

Quantum Theory of Materials

Introduction to Density Functional Theory and its Computational Challenges

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*In Quantum Chemistry and Material Science the objective is to derive chemical and **physical properties** of complex materials (total energy, energy derivatives respect to nuclei positions, band energy gaps, conductivity, etc..).*

*This goal is pursued through the investigation of the electronic structure and its achievement can be **very challenging**.*

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- 2 Many-electron problem
- 3 Kohn-Sham scheme and DFT
- 4 Methods overview
- 5 Full-Potential Linearized Augmented Plane-Wave Method (FLAPW)
- 6 Introduction to reverse simulation
- 7 Sequences of Eigenproblems
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The (time-independent) Schrödinger equation

general form and properties

$$\hat{H} \psi(\mathbf{x}) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \right) \psi(\mathbf{x}) = E \psi(\mathbf{x})$$

\hat{H} = Hamiltonian of a physical system:

- Hermitian operator
- In stationary cases it represents the (constant) energy of the system
- It is composed of a Kinetic ($-\frac{\hbar^2}{2m} \nabla^2$) and a Potential ($V(\mathbf{x})$) energy term.

$\psi(\mathbf{x})$ = Wavefunction:

- one-dimensional complex value function of many variables
- It is interpreted as probability amplitude so that its square is a density distribution
 $\Rightarrow \int |\psi(\mathbf{x})|^2 d\mathbf{x} = 1$
- It generally depends on a set of discrete countable numbers (for bounded systems)

The (time-independent) Schrödinger equation

general form and properties

$$\hat{H} \psi(\mathbf{x}) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \right) \psi(\mathbf{x}) = E \psi(\mathbf{x})$$

E = Energy eigenvalues:

- the time-independent Schrödinger equation is nothing else than an operatorial eigenvalue equation
- E as well as ψ depend generically on a set of discrete numbers (for bounded systems)
- The set of discrete numbers are called quantum numbers and are the consequence of the so-called first quantization

$$[\mathbf{x}, \mathbf{k}] = \mathbf{x} \cdot \mathbf{k} - \mathbf{k} \cdot \mathbf{x} = i\hbar \quad ; \quad \mathbf{k} = i\hbar \nabla$$

The (time-independent) Schrödinger equation

Example 1: one dimensional infinite well

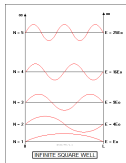
$$V(x) = \begin{cases} \infty & x < 0 \text{ and } x > L \\ 0 & 0 \leq x \leq L \end{cases} \implies -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E \psi(x)$$

Wave equation generic solution

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\psi(0) = \psi(L) = 0$$



Solution after boundary conditions

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2m L^2}$$

- 1 There are an infinite countable number of solutions parametrized by $n \in \mathbb{N}$
- 2 Wavefunctions with different quantum numbers are orthogonal $\int \Psi_m^* \Psi_n = \delta_{mn}$
- 3 Each Ψ_n has $n - 1$ nodes \implies for $n \gg 1$ Ψ_n oscillate very wildly
- 4 $n = 1$ solution is the so-called ground state: most symmetric and stable

The (time-independent) Schrödinger equation

Example 2: Hydrogen atom

$$V(\mathbf{r}) = -\frac{e^2}{4\pi \epsilon_0 r} \quad \Rightarrow \quad -\frac{\hbar^2}{2\mu} \frac{1}{r^2 \sin\theta} \left[\sin\theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin\theta} \frac{\partial^2}{\partial \phi^2} \right] \Psi(r, \theta, \phi) +$$
$$-\frac{e^2}{4\pi \epsilon_0 r} \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

Due to spherical potential depending only on radial coordinate the solution is separable

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Stability of the atom requires quantization of angular momentum $\Rightarrow L^2 = \ell(\ell + 1)\hbar^2$

$$R_{n\ell}(r) = r^\ell L_{n-\ell-1} e^{-\frac{r}{n}} \quad ; \quad Y_{\ell m}(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \left[\frac{2\ell + 1}{2} \frac{(\ell - m)!}{(\ell + m)!} \right]^{\frac{1}{2}} P_{\ell m} e^{im\phi}$$

$L_{n-\ell-1}$ associated Laguerre polynomials and $P_{\ell m}$ associated Legendre polynomials

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 \hbar^2 n^2} \quad ; \quad n = 1, 2, \dots \quad ; \quad \ell = 1, 2, \dots, n-1 \quad ; \quad m = -\ell, \dots, 0, \dots, \ell$$

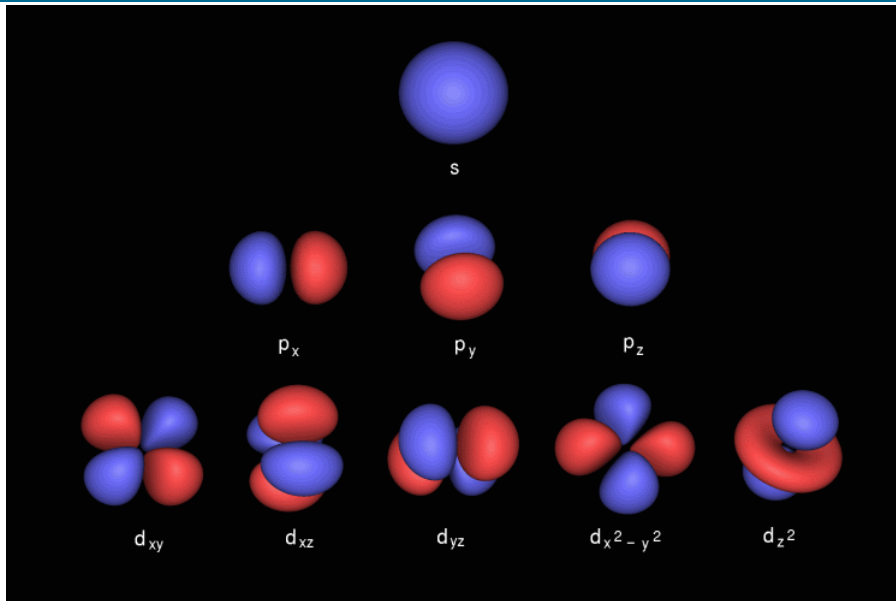
The (time-independent) Schrödinger equation

Example 2: Hydrogen atom

- $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$ are called orbitals
- Orbitals with $\ell = 0$ have spherical symmetry all the others have, at best, cylindrical symmetry
- High quantum numbers orbitals have many “lobes” \rightarrow oscillate wildly closer to r
- Relativistic effects, spin-orbit interactions, etc., force E to be dependent also on ℓ
- For each orbital you can accommodate two opposite spins (Pauli's principle): one \uparrow and one \downarrow
- Again the ground state is the most symmetric and stable state
- The spin orbitals constitute an orthogonal complete set of wavefunctions
- Open shells and closed shells: systematics of orbitals (core vs valence orbitals, s,p,d,...)

