

Penn State QE workshop



An introduction to Density Functional Theory and Simulations

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Marco Buongiorno Nardelli – QE workshop – PSU 2014

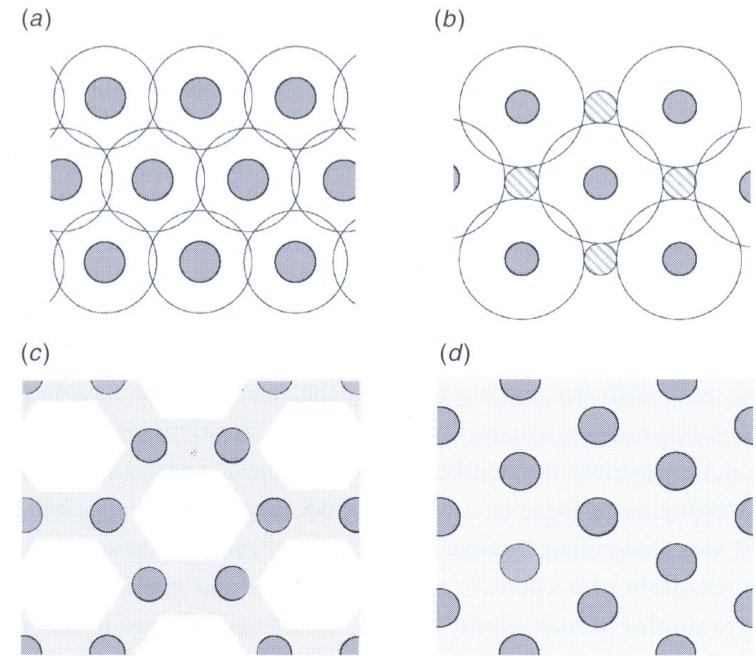


Overview

- 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 ground state properties, and we will cover the basic principles underlying the computational approaches, and we will learn how to compute some of the above properties using a state-of-the-art scientific software package: Quantum-ESPRESSO!

Electronic ground state

- Stable structure of solids are classified on the basis of their electronic ground state, which determines the minimum energy equilibrium structure, and thus the characteristics of the bonding between the nuclei
 - Closed-shell systems: rare gases and molecular crystals. They remain atom-like and tend to form close-packed solids
 - Ionic systems: compound formed by elements of different electronegativity. Charge transfer between the elements thus stabilizes structures via the strong Coulomb (electrical) interaction between ions
 - Covalent bonding: involves a complete change of the electronic states of the atoms with pair of electrons forming directional bonds
 - Metals: itinerant conduction electrons spread among the ion cores. Electron “gas” as electronic glue of the system



Electronic ground state

- From the above discussion it starts to appear clearly the fundamental role played by the electrons, and in a broader sense, by the “electron density”, in determining the properties of real materials.
- The electron density, $n(\mathbf{r})$, can be measured experimentally, providing support for the bonding picture in different materials.
- Since the electron density determines the ground state properties of the material, its knowledge determines also the stable structure of the system: Knowledge of the stable structure of the system as a function of pressure or temperature is perhaps the most fundamental property of condensed matter: the equation of state
 - Electronic structure theory is able to predict the electronic density that corresponds to the minimum energy of the system as a function of volume (Ω), so, in particular, it is straightforward to compute:

$$E = E(\Omega) \equiv E_{total}(\Omega)$$

$$P = -\frac{dE}{d\Omega}$$

$$B = -\Omega \frac{dP}{d\Omega} = \Omega \frac{d^2E}{d\Omega^2}$$

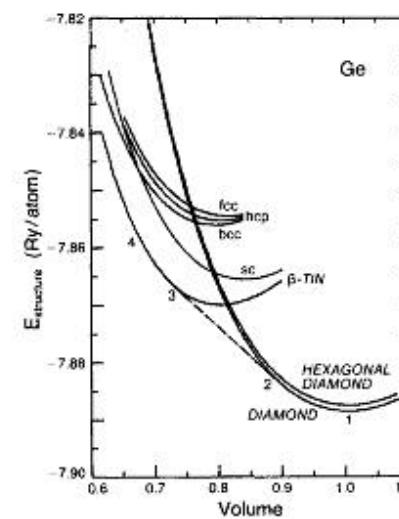
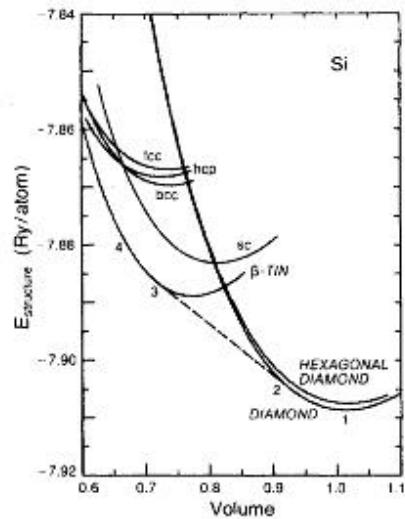
E = total energy of the
ground state

P = pressure

B = bulk modulus

Electronic ground state

- Large variations in volume (thus in pressure) can give rise to phase transitions in materials: at a given pressure a different structural phase becomes more stable than the “natural” one.
- Predictive power of electronic structure calculations in finding new structures of matter under different external conditions: the quantity to compute then becomes the enthalpy, $H=E+PV$.
- Example: Si and Ge phase diagram. Upon increasing pressure Si(Ge) changes its equilibrium structure from diamond to β -tin.



