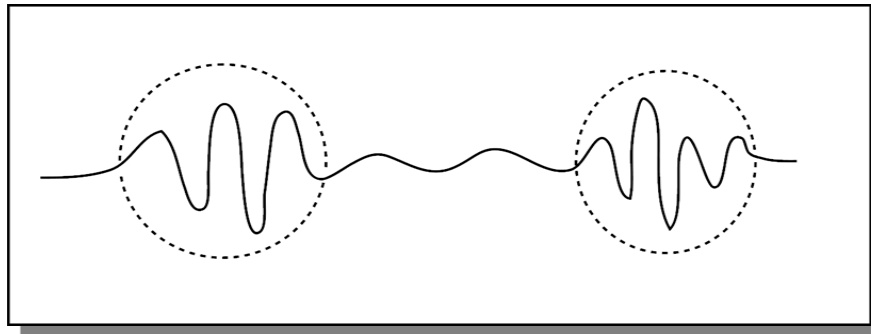
Pseudopotentials

The pseudopotential method is based on two observations.

First, in almost any system one could identify a set of the so-called core orbitals which change little from their atomic counterparts.

Second, the remainder, the so-called valence orbitals, acquire their oscillating behavior mainly due to Pauli exclusion principle or, in plain words, orthogonality constraints to the core orbitals.

In pseudopotential approximation the original atoms that constitute a given chemical system are modified by removing core energy levels and enforcing the Pauli exclusion principle via repulsive pseudopotential. This removes the wiggles from the atomic valence orbitals and allows efficient application of plane wave basis set expansion. The resulting pseudoatoms will in general acquire a nonlocal potential term.



Pseudopotentials

- The core electrons of an atom are computationally expensive with planewave basis sets
 - Large number of planewaves are required to expand their wavefunctions
 - Contributions of core electrons versus valence electrons to bonding is usually negligible
- To address this, we replace the atomic potential due to core electrons with a *pseudopotential* which has the same effect on valence electrons: (see also “Efficient pseudopotentials for plane-wave calculations by Troullier and Martins:
 - <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.43.1993>)

END

Thanks for your attention