The (time-independent) Schrödinger equation

Example 2: Hydrogen atom



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Intro to Many-electron problem

Full Hamiltonian (neglecting spin and relativistic terms)

Atoms, molecules and solids are composed of many interacting electrons and nuclei

$$\hat{H}_{tot} = \sum_i \frac{\mathbf{p}_i^2}{2m} - \sum_{i,I} \frac{z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_I \frac{\mathbf{P}_I^2}{2M_I} + \frac{1}{2} \sum_{I \neq J} \frac{z_I z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- First 3 terms constitute the so-called electronic Hamiltonian – last two terms describe nuclei dynamics
- 1st and 4th term represent the kinetic energy of electrons and nuclei respectively ($\mathbf{p} = i\hbar\nabla$)
- 2nd term describes the Coulomb potential well experienced by electrons
- 3rd and 5th terms describe repulsion (due to same charge) between electrons and nuclei respectively

Note: Dynamics of electrons and nuclei are somewhat separated if it wasn't for the presence of the Coulomb potential

Consideration: Since $M_I \gg m_i \Rightarrow K_i \gg K_I$, it is possible to decouple the dynamics of fast variables (electrons) from the one of slow variables (nuclei)

This is at the base of the so-called adiabatic procedure also known as

Born-Oppenheimer approximation (1927)

- Nuclei are supposed fixed in a selected spatial configuration
- Attention is only focused on electronic eigenvalues as functions of the chosen nuclear coordinates
- The approximation introduces the concept of adiabatic potential-energy surfaces

Note: Usually the main interest is in the *ground adiabatic sheet*. This is usually non-degenerate and has a minimum \Rightarrow “fixed” lattice leading to an adiabatic or electronic Hamiltonian

$$\hat{H}_{el} = - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \sum_{i,I} \frac{z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Electronic Schrödinger Equation

$$\hat{H}_{\text{el}} \Psi(\mathbf{r}_1; \sigma_1, \mathbf{r}_2; \sigma_2, \dots, \mathbf{r}_N; \sigma_N) = E \Psi(\mathbf{r}_1; \sigma_1, \mathbf{r}_2; \sigma_2, \dots, \mathbf{r}_N; \sigma_N)$$

$\Psi : \left(\mathbb{R}^3 \times \left\{ \pm \frac{1}{2} \right\} \right)^N \longrightarrow \mathbb{R}$ high-dimensional anti-symmetric function.

One electron approximation:

- Hartree-Fock (occupied states only)

Configuration Interaction (CI)

- Coupled Clusters (CC)

etc.

} ← (incl. excited states) Quantum Chemistry

Electron density:

- Ground state → Density Functional Theory (DFT)
- Nuclei dynamics → Molecular Dynamics (MD)

Intro to Many-electron problem

Basic Hartree-Fock: a simple self-consistent example

- Identical particles
- Antisymmetry for interchange of coordinates (spin included)
- Orthonormal one-particle functions base

$$\Psi(\mathbf{r}_1; \sigma_1, \mathbf{r}_2; \sigma_2, \dots, \mathbf{r}_N; \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(\mathbf{r}_1; \sigma_1) & \Psi_1(\mathbf{r}_2; \sigma_2) & \dots & \Psi_1(\mathbf{r}_N; \sigma_N) \\ \Psi_2(\mathbf{r}_1; \sigma_1) & \Psi_2(\mathbf{r}_2; \sigma_2) & \dots & \Psi_2(\mathbf{r}_N; \sigma_N) \\ \dots & \dots & \dots & \dots \\ \Psi_N(\mathbf{r}_1; \sigma_1) & \Psi_N(\mathbf{r}_2; \sigma_2) & \dots & \Psi_N(\mathbf{r}_N; \sigma_N) \end{vmatrix}$$

Hartree self-consistent approximation: Each electron moves in the effective field corresponding to the Coulomb potential generated by the charge distribution of all the other $N - 1$ electrons

$$V_H(\mathbf{r}) = \int \rho(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \quad ; \quad \rho(\mathbf{r}) = -e \sum_j^{(occ)} \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}) (= \text{charge density})$$

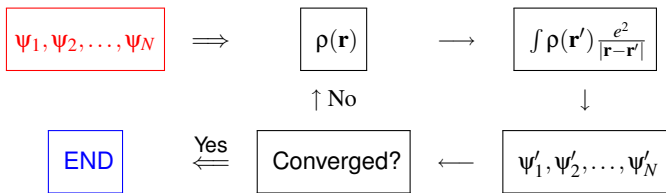
The one-electron spin orbitals making up Ψ , satisfy the Hartree equation

$$\left[\frac{\mathbf{p}^2}{2m} - \frac{z e^2}{|\mathbf{r} - \mathbf{R}|} + V_H(\mathbf{r}) \right] \psi_i = \varepsilon_i \psi_i$$

Intro to Many-electron problem

Basic Hartree-Fock: continued

$$\left[\frac{\mathbf{p}^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right] \psi_i = \epsilon_i \psi_i; \quad \rho(\mathbf{r}) = -e \sum_{j \neq i}^{(\text{occ})} \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}); \quad V_{\text{H}}(\mathbf{r}) = \int \rho(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$



Cycles are *repeated* up to self-consistency of input and output functions and potentials

Because of the effective Hartree potential V_{H} this system is also referred to as
“**non-interacting**”

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We split the adiabatic Hamiltonian in *internal* and *external* terms

$$\hat{H}_{\text{el}} = \hat{H}_{\text{int}} + V_{\text{ext}} \iff \begin{cases} \hat{H}_{\text{int}} = K + V_{\text{ee}} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ V_{\text{ext}} = \sum_i v_{\text{ext}}(\mathbf{r}) = - \sum_I \sum_l \frac{z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \end{cases}$$

HK Theorem statement (1964)

There is one-to-one correspondence between the ground-state density $n_0(\mathbf{r})$ of a N electron system and the external potential acting on it. $n_0(\mathbf{r})$ is then said to be v -representable

- i) $n_0(\mathbf{r}) \iff v_{\text{ext}}(\mathbf{r})$ $n_0(\mathbf{r})$ is the ground state density
- ii) $\mathcal{E}_{\text{HK}}[n, v_{\text{ext}}] = \mathcal{F}_{\text{HK}}[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})$ unique functional
- iii) $E_0 = \min_n \mathcal{E}_{\text{HK}}[n, v_{\text{ext}}]$ minimum at the exact ground state density
- vi) $K[n] + V_{\text{ee}}[n] = \mathcal{F}_{\text{HK}}[n]$ universal (v -independent)

$$\begin{array}{ccc} V_{\text{ext}}(\mathbf{r}) & \xleftarrow{\text{HK}} & n_0(\mathbf{r}) \\ \downarrow & & \uparrow \\ \Psi_i(\{\mathbf{r}\}) & \rightarrow & \Psi_0(\{\mathbf{r}\}) \end{array}$$

- Any property of a system of many interacting particles can be viewed as a functional of $n_0(\mathbf{r})$
- The H-K proves the existence of such functionals
- H-K does not provide any method to compute such functionals exactly
- In many cases these are non-local functionals depending simultaneously upon $n_0(\mathbf{r})$ at different positions \mathbf{r}
- Even if $\mathcal{F}_{\text{HK}}[n]$ is a universal functional there is no known approach that allows to go, for example, from density to kinetic energy

H-K theorem by itself does not provide an **operative** way to use density functional theory in practical problem

K-S ansatz (1965)

Interactive v -representable charge density $n_0(\mathbf{r})$ are also non-interactive v -representable.