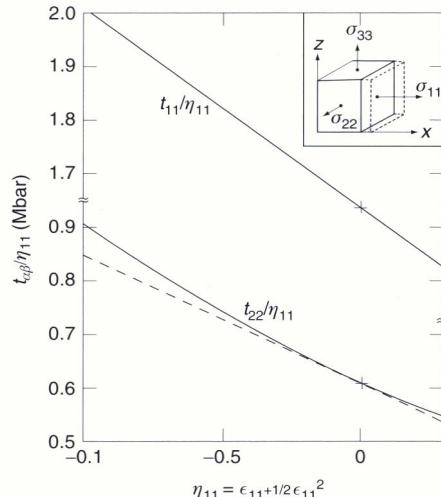
Electronic ground state

- Elasticity: stress-strain relations in materials depend on the electronic ground state and can be obtained via electronic structure methods
- Variation of the total energy with respect to specific deformation of the shape of the materials gives direct information on elasticity properties:

$$\sigma_{\alpha\beta} = -\frac{1}{\Omega} \frac{\partial E}{\partial u_{\alpha\beta}}$$

$u_{\alpha\beta}$ is the symmetric stress tensor that defines the deformation

- Example: stress in Si as a function of strain along the (100) direction:



Electronic ground state

- Equilibrium atomic geometries and atomic vibrations: simply obtained by the electronic ground state
- Given a geometrical configuration of nuclei:

$$E = E(\{\mathbf{R}_i\})$$

$$\mathbf{F}_i = -\frac{dE}{d\mathbf{R}_i}$$

$$C_{i,j} = -\frac{d\mathbf{F}_i}{d\mathbf{R}_j} = -\frac{d^2E}{d\mathbf{R}_i d\mathbf{R}_j}$$

- Where \mathbf{F}_i is the force on nucleus i and $C_{i,j}$ are the force constants for lattice dynamics
- Knowing the force on each nucleus for any configuration, allows us to search for
 - The ground state of the complete (electrons+nuclei) system
 - The dynamical evolution at finite temperature (through a molecular dynamics simulation)
 - The vibrational spectrum of the system

A Density Functional Theory Primer

The Theory of Everything

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi$$

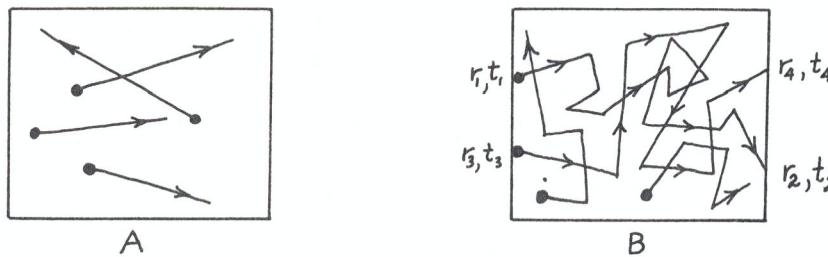
$$\begin{aligned} \mathcal{H} = & - \sum_j^N \frac{k^2}{2m} \nabla_j^2 - \sum_\alpha^M \frac{k^2}{2M_\alpha} \nabla_\alpha^2 - \sum_j^N \sum_\alpha^M \frac{Z_\alpha e^2}{|r_j - R_\alpha|} \\ & + \sum_{j < k}^N \frac{e^2}{|r_j - r_k|} + \sum_{\alpha < p}^M \frac{Z_\alpha Z_p e^2}{|R_\alpha - R_p|} \end{aligned}$$

* Air	* Steel	* Paper	* Vitamins
* Water	* Plastic	* Dynamite	* Ham Sandwiches
* Fire	* Glass	* Antifreeze	* Ebola Virus
* Rocks	* Wood	* Glue	* Economists
* Cement	* Asphalt	* Dyes	* ...

From R.B. Laughlin Nobel lecture, 1998, <http://large.stanford.edu/prizes/nobel/lecture/>

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 ($\{\mathbf{R}_j\}$)

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

The many-body problem

- Electronic terms:

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

- Nuclear terms:

$$-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- 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

- The last term remains to insure charge neutrality, but it is just a classical term (Ewald energy)

The electronic Hamiltonian

- The Born-Oppenheimer approximation justifies the separation of electronic and ionic variables due to the different time-scales of the relative motion
- Electrons remain in their ground state as ions move:
 - Ions are responsible for the fixed external potential in which electrons move

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_{\parallel}$$

where T is the kinetic energy of the electrons, V_{ext} is the potential acting on the electrons due to the nuclei

$$\hat{V}_{\text{ext}} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|)$$

V_{int} is the electron-electron interaction term and E_{\parallel} is the classical energy term of the system of ionic point charges

(Here we take $\hbar = m_e = 1$)

The electronic Hamiltonian

- In quantum mechanical terms, the system of the electrons in the external potential of the atoms is described by the many-body wavefunction of the system

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_N) = \Psi(\{\mathbf{r}_i; \mathbf{s}_i\})$$

where

$$|\Psi(\{\mathbf{r}_i; \mathbf{s}_i\})|^2 d\mathbf{r}^N$$

is the quantum mechanical probability of finding the systems of electrons with coordinates within $\{\mathbf{r}, \mathbf{r}+d\mathbf{r}^N\}$ and spin \mathbf{s}^N

- The many-body wavefunction for the electrons can be obtained solving the Schroedinger equation for the system:

$$\hat{H}\Psi = E\Psi$$

where E is the ground state energy of the system in the external potential of the ions.

The many-body electron wavefunction

- The fundamental problem of electronic structure theory is the evaluation of the many-body electron wavefunction
- Knowledge of Ψ allows us to evaluate all the fundamental properties of the system as expectation values of quantum mechanical operators

$$O = \frac{\langle \Psi | \hat{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \frac{\int d^3r_1 d^3r_2 \cdots d^3r_N \Psi^*(\{\mathbf{r}\}) \hat{O} \Psi(\{\mathbf{r}\})}{\int d^3r_1 d^3r_2 \cdots d^3r_N |\Psi(\{\mathbf{r}\})|^2}$$

- For example, a quantity of great relevance in the description of the electronic system is the density of particles (electron density)

$$n(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \frac{\int d^3r_1 d^3r_2 \cdots d^3r_N \sum_s |\Psi(\{\mathbf{r}\})|^2}{\int d^3r_1 d^3r_2 \cdots d^3r_N |\Psi(\{\mathbf{r}\})|^2}$$

that is the expectation value of the density operator

$$\hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) = \begin{cases} 1 & \text{if } \mathbf{r} = \mathbf{r}_i \\ 0 & \text{if } \mathbf{r} \neq \mathbf{r}_i \end{cases}$$