In other words, for each interactive system described by the charge density $n_0(\mathbf{r})$, it exists an auxiliary non-interactive system described by the same charge density.

$$\begin{array}{ccccccc}
 V_{\text{ext}}(\mathbf{r}) & \xleftarrow{\text{HK}} & n_0(\mathbf{r}) & \xleftrightarrow{\text{KS}} & n_0(\mathbf{r}) & \xrightarrow{\text{HK}_0} & V_{\text{KS}}(\mathbf{r}) \\
 \downarrow & & \uparrow & & \uparrow & & \downarrow \\
 \Psi_i(\{\mathbf{r}\}) & \rightarrow & \Psi_0(\{\mathbf{r}\}) & & \Psi_{i=1, N_e}(\mathbf{r}) & \leftarrow & \Psi_i(\mathbf{r})
 \end{array}$$

Interacting system

$$V_{\text{ee}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Non-interacting system

$$V_{\text{H}} = \int n_0(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

\iff

The Kohn-Sham scheme allows for a practical application of the Hohenberg-Kohn theorem through a set of non-linear coupled equations

Interacting system

Non-interacting system

$$\mathcal{E}_{\text{HK}}[n] = \mathcal{F}_{\text{HK}}[n] + \int v_{\text{ext}}([n], \mathbf{r})n(\mathbf{r}) \iff \mathcal{E}_0[n] = K_0[n] + \int v_{\text{ext}}([n], \mathbf{r})n(\mathbf{r}) + E_{\text{H}}[n] + E_{\text{xc}}[n]$$

The K-S equations

- 1 $v_0([n], \mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int v_{\text{H}}(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') + v_{\text{xc}}([n], \mathbf{r})$
- 2 $\hat{H}_{\text{KS}}\psi_i(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + v_0(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}); \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots$
- 3 $n_0(\mathbf{r}) = \sum_i^{N_e} |\psi_i(\mathbf{r})|^2$
- 4
$$\begin{cases} v_{\text{xc}}([n], \mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} & \text{Exchange potential} \\ E_{\text{xc}}[n] = \mathcal{F}_{\text{HK}}[n] - \left(\frac{1}{2} \int n(\mathbf{r}')v_{\text{H}}(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') + K_0[n]\right) \end{cases}$$

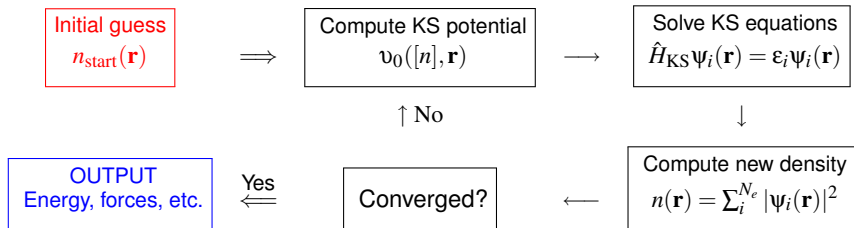
- The kinetic energy $K_0[n]$ is now **computable** directly from the orbital functions $\psi_i(\mathbf{r})$
- The ground state energy now can be *operatively* computed from $\mathcal{E}_0[n]$

$$E_0 = \mathcal{E}_0[n_0] = \sum_{i=1}^{N_e} \epsilon_i - \frac{1}{2} \int n_0(\mathbf{r}') v_H(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}) + E_{xc}[n_0] - \int v_{xc}([n], \mathbf{r}) n_0(\mathbf{r})$$

- All the complex many-body contributions are now incorporated in an *exchange-correlation functional of the density*
- $E_{xc}[n]$ can be reasonably approximated as a local or nearly local functional of the charge density
- Many approximations - LDA, GGA, OEP, EXX, Hybrid, etc.

▶ see appendix C

Conceptually similar to the self-consistent cycle of Hartree-Fock methods



In practice this iterative cycle is much more computationally challenging.

- 1 Educated guess for $n_{\text{start}}(\mathbf{r})$. For example in molecular or solid state systems it is usually constructed from an opportunely tuned sum of atomic densities

$$n_{\text{start}}(\mathbf{r}) = \sum_{\alpha} n_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha}); \quad \alpha = \text{nuclei index}$$

- 2 Each component of $v_0([n], \mathbf{r})$ is computed separately and poses a different numerical problem.

- The external potential can be a sum of atomic potentials $v_{\text{ext}}(\mathbf{r}) = \sum_{\alpha} v_{\alpha}(\mathbf{r} - \mathbf{R}_{\alpha})$. In many cases the use of the Coulomb potential is unfeasible \rightarrow Pseudo-potentials
- Hartree potential is computed either by direct integration (atomic cases) or by solving the associated Poisson equation

$$\nabla^2 v_{\text{H}}(\mathbf{r}) = -4\pi n(\mathbf{r})$$

- The xc potential is formally a functional derivative of the $E_{\text{xc}}[n]$ functional. Hundreds of approximate xc functional have appeared in the last 30 years

- 3 The goal of solving the KS equations is to find the lowest N_e eigenstates of the Hamiltonian \hat{H}_{KS} .
- For atomistic systems it is reduced to a one-dimensional equation \rightarrow efficient integration method
 - For all the other cases a basis set is used leading to the diagonalization of \hat{H}_{KS} . Such an operation makes use of different methods depending on the sparsity of the Hamiltonian as well as the size of the basis set.
- 4 Convergence: the two most common methods are based on the difference of total energies or densities between iterations i and $i - 1$

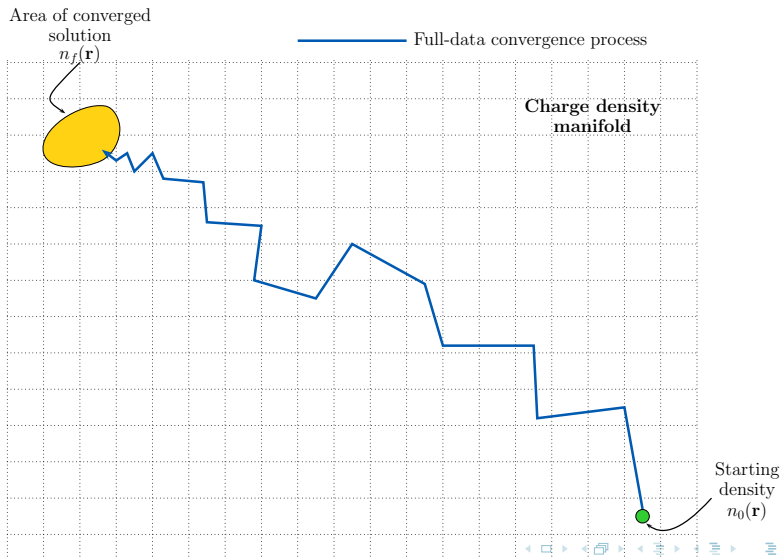
$$\left| E_0^{(i)} - E_0^{(i-1)} \right| < \eta_E \quad \text{or} \quad \left| n_0^{(i)} - n_0^{(i-1)} \right| < \eta_n$$

If the criterium has not been fulfilled, the cycle is started with a new density. Usually, to avoid instabilities, it is a mix of new and old density.