The many-body electron wavefunction

- Main quantity is indeed the ground state energy E that is calculated as the expectation value of the Hamiltonian (it follows from the Schrödinger equation):

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r})$$

- The ground state wavefunction Ψ_0 is the one that corresponds to the state with the lowest energy that obeys all symmetries of particles and conservation laws
- It allows us to introduce a “variational principle” for the ground state:

$$\begin{aligned} E[\Psi] &\geq E_0 \\ E_0 &= \min_{\Psi} E[\Psi] \end{aligned}$$

Ground state properties

- Ground state properties, determined by the knowledge of the ground state wavefunction, include total energy, electron density and correlation function for the system of the electrons in the external potential of the atoms
- In the limit of small perturbations, also excited state properties can be derived, using what, in quantum mechanics, is called “perturbation theory”
- For instance, small ionic displacements around the equilibrium positions will give us information on the forces acting on the atoms, or more in general, on the vibrational properties of the system
- **Force theorem** (aka Hellman-Feynman theorem), one of the most fundamental theorems in quantum mechanics

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \mathbf{R}_I} \right| \Psi \right\rangle - \left\langle \frac{\partial \Psi}{\partial \mathbf{R}_I} \left| \hat{H} \right| \Psi \right\rangle - \left\langle \Psi \left| \hat{H} \right| \frac{\partial \Psi}{\partial \mathbf{R}_I} \right\rangle - \frac{\partial E_{II}}{\partial \mathbf{R}_I}$$

- Since the middle terms cancel at the ground state (by the definition of ground state wavefunction):

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int d^3r n(\mathbf{r}) \frac{\partial V_{ext}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{II}}{\partial \mathbf{R}_I}$$

Forces depend on the ground state electron density!

Electronic structure methods

- Independent electron approximations → the electronic structure problem involves the solution of a Schroedinger-like equation for each of the electrons in the system – treated independently!

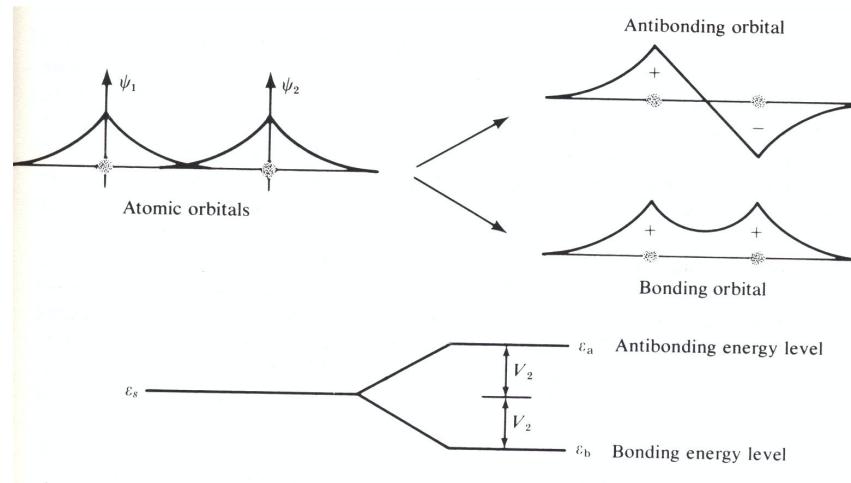
$$\hat{H}_{\text{eff}} \psi_i^s(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}^s(\mathbf{r}) \right] \psi_i^s(\mathbf{r}) = \varepsilon_i^s \psi_i^s(\mathbf{r})$$

- In this formalism, the ground state energy is found populating the lowest eigenstates according to the Pauli exclusion principle
- Central equation in electronic structure theory. Depending on the level of approximation we find this equation all over:
 - Semi-empirical methods (empirical pseudopotentials, tight-binding)
 - Density Functional Theory
 - Hartree-Fock and beyond
- Mathematically speaking, we need to solve a generalized eigenvalue problem using efficient numerical algorithms

The tight-binding method

- Solution of an effective Hamiltonian obtained as a superposition of Hamiltonians for isolated atoms plus corrections coming from the overlap of the wavefunctions (atomic orbitals)

$$\hat{H}_{\text{eff}} = \sum \hat{H}_{\text{atom}} + \Delta U(\mathbf{r})$$



- Very efficient from a computational point of view
- can handle reasonably large systems (between ab initio and atomistic)
- Needs parameters from experiments or ab initio calculations

Hartree-Fock methods

- Standard method for solving the many-body wavefunction of an electronic system starting from a particular ansatz for the expression of Ψ
- A convenient form is to write a properly antisymmetrized (to insure the Pauli principle is satisfied) determinant wavefunction for a fixed number of electrons with a given spin (Slater determinant), and find the single determinant that minimizes the total energy for the full interacting Hamiltonian

$$\Psi = \frac{1}{(N!)^{\frac{1}{2}}} \det \begin{pmatrix} \psi_1^1 & \psi_2^1 & \dots \\ \psi_1^2 & \psi_2^2 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

- Use of this wavefunction ansatz gives rise to equations of the form of non-interacting electrons where the effective potential depends upon the particular electronic state
- Methodologies to solve these equations have been developed mostly in the framework of quantum chemistry calculations (J. Pople, Nobel prize for Chemistry, 1998 - GAUSSIAN: quantum chemistry code, <http://www.gaussian.com>)

“Exchange” and “Correlation”