- Simplest scheme - linear mixing $n_0^{(i+1)} = \beta n' + (1 - \beta)n_0^{(i)}$
- More sophisticated schemes use extrapolation of several iterations and more complex methods

Kohn-Sham scheme and DFT

The process of convergence



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The different methods stem from the fact that the Kohn-Sham equations must be “discretized” before they can be numerically solved

- 1 **Plane Waves:** uses plane wave basis expansions and a variety of different ways to express $v_{\text{ext}}[n]$
- 2 **Localized orbitals:** uses specialized functions such as exponential or Gaussian orbitals
- 3 **Real-Space methods:** does not use an explicit basis but discretizes the equations in real space

Plane wave expansions of the K-S eq. take advantage of the **periodicity** of the crystal.

In the case of one-dimensional Schrödinger equation:

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E \psi(x); \quad V(x) = \sum_{n=-\infty}^{+\infty} V_n e^{ih_n x}; \quad h_n = \frac{2\pi n}{a}$$

Applying the Hamiltonian to a normalized plane wave $W_k(x) = \frac{1}{\sqrt{L}} e^{ikx}$

$$\hat{H}W_k(x) \subset \mathbf{S}_k \equiv \{W_k(x), W_{k+h_1}(x), W_{k-h_1}(x), W_{k+h_2}(x), W_{k-h_2}(x), \dots\}$$

A generic wavefunction $\psi(x)$ can be obtained diagonalizing \hat{H} on the subspace \mathbf{S}_k and expressed as a linear combination

$$\psi_k(x) = \frac{1}{\sqrt{L}} \sum_n c_n(k) e^{i(k+h_n)x} \quad ; \quad \psi_k(x+ma) = e^{ikma} \psi_k(x)$$

$$k \in \text{BZ} \equiv \left\{ k : -\frac{\pi}{a} < k \leq \frac{\pi}{a} \right\} \quad \text{First Brillouin Zone}$$

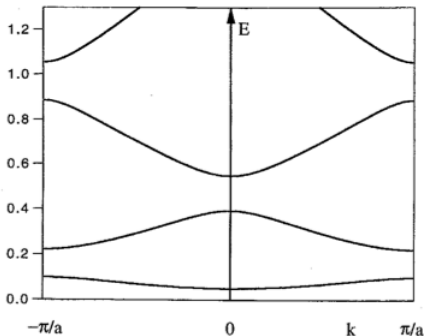
DFT methods overview

Plane wave expansion: Bloch theorem... cont.

- $\psi_k(x) = u_k(x) e^{ikx}$ is a travelling wave function modulated, on the microscopic scale by an appropriate function with lattice periodicity
- in general, the energy spectrum $E(k)$ consists of allowed regions separated by energy gaps. These are usually referred to as **Energy Bands**
- In one dimension it is possible to demonstrate that these bands do not cross each other
- In solids these bands can be quite completed

Example of periodic array of quantum wells (Kronig-Penney model)

Grosso and Parravicini



DFT methods overview

Plane waves: calculating \hat{H}_{KS}

In 3D the Bloch theorem is easily generalized

$$\phi_{\mathbf{k}}(x) = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k},\nu}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} \quad ; \quad \begin{array}{l} \mathbf{G} = \text{reciprocal lattice vector} \\ \nu = \text{energy band index} \end{array}$$

All the quantities of interest are computed in Fourier space using FFT. There are only two parameters that need to be fine-tuned for every calculations:

- The Brillouin zone sampling (using space group lattice and special points)
 - Cut-off \mathbf{G}_{\max} in order to truncate the sums over reciprocal lattice vectors \mathbf{G}
- 1 Density – the $f(\epsilon_{\mathbf{k},\nu})$ denotes the occupation numbers for the K-S energies $\epsilon_{\mathbf{k},\nu}$

▶ see appendix A

$$n(\mathbf{G}) = \sum_{\mathbf{k},\nu} \sum_{\mathbf{G}'} f(\epsilon_{\mathbf{k},\nu}) c_{\mathbf{k},\nu}^*(\mathbf{G}' - \mathbf{G}) c_{\mathbf{k},\nu}(\mathbf{G})$$

2 The Kinetic energy

$$K = \frac{1}{2} \sum_{\mathbf{k},\nu} \sum_{\mathbf{G}} f(\epsilon_{\mathbf{k},\nu}) |c_{\mathbf{k},\nu}(\mathbf{G})|^2 |\mathbf{k} + \mathbf{G}|^2$$

3 The K-S potential $v_0[n]$

- Calculating the Hartree v_H , the external potential v_{ext} and the nuclei interaction presents some issues due the divergence of the potential at $\mathbf{G} = 0 \Rightarrow$ however the sum of three divergences is a constant (Ewald)
- Valence orbitals of high atomic number z atoms oscillates wildly (remember 1D case) in the vicinity of the atomic nucleus due to orthogonalization respect to inner core orbitals \Rightarrow large numbers of plane waves required!
- Description of atom based only on valence orbitals \Rightarrow introduction of an effective potential **Pseudo-potential** that takes into account the nuclei as well as the core electrons.

▶ see appendix B

Finally the K-S equations become

$$\sum_{\mathbf{G}'} \hat{H}_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) c_{\mathbf{k},\nu}(\mathbf{G}') = \epsilon_{\mathbf{k},\nu} c_{\mathbf{k},\nu}(\mathbf{G})$$

$$\hat{H}_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + v_{ext}^{eff}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') + v_H(\mathbf{G} - \mathbf{G}') + v_{xc}(\mathbf{G} - \mathbf{G}')$$

Eigenvalue equation $Ax = \lambda x$ where $A = \hat{H}$, $x = c_{\mathbf{k},\nu}$, and $\lambda = \epsilon_{\mathbf{k},\nu}$.

- The Laplacian term (kinetic energy) of the Hamiltonian is represented by a **diagonal** matrix
- The potential $v_0[n]$ gives rise to a **dense** matrix. Its computation can be a very expensive task.
- For each vector \mathbf{k} there is an independent eigenvalue equation
- Each FFT performed costs $q \log q$ operation where q is the number of plane waves. For large q this can be costly.
- The most costly operation is the diagonalization, contributing with a G_{\max}^3 cost.
- The plane wave expansion is quite effective for periodic systems. For nonperiodic systems such as clusters, liquids can be combined with supercell methods that repeat local configuration to impose periodicity.

In this approach to each atom labeled by α is associated a set of functions which combine radial functions with spherical harmonics

$$\psi_{n\ell m}^{\alpha}(\mathbf{r}) = \phi_{n\ell}^{\alpha}(\mathbf{r}_{\alpha}) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) \quad ; \quad \mathbf{r}_{\alpha} = \mathbf{r} - \mathbf{R}_{\alpha}$$

The radial functions $\phi_{n\ell}^{\alpha}(\mathbf{r}_{\alpha})$ are the solution of 1D equation. They can be exponentials, Gaussians or any set of localized functions.

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + \frac{\ell(\ell+1)}{2r^2} + v_{\text{KS}} \right] \phi_{n\ell}^{\alpha}(\mathbf{r}_{\alpha}) = \epsilon_{n\ell} \phi_{n\ell}^{\alpha}(\mathbf{r}_{\alpha})$$

Gaussians, for example:

- yield analytical matrix elements for \hat{H}_{KS} provided also the potential are expanded in terms of Gaussians
- basis set size produces much smaller matrices than plane wave
- requires many indices to label state, orbitals and basis set increasing dramatically the “bookkeeping” operations
- convergence is not controlled by a single parameter; if atoms in a solid are slightly moved, the basis should be re-optimized for the new geometry

Functions $\psi_{\mathbf{k}\nu}(\mathbf{r})$ are not expanded in a basis set but just sampled on a real-space mesh. This property overcomes many complications arising from non-periodic physical systems

- 1 Kinetic energy results from the discretization of the Laplacian using a finite M-order rule

$$\nabla^2 \psi_{\mathbf{k}\nu}(\mathbf{r}) \Big|_{\mathbf{r}=(x_i, y_j, z_k)} = \sum_{n_x=-M}^M C_{n_x} \psi_{\mathbf{k}\nu}(x_i + n_x a, y_j, z_k) + (\text{same for } y_j \text{ and } z_k) + O(a^{2M+2})$$

- 2 The potential term $v_0[n]$ is mostly diagonal.

When the pseudo-potential and/or a non-simple xc potential are used there is the possibility of non-local term. In discrete form the non-local contribution becomes a sum of rank-one updates over all atoms:

$$\sum_{\alpha, \ell, m} d_{\alpha, \ell, m} \mathbf{U}_{\alpha, \ell, m} \mathbf{U}_{\alpha, \ell, m}^T \quad ; \quad \mathbf{U}_{\alpha, \ell, m} = \text{sparse vectors}$$

The v_H is usually obtained by efficiently by solving Poisson eq. in Fourier space and transforming back (or by multi-grid techniques)

The main advantages of the real-space methods is the simplicity and intuitiveness of the whole procedure. There are also some drawbacks

- Higher order finite differences can improve convergence
- The matrix \hat{H}_{KS} is usually bigger than in the plane waves method but quite sparse. Consequently the solution of the eigenvalue problem is achieved through iterative methods.
- There is no need to store the Hamiltonian explicitly as a sparse matrix
- The convergence depends only on one parameter: the grid spacing
- most of the implementations are not variational \rightarrow computed ground energy may be lower than true energy
- it breaks translational symmetry \rightarrow artificial lifting of some energy degeneracies

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Introduction to FLAPW

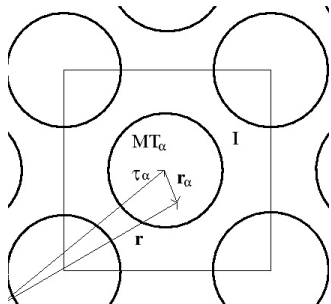
Linearized augmented plane wave (LAPW) in a Muffin Tin (MT) geometry

Lapw

$$\psi_{\mathbf{k},\nu}(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| \leq \mathbf{G}_{max}} c_{\mathbf{k},\nu}^{\mathbf{G}} \phi_{\mathbf{G}}(\mathbf{k}, \mathbf{r})$$

\mathbf{k} Bloch vector
 ν band index

$$\phi_{\mathbf{G}}(\mathbf{k}, \mathbf{r}) = \begin{cases} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} & \text{Interstitial (I)} \\ \sum_{\ell,m} \left[a_{\ell m}^{\alpha,\mathbf{G}}(\mathbf{k}) u_{\ell}^{\alpha}(r) + b_{\ell m}^{\alpha,\mathbf{G}}(\mathbf{k}) \dot{u}_{\ell}^{\alpha}(r) \right] Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{Muffin Tin} \end{cases}$$



boundary conditions

Continuity of wavefunction and its derivative at MT boundary

$$a_{\ell m}^{\alpha,\mathbf{G}}(\mathbf{k}) \quad \text{and} \quad b_{\ell m}^{\alpha,\mathbf{G}}(\mathbf{k})$$

Introduction to FLAPW

Linearized augmented plane wave (LAPW) in a Muffin Tin (MT) geometry... cont.

The radial functions $u_\ell^\alpha(r)$ are the solutions of the atomic Schrödinger equations where the potential retains only the spherical part.

$$\hat{H}_{\text{sph}}^\alpha u_\ell^\alpha(r) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} + v_{\text{sph}}^\alpha(r) \right] r u_\ell^\alpha(r) = E_\ell u_\ell^\alpha(r)$$

where the \dot{u} can be determined from the energy derivative of the Schrödinger-like equation

$$\hat{H}_{\text{sph}}^\alpha \dot{u}_\ell^\alpha = E_\ell \dot{u}_\ell^\alpha + u_\ell^\alpha$$

- E_ℓ is a parameter and it is predetermined by optimization
- like the plane wave case there is a cut-off \mathbf{G}_{max} (typically $\sim 3.5 - 4.0$)
- unlike the plane waves there is also a cut-off (for open-shell atoms) on ℓ_{max} (typically ~ 8)
- unlike the plane waves this set of basis functions is overcomplete \Rightarrow it is NOT an orthogonal set
- it is one of the *most accurate* implementation of ab initio methods

The Kohn-Sham equations receive contributions from the Interstitial as well as the Muffin-Tin regions. These can be treated separately

$$\hat{H}_{\mathbf{G}\mathbf{G}'}^{\text{MT}} + \hat{H}_{\mathbf{G}\mathbf{G}'}^{\text{I}}$$

Both the density and the K-S potential are expanded in the same fashion as the wave functions

$$v_{\text{KS}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} v_{\text{I}}^{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \\ \sum_{\ell m} v_{\text{MT}}^{\ell m}(r) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) \end{cases} \quad n(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} n_{\text{I}}^{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} & \text{Interstitial} \\ \sum_{\ell m} n_{\text{MT}}^{\ell m}(r) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{MT} \end{cases}$$

- 1 Kinetic energy for Interstitial and MT give diagonal matrix entries
- 2 The spherical part of the potential, inside MT, are also diagonal by construction. The non-spherical part (like v_{H}) are more complicated to compute (Pseudo-charge method) and in general result in a dense matrix.

▶ see appendix D

- 3 In the FLAPW framework the Kohn-Sham equations translate to **generalized eigenvalue equations**.

Inserting the LAPW expansion in the equations

$$\phi_{\mathbf{G}}^*(\mathbf{k}, \mathbf{r}) \sum_{\mathbf{G}'} \hat{H}_{\text{KS}} c_{\mathbf{k}, \mathbf{v}}^{\mathbf{G}'} \phi_{\mathbf{G}'}(\mathbf{k}, \mathbf{r}) = \lambda_{\mathbf{k}, \mathbf{v}} \phi_{\mathbf{G}}^*(\mathbf{k}, \mathbf{r}) \sum_{\mathbf{G}'} c_{\mathbf{k}, \mathbf{v}}^{\mathbf{G}'} \phi_{\mathbf{G}'}(\mathbf{k}, \mathbf{r}),$$

defining the matrix entries for the left and right hand side respectively as Hamiltonian $A(\mathbf{k})$ and overlap matrices $B(\mathbf{k})$

$$\{A(\mathbf{k}), B(\mathbf{k})\} = \sum_{\alpha} \int \phi_{\mathbf{G}}^*(\mathbf{k}, \mathbf{r}) \{\hat{H}_{\text{KS}}, \hat{\mathbb{1}}\} \phi_{\mathbf{G}'}(\mathbf{k}, \mathbf{r})$$

and remembering that the basis set is overcomplete ($\Rightarrow B \neq \text{diag}$)