- The basic equations that define the Hartree-Fock method are obtained plugging the Slater determinant into the electronic Hamiltonian to derive a compact expression for its expectation value

$$\begin{aligned}\langle \Psi | \hat{H} | \Psi \rangle = & \sum_{i,s} \int d\mathbf{r} \psi_i^{s*}(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) \right] \psi_i^s(\mathbf{r}) + E_H \\ & + \frac{1}{2} \sum_{i,j,s_i,s_j} \int d\mathbf{r} d\mathbf{r}' \psi_i^{s_i*}(\mathbf{r}) \psi_j^{s_j*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i^{s_i}(\mathbf{r}) \psi_j^{s_j}(\mathbf{r}') \quad \text{Direct term} \\ & - \sum_{i,j,s} \int d\mathbf{r} d\mathbf{r}' \psi_i^{s*}(\mathbf{r}) \psi_j^{s*}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^s(\mathbf{r}) \psi_i^s(\mathbf{r}') \quad \text{Exchange term}\end{aligned}$$

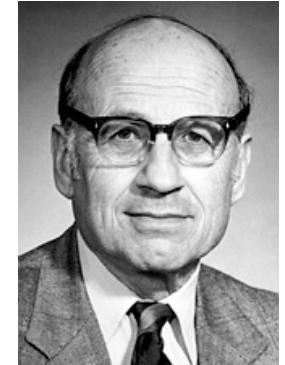
- Direct term is essentially the classical Hartree energy (acts between electrons with different spin states ($i=j$ terms cancel out in the direct and exchange terms))
- Exchange term acts only between same spin electrons, and takes care of the energy that is involved in having electron pairs with parallel or anti-parallel spins together with the obedience of the Pauli exclusion principle

“Exchange” and “Correlation”

- Exchange term is a two-body interaction term: it takes care of the many-body interactions at the level of two single electrons.
- In this respect it includes also correlation effects at the two-body level: it neglects all correlations but the one required by the Pauli exclusion principle
- Since the interaction always involve pairs of electrons, a two-body correlation term is often sufficient to determine many physical properties of the system
- In general terms it measures the joint probability of finding electrons of spin s at point \mathbf{r} and of spin s' at point \mathbf{r}'
- Going beyond the two-body treatment of Hartree-Fock introduces extra degrees of freedom in the wavefunctions whose net effect is the reduction of the total energy of any state
- This additional energy is termed the “correlation” energy, E_c and is a key quantity for the solution of the electronic structure problem for an interacting many-body system

A Density Functional Theory Primer

- 1998 Nobel Prize in Chemistry to Walter Kohn and John Pople
- **Key point** - the ground state energy for the hard many-body problem can in principle be found by solving non-interacting electron equations in an effective potential determined only by electron density



Walter Kohn

$$\left(-\frac{1}{2} \nabla^2 + V_{eff} \right) \psi_i = \epsilon_i \psi_i$$

- The effective potential contains all the information on the external potential and the many-body electron interactions - needs to be approximated! Accurate approximations for the functionals of the density exist: LDA, LSDA, GGA.
- Ab initio pseudopotentials to describe the ions (or all electron calculations possible)

Definitions

Function: a prescription which maps one or more numbers to another number:

$$y = f(x) = x^2$$

Operator: a prescription which maps a function onto another function:

$$O = \frac{\partial^2}{\partial x^2} \text{ so that } Of(x) = \frac{\partial^2}{\partial x^2} f(x)$$

Functional: A functional takes a function as input and gives a number as output:

$$F[f(x)] = y$$

Here $f(x)$ is a function and y is a number.

An example is the functional to integrate x from $-\infty$ to ∞ :

$$F[f(x)] = \int_{-\infty}^{\infty} f(x) dx$$

The Hohenberg-Kohn theorems

- The revolutionary approach of Hohenberg and Kohn in 1964 was to formulate DFT as an exact theory of a many-body system
- The formulation applies to any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, including any problem of electrons and fixed nuclei, where the hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_i V_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Foundation of Density Functional Theory is in the celebrated Hohenberg and Kohn theorems:
 - **Theorem 1:** There cannot be two different external potentials differing by more than a constant which give rise to the same non-degenerate ground state charge density.
 - The density uniquely determines the external potential to within a constant.
 - **Theorem 2:** A universal functional of the energy $E[n]$ can be defined in terms of the density $n(r)$, valid for any external potential $V_{ext}(r)$. For any particular V_{ext} the exact ground state of the system is determined by the global minimum value of this functional
 - Among all the solutions which are consistent with the given density, the unique ground state wavefunction is the one that has the lowest energy.

Hohenberg-Kohn theorems

- Proofs of H-K theorems are exceedingly simple, and both based on a simple *reduction ad absurdum* argument
- Proof of Theorem 1: suppose there were two different external potentials V_{ext}^1 and V_{ext}^2 with same ground state density, $n(r)$.
The two potentials lead to two different Hamiltonians with different wavefunctions, that are hypothesized to lead to the same density. Then:

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle$$

which leads to

$$E^{(1)} < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)} + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle = E^{(2)} + \int d^3r \{ V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \} n(\mathbf{r})$$

But changing the labelling we can equally say that

$$E^{(2)} < E^{(1)} + \int d^3r \{ V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r}) \} n(\mathbf{r})$$

Summing the above expression we get the absurd result

$$E^{(1)+} E^{(2)} < E^{(2)+} E^{(1)}$$

Hohenberg-Kohn theorems

- Theorem 2 gives us a first step towards an operative way to solve the problem
- Theorem 2 can be proved in a very similar way, and the demonstration leads to a general expression for the universal functional of the density in DFT

$$\begin{aligned} E_{HK}[n] &= T[n] + E_{int}[n] + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{\parallel} \\ &\equiv F_{HK}[n] + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{\parallel} \end{aligned}$$

- $F_{HK}[n]$ is a universal functional of the density that determines all the many-body properties of the system

$$F_{HK}[n] = T[n] + E_{int}[n]$$

- PROBLEM: we do not know what is this functional!

We only know that:

- is a functional of the density alone
- is independent on the external potential (thus its universality)
- It follows that if the functional $F_{HK}[n]$ were known, then by minimizing the total energy of the system with respect to variations in the density function $n(\mathbf{r})$, one would find the exact ground state density and energy.