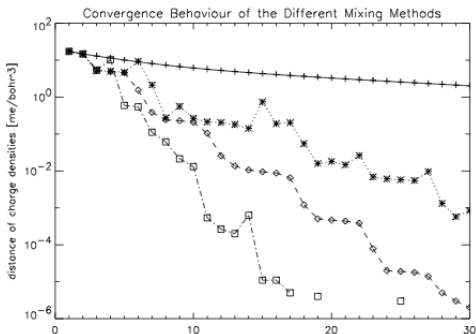
$$\sum_{\mathbf{G}'} A_{\mathbf{G}\mathbf{G}'}(\mathbf{k}) c_{\mathbf{k}, \mathbf{v}}^{\mathbf{G}'} = \lambda_{\mathbf{k}, \mathbf{v}} \sum_{\mathbf{G}'} B_{\mathbf{G}\mathbf{G}'}(\mathbf{k}) c_{\mathbf{k}, \mathbf{v}}^{\mathbf{G}'}$$

- 4 The started density is constructed from a superposition of atomic densities. The process of minimization of the energy functional E_0 determines a fix-point map

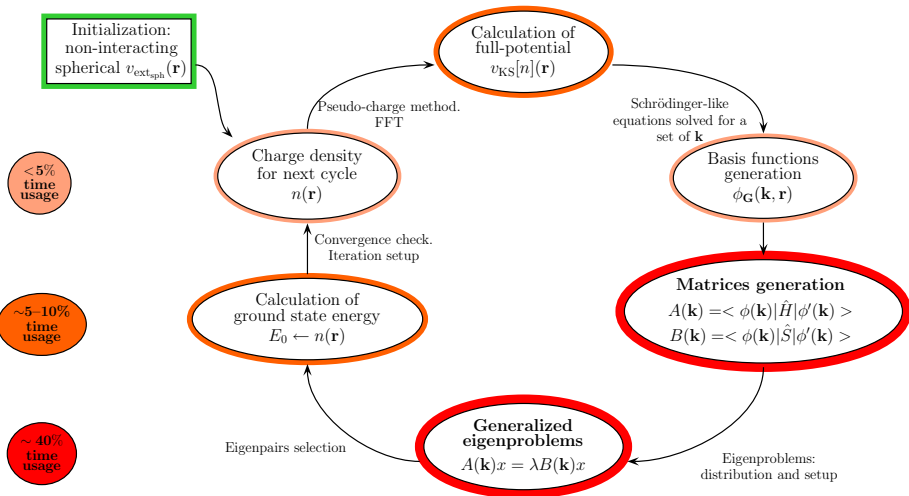
$$E_0 = \min_n \mathcal{E}_{\text{KS}}[n, v_{\text{ext}}] \implies n^{(i+1)} = F\{n^{(i)}\}$$

In order to find the fixed point of F several methods can be used

- linear mixing \rightarrow linear convergence
- Newton-Raphson methods \rightarrow quadratic convergence, Jacobian computationally demanding
- Quasi-Newton methods \rightarrow superlinear convergence, local Jacobian



FLAPW self-consistent cycle



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The “self-made man” approach

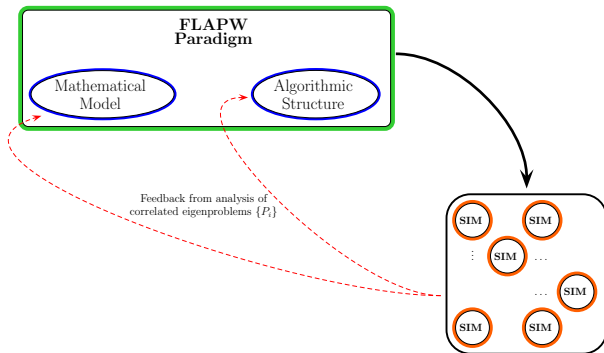
Mathematical Model \implies Algorithmic Structure \implies Simulations \implies Physics

- 1 **Math** \implies **Algorithm** – Often a sort of “mechanical” one-way process with little room for optimization;
- 2 **Algorithm** \implies **Sim** – The simulation is considered an end product, the successful translation of an algorithm into a series of machine accessible operations resulting in the computation of meaningful physical quantities;
- 3 **Math** \implies **Sim** – The mathematical model and the simulation are considered as practically disjoint.

Reverse Simulation

A different approach

Simulations \implies $\left\{ \begin{array}{l} \text{Mathematical model} \\ \text{Algorithmic structure} \end{array} \right.$



An Example: Sequences of eigenproblems in Density Functional Theory

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A (mostly) converging process

The traditional approach

Initialization: At every iteration of the cycle all numerical quantities are entirely re-computed

- A new set of basis functions is assembled at each iteration cycle (Math \nleftrightarrow Sim)
- The entries of the matrices A and B are re-initialized at each iteration cycle (Algorithm \nleftrightarrow Sim)

Eigenproblems: Each eigenproblem $P^{(i)} : A^{(i)}x = \lambda B^{(i)}x$ at iteration i is solved in total independence from the eigenproblem $P^{(i-1)}$ of the previous iteration (Algorithm \nleftrightarrow Sim)

Convergence: Starting with a electron density close enough to the one minimizing the energy E_0 it is likely to reach convergence within few tens of iterations. Unfortunately there is no general theorem establishing the converging conditions

- # of steps is still uncertain. They depend on the material and the initial guess (area of convergence) (Math \nleftrightarrow Sim)
- $|n'(\mathbf{r}) - n(\mathbf{r})|$ undergo relatively small decreasing oscillations (Math \nleftrightarrow Sim)

Sequences of eigenproblems

- Consider the set of generalized eigenproblems $P^{(1)} \dots P^{(i)} P^{(i+1)} \dots P^{(N)} \neq (P)^N$
- Could this sequence $\{P^{(i)}\}$ of eigenproblems **evolve** following a convergence pattern in line with the convergence of $n(\mathbf{r})$?

Investigating evidence of evolution

- (a) Eigenvectors transformation from one iteration to the next
- (b) Distance between successive Hamiltonian matrices A_k

Sequences of eigenproblems

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Investigating evidence of evolution

- (a) Eigenvectors transformation from one iteration to the next
- (b) Distance between successive Hamiltonian matrices $A_{\mathbf{k}}$

$$\sum_{\mathbf{G}'} [A_{\mathbf{G}\mathbf{G}'}(\mathbf{k}) - \lambda_{\mathbf{k}\nu} B_{\mathbf{G}\mathbf{G}'}(\mathbf{k})] c_{\mathbf{k}\nu}^{\mathbf{G}'} = 0$$

Reminder:

- the eigenvectors x , solving for each problem P , are vectors of coefficients $c_{\mathbf{k}\nu}^{\mathbf{G}}$ expressing orbital wave functions $\psi_{\mathbf{k},\nu}(\mathbf{r})$ as a linear combination of basis wave functions $\phi_{\mathbf{G}}(\mathbf{k}, \mathbf{r}) \rightarrow$ eigenvectors are seemingly uncorrelated across iterations
- # of \mathbf{k} = 1:10-100 ; # of i = 1:20-50 ; size of A : 1,000 - 20,000

Actions:

- study the evolutions of the angles b/w eigenvectors of successive iterations
- develop a method that establishes systematically a one-to-one correspondence b/w eigenvectors
- collect data on eigenvectors deviation angles

Analysis:

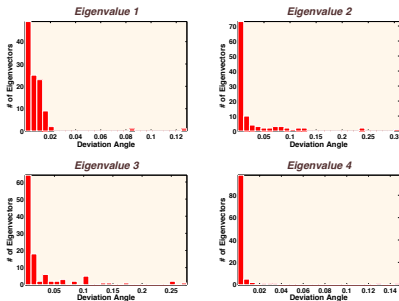
- 1 i and λ fixed \Rightarrow distribution among $\mathbf{k}s$
- 2 fix $\mathbf{k} \Rightarrow$ multi-plot on evolution for all λs
- 3 fix $\lambda \Rightarrow$ multi-plot on evolution for all $\mathbf{k}s$

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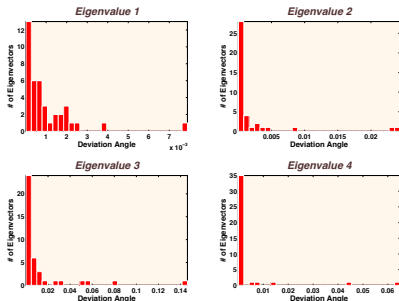
Eigenvectors evolution - Histograms

fixed λ and i

Cu bulk



Zinc Oxide



Considerations:

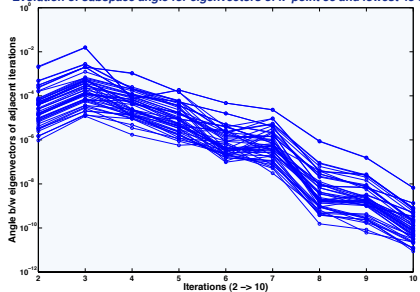
- 1 Distribution of deviation angles peaked on lowest end of the interval with small tail
- 2 “Democratic” contribution of eigenvectors to convergence process

Eigenvectors evolution - Multiplot

fixed k

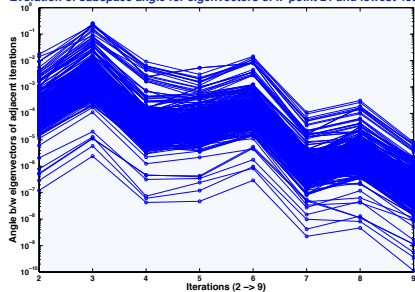
Cu bulk

Evolution of subspace angle for eigenvectors of k-point 33 and lowest 48 e_i



Zinc Oxide

Evolution of subspace angle for eigenvectors of k-point 21 and lowest 485 e_i



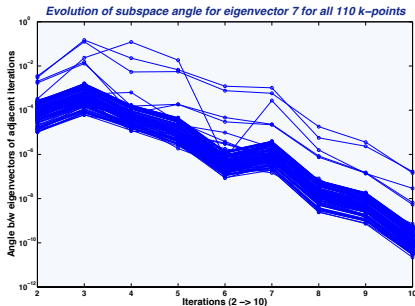
Considerations:

- 1 Angles decrease monotonically with some oscillation (excess of localized charge)
- 2 Majority of angles are small after the first few iterations
- 3 “Universal” behaviour

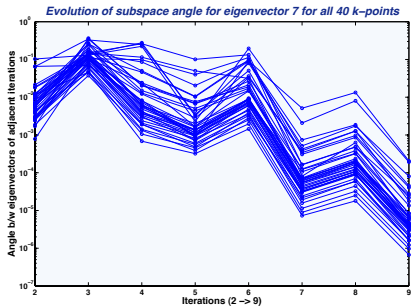
Eigenvectors evolution - Multiplot

fixed λ

Cu bulk



Zinc Oxide



Considerations:

- 1 some k-points contribute slightly more \rightarrow Help identify sensitive areas of the reciprocal lattice
- 2 In line with the “democratic” principle

- There is a strong correlation between eigenvectors of successive eigenproblems $x^{(i-1)}$ and $x^{(i)}$
- It validates the importance of looking at the set of eigenproblems as a sequence $\{P^{(i)}\}$

Can we exploit this result?

Use an iterative solver where the eigenvectors of $P^{(i-1)}$ are fed to solve $P^{(i)}$

Exploratory study using SLEPc framework:

- 1 Subspace Iteration Method
- 2 Implicit Restarted Arnoldi Method
- 3 Krylov-Schur Method

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Molecule: an example of high-T superconducting material

Matrix size: 2628

Num of fixed-point iterations: 32

Num of k-points: 27

B ill-conditioned

B is in general almost singular. Ex:

$$\text{size}(A) = 50 \rightarrow \kappa(A) \approx 10^4 \quad \text{size}(A) = 500 \rightarrow \kappa(A) \approx 10^7$$

We used the standard form for the problem

$$Ax = \lambda Bx \rightarrow A'y = \lambda y \quad \text{with} \quad A' = L^{-1}AL^{-T} \quad \text{and} \quad y = L^T x$$

TOL:

$$\frac{\|Ax - \lambda x\|}{\|\lambda x\|} = 1e - 07$$

N_{ev} = Number of searched eigenpairs

N_{vc} = size of subspace

$$N_{vc} \geq \max[2 \times N_{ev}, N_{ev} + 15]$$

for random vectors

Subspace Iteration Method

This method is based on

- Inner loop $V \leftarrow A'V$
- A refinement loop using a Rayleigh-Ritz quotient

It can accept, as initial guess, the entire set of vectors V

Iter cycle	Nev=5, Nvc=20 random	Nev=5, Nvc=20 feed-in	Nev=10, Nvc=25 random	Nev=10, Nvc=20 feed-in
10	75.43 s	52.31 s	114.60 s	80.17 s
20	74.89 s	50.74 s	113.05 s	82.64 s
30	74.93 s	51.56 s	112.15 s	79.49 s

Considerations:

- 1 30% speed-up independently from Nev search space
- 2 Nvc for the feed-in can be adjusted for better exploitation
- 3 Still very slow and not competitive with the other methods

They can accept, as initial guess, only **one vector** (we chose the dominant one)

Iter cycle	Nev=4, Nvc=20 IRAM random	Nev=4, Nvc=20 IRAM feed-in	Nev=10, Nvc=25 (K-S) random	Nev=10, Nvc=25 (K-S) feed-in
10	5.37 s	3.37 s	3.37 s	2.54 s
20	5.37 s	3.34 s	3.39 s	2.51 s
30	5.37 s	3.36 s	3.39 s	2.55 s

Considerations:

- 1 between 25% and 35% speed-up
- 2 Results depend on the Nev (speed up decreases as Nev increase)
- 3 Convergence in IRAM-random seems to be influenced by the clustering of eigenvalues

1 Feeding eigenvectors:

- All methods experience between 25% and 35% speed-up
- Due to the different number of eigenvectors that can be “seeded”, the speed up for IRAM and K-S is limited to few sought after eigenpairs
- Subspace Iteration does not have limits but it is still not competitive

2 Direct vs Iterative:

- Preliminary results, using IRAM, show that iterative methods for dense matrices can be competitive if a portion 10% or lower of the spectrum is sought after
- Iterative methods become competitive for large systems (size > 10000)
- When GPUs are factored in, iterative methods may be competitive even for higher portion of the spectrum.