Kohn and Sham ansatz

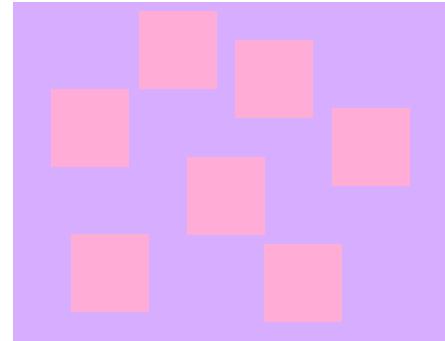
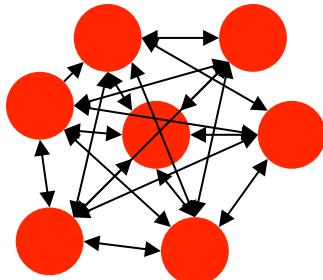
- H-K theory is in principle exact (there are no approximations, only two elegant theorems) but impractical for any useful purposes
- Kohn-Sham ansatz: replace a problem with another, that is the original many-body problem with an auxiliary independent-particle model
- **Ansatz:** K-S assume that the 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.
 - 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

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

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

Kohn and Sham ansatz

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:

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

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

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

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

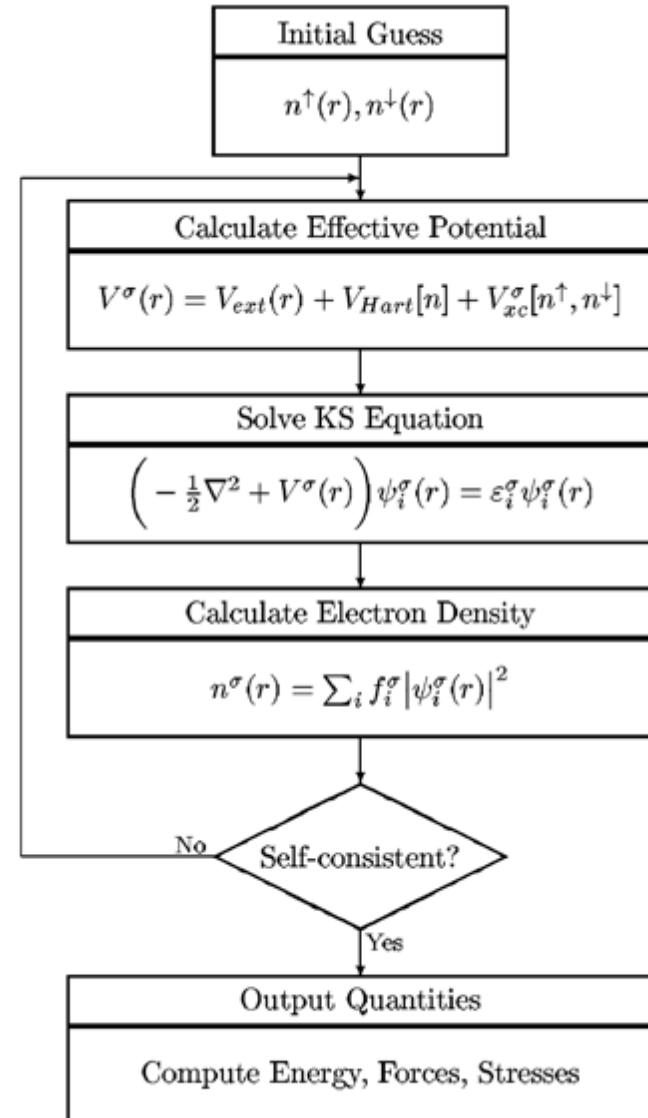
$$H_{KS}^\sigma(\mathbf{r}) = -\frac{1}{2} \nabla^2 + V_{KS}^\sigma(\mathbf{r})$$

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

- 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 wavefunctions 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



Kohn and Sham equations

- The great advantage of recasting the H-K functional in the K-S form is that separating the independent particle kinetic energy and the long range Hartree terms, the remaining exchange and correlation functional can be reasonably approximated as a local or nearly local functionals of the electron density
- **Local Density Approximation (LDA):** $E_{xc}[n]$ is a sum of contributions from each point in space depending only upon the density at each point independent on other points

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

where $\varepsilon_{xc}(n)$ is the exchange and correlation energy per electron.

- $\varepsilon_{xc}(n)$ is a universal functional of the density, so must be the same as for a homogeneous electron gas of given density n
- The theory of the homogeneous electron gas is well established and there are exact expression (analytical or numerical) for both exchange and correlation terms
- Exchange as $\varepsilon_x(n) = -\frac{0.458}{r_s}$ where r_s is defined as the average distance between electrons at a given density n : $\frac{4\pi}{3} r_s^3 = \frac{1}{n}$
- Correlations from exact Monte Carlo calculations (Ceperley, Alder, 1980)

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)

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

- 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 loosing much of the computational appeal of a local form

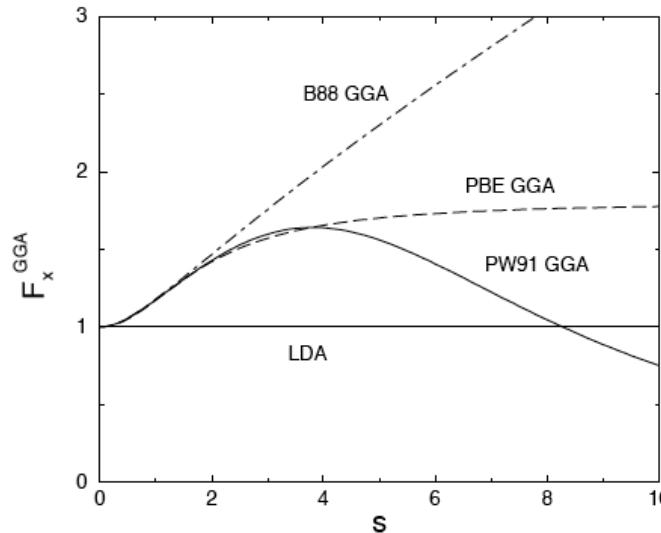
Generalized Gradient Approximations

- 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:

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

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

- Orbital dependent functionals: mostly useful for systems where electrons tend to be localized and strongly interacting
 - LDA+U - local functional + orbital-dependent interaction for localized atomic orbitals (Hubbard U)
 - EXX (exact exchange) - functionals that include explicitly the exact exchange integral of Hartree-Fock
 - Hybrid functionals (PBE0, HSE, B3LYP) - combination of orbital-dependent Hartree-Fock and explicit DFT. Most accurate functional on the market - most preferred for chemistry calculations – not “purely” ab initio, since the fraction of exact exchange in the functional is decided a priori

Numerical Solution: Plane Waves

$$\hat{H}_{\text{eff}} \psi_i(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- To be tractable in a computer, the problem needs to be discretized via the introduction of a suitable representation of all the quantities involved
- In periodic solids, plane waves of the form $e^{i\mathbf{q}\cdot\mathbf{r}}$ are most appropriate representation since they reflect the periodicity of the crystal and periodic functions can be expanded in the complete set of Fourier components through orthonormal PWs

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{i,\mathbf{q}} \times \frac{1}{\Omega} e^{i\mathbf{q}\cdot\mathbf{r}} = \sum_{\mathbf{q}} c_{i,\mathbf{q}} \times |\mathbf{q}\rangle$$

- In Fourier space, the K-S equations become

$$\sum_{\mathbf{q}} \langle \mathbf{q}' | \hat{H}_{\text{eff}} | \mathbf{q} \rangle c_{i,\mathbf{q}} = \varepsilon_i \sum_{\mathbf{q}} \langle \mathbf{q}' | \mathbf{q} \rangle c_{i,\mathbf{q}} = \varepsilon_i c_{i,\mathbf{q}'}$$

- Kohn and Sham equations can then be written as matrix equations:

$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k})$$

$$H_{m,m'}(\mathbf{k}) = |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{\text{eff}}(\mathbf{G}_m - \mathbf{G}_{m'})$$

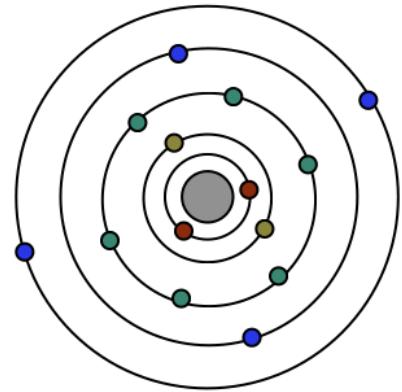
Need to
truncate the
sum = kinetic
energy cutoff

We have effectively transformed a differential problem into one that we can solve using linear algebra algorithms!

Atoms and pseudopotentials

- IDEA: group all the electrons around the nuclear core into an effective ionic core, where all the strong oscillations close to the nuclei are damped, and leave out only the valence electrons that contribute to the bonding of the solid. Core electrons are left basically unchanged going from the atom to the solid