3 Future work:

- Using block Krylov-Schur methods will allow “seeding” the eigensolver with more eigenvectors. This should provide extra speed-up
- Experiments on large parallel architectures need to be performed
- Evolution of the sequence still to be factored in

Distance between Hamiltonians

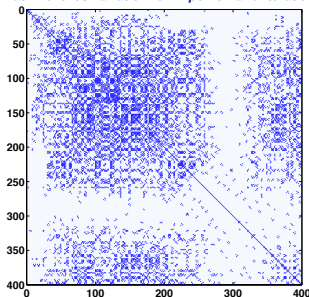
Matrix entries

Hamiltonians $A^{(i)}$ across iterations are completely re-computed. If there is correlation among eigenvectors, the Hamiltonian may not be completely independent across iterations.

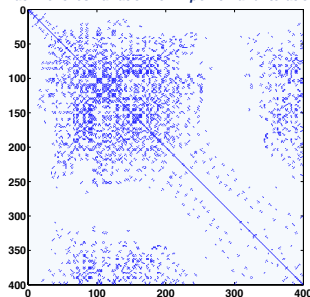
A simple comparison through entry subtraction can be used

$$\tilde{A}_{\mathbf{k}}^{(i)} = \frac{|A_{\mathbf{k}}^{(i+1)} - A_{\mathbf{k}}^{(i)}|}{\delta^{(i)}} \quad ; \quad \delta^{(i)} = \max(|A_{\mathbf{k}}^{(i+1)} - A_{\mathbf{k}}^{(i)}|)$$

Matrix entries variation for k-point 1 and iteration 4



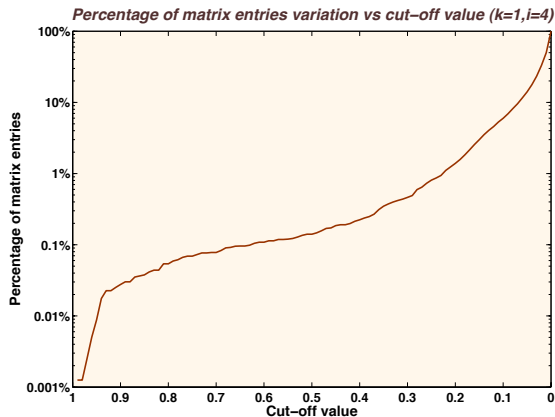
Matrix entries variation for k-point 1 and iteration 4



Distance between Hamiltonians

Threshold map

each entry of $\tilde{A}_{\mathbf{k}}^{(i)}$ is a map onto the $[0, 1]$ interval. Measuring the threshold as a fraction of δ_i , one can look at the percentage of entries that vary as a function of the cut-off value, p_t



the lower the cut-off value p_t , the greater the number of non-zero entries of \tilde{A} is.

Conclusions on ALGORITHM \leftrightarrow SIM

- Feeding eigenvectors of $P^{(i-1)}$ speed-ups the iterative solver for $P^{(i)}$
- Iterative methods seem to be competitive than direct methods for medium/large problems
- The algorithmic structure of FLAPW need to be re-thought to take into consideration these results

Future scientific directions

- Analysis on the structure of the entries of A and B across adjacent iteration seems to suggest quite a bit of computational time can be spared in initializing the matrices (ALGORITHM \leftrightarrow SIM)
- An ongoing study on mixed overlap matrices \tilde{B} may show that there is no need to re-calculate all the basis wave functions at each new iteration cycle (MATH \leftrightarrow SIM)
- A complete study on convergence is still missing. A great deal of increase in efficiency of the simulation can be reached if the convergence process is optimized (MATH \leftrightarrow SIM)

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Thanks to...

- the audience to put up with listening to so much Physics
- VolkswagenStiftung for supporting this research through the fellowship "Computational Sciences"
- The AICES (RWTH Aachen University) for inviting me to give this lecture

- F. Nogueira, et Al. - *A tutorial on Density Functional Theory* Springer (2003)
- Y. Saad, et Al. - *Numerical Methods for Electronic Structure Calculation* Materials Siam Review 52, 1 (2010)
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The simplest atomic pseudo-potential was introduced by Fermi and re-proposed by Hellman in 1935

$$v(r) = -\frac{1}{r} + \frac{2.74}{r} e^{-1.16r}$$

for a valence atom of Potassium (K).

The generic concept is based on the substitution the interaction of valence electrons with nuclei and core electrons with a function that smoothes away the strong oscillation of the valence wavefunctions close to the nuclei core. The result is an energy dependent potential that is generically represented as

$$v_{\text{PK}}(E) = v_0 - \sum_c (E_c - E) |\Psi_c\rangle \langle \Psi_c| \quad ; \quad E_c = \text{energy of core orbitals}$$

At a certain distance from the core $v_{\text{PK}}(E)$ becomes v_0 due to the decay of the core orbitals wavefunctions. The second term in the equation represents a **repulsive** effect, making the potential much weaker than the true potential in the vicinity of the core

◀ Return

The first and most simple exchange-correlation potential is the Local Density Approximation (LDA)

$$E_{xc}^{LDA}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{\text{hom}}(n(\mathbf{r}))$$

where $\epsilon_{xc}^{\text{hom}}$ is the exchange-correlation energy density of an homogeneous electron gas with density $n(\mathbf{r})$ at each point (that can be found analytically).

The Generalized Gradient Approximation (GGA) introduces in ϵ_{xc} a dependence on the gradient of the charge density $\nabla n(\mathbf{r})$.

Advanced Hybrid functional have been recently introduced, that mix parametrically ($\lambda \in [0, 1]$) HF with LDA or GGA

$$E_{xc} = \lambda E_{xc}^{\text{HF}} + (1 - \lambda) E_{xc}^{\text{DFA}}$$

They are computationally challenging having non-local contributions. They can be very useful in helping to predict excitation energies.

[Return](#)

No shape approximations

$$v_{\text{ext}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} v_{\mathbf{I}}^{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} & \text{Interstitial warped potential} \\ \sum_{\ell m} v_{\text{MT}}^{\ell m}(r) Y_{\ell m}(\hat{\mathbf{r}}_{\alpha}) & \text{MT (includ. non spherical terms)} \end{cases}$$

Pseudocharge method (Weinert 1981)

- $n_{\text{MT}}(\mathbf{r}_{\alpha}) \implies q_{l,m}$ (multiple moments) & $n_{\mathbf{I}}(\mathbf{r}) \implies v_{\mathbf{I}}(\mathbf{r})$ (interstitial potential)
- $n_{\text{MT}}(\mathbf{r}_{\alpha}) \xrightarrow{\text{subs with}} \tilde{n}_{\text{MT}}(\mathbf{r}_{\alpha})$ rapidly convergent same $q_{l,m} \implies v_{\mathbf{I}}(\mathbf{r}) = \sum_{\mathbf{G} \neq \mathbf{0}} \frac{4\pi n(\mathbf{G})}{G^2} e^{i\mathbf{G}\mathbf{r}}$
- $v_{\mathbf{I}}(\mathbf{r})|_{\partial\text{MT}@}\alpha \implies v_{\text{MT}}(\hat{\mathbf{r}}_{\alpha})$ **Green's function method**

◀ return