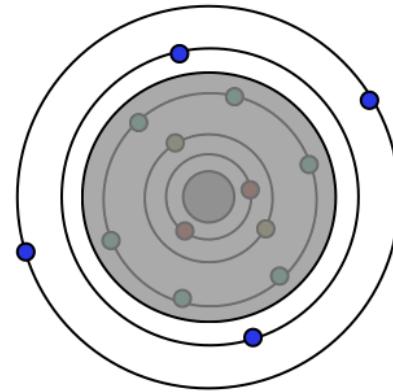
Si: $1s^2 2s^2 2p^6 3s^2 3p^2$



14 electrons

$$V_{ext}(\mathbf{r}) = \frac{-14e}{r}$$

Si: (pseudo core) $3s^2 3p^2$



4 (valence) electrons

$$V_{ext}(\mathbf{r}) = V_{ps}(\mathbf{r})$$

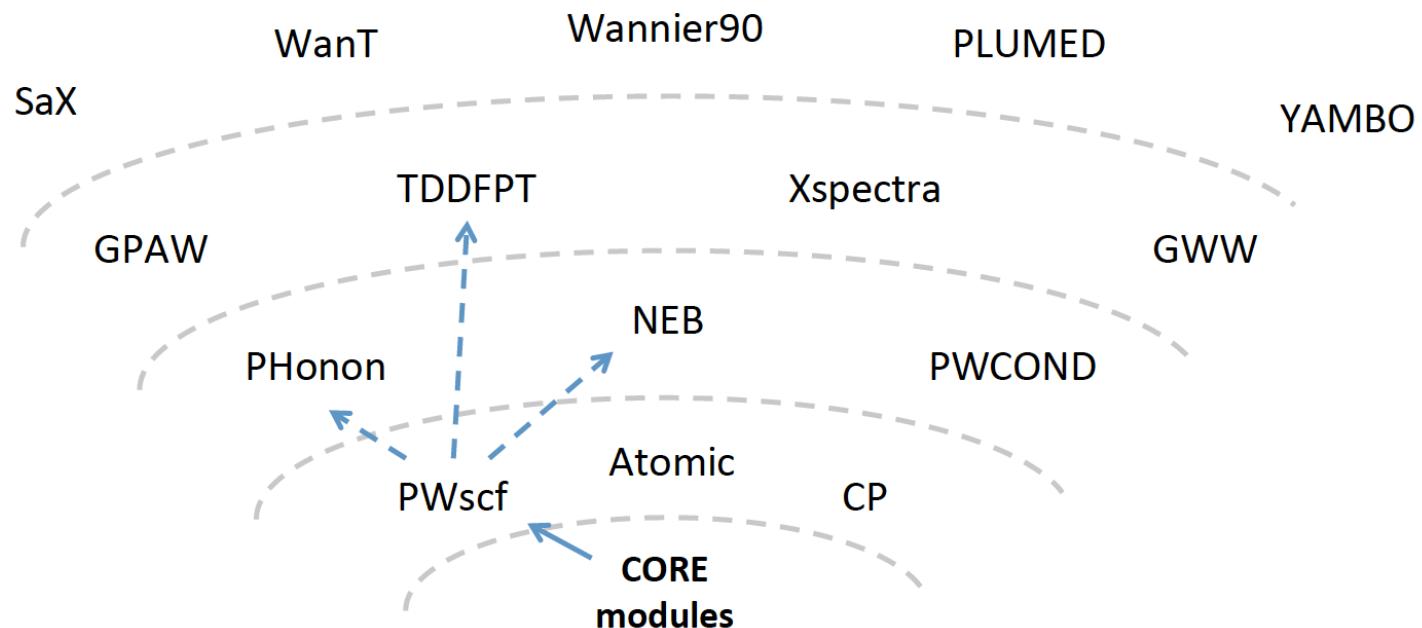


integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

- Quantum ESPRESSO is not a monolithic application, but an integrated ecosystem thriving around a small number of core components developed and maintained by a small number of developers
- the ecosystem is designed so as to be alien-friendly: a number of third-party QE-compatible applications and add-ons, often designed to be code-agnostic, are distributed with QE (notable examples include *WanT*, *yambo*, *EPW*, *Wannier90*, *XCrysDen*, ...)
- the environment that allows the ecosystem to prosper is provided by the qe-forge.org platform, freely available to researchers and developers from all over the world



integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.





300,000+ lines of FORTRAN/C code

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1600+ registered users

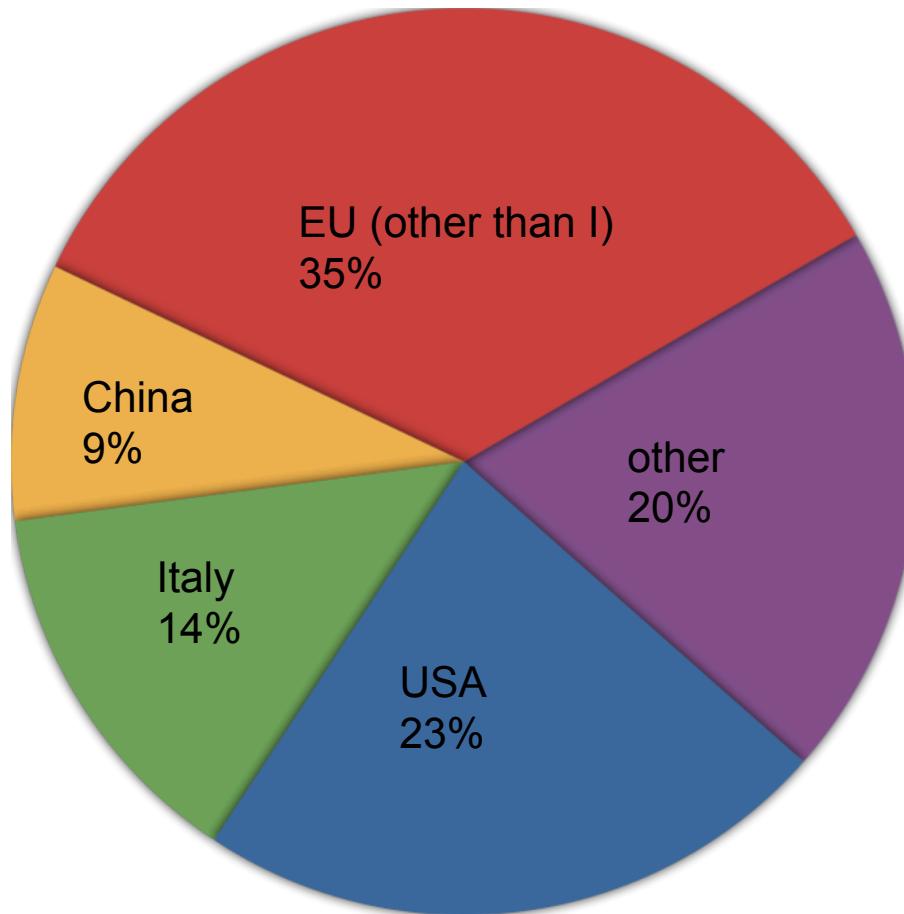
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3 web sites (quantum-espresso.org & qe-forge.org, foundation.quantum-espresso.org)

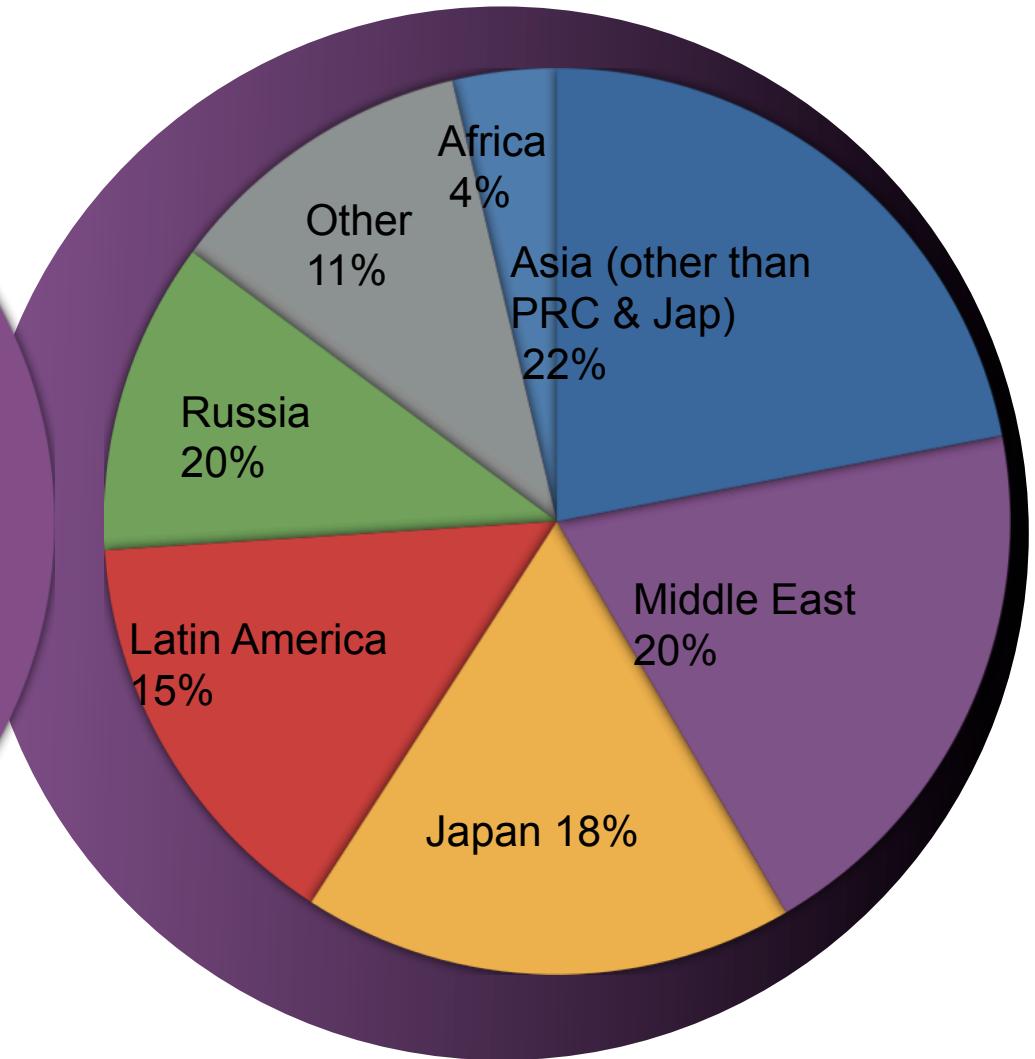
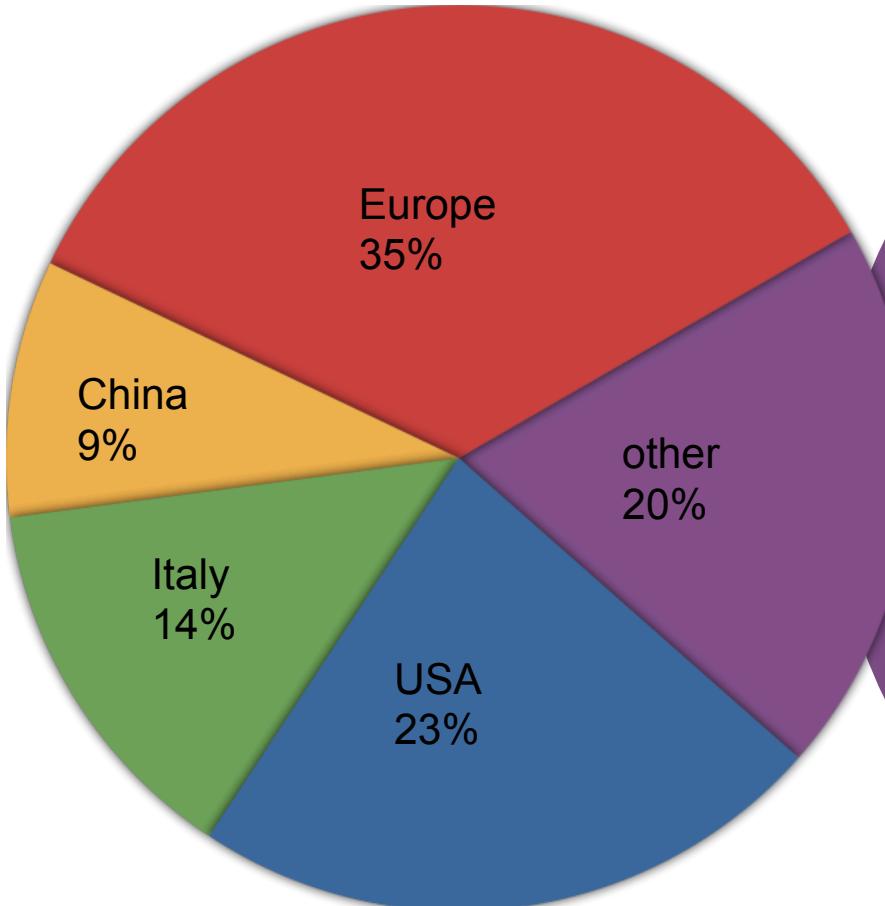
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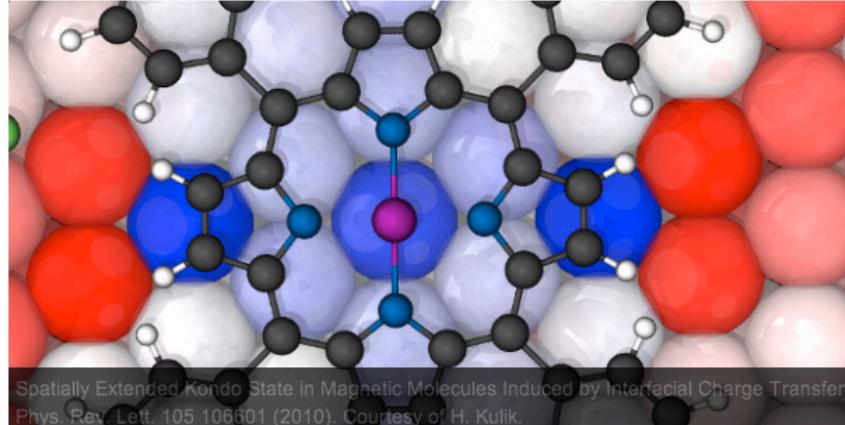
Computer modelling of materials at the nanoscale: An introduction and hands-on tutorial with the QUANTUM ESPRESSO distribution & YAMBO code, The University of Tokyo, Hongo campus, 23-26th April (program)

Quantum ESPRESSO Workshop, Penn State University, 16-20 June.

ICTP activities that include a Quantum ESPRESSO tutorial:

3rd African School on Electronic Structure Methods and Applications, Abuja, Nigeria, 9-21 June

Summer School on Atomistic Materials Modelling, Pune, India, 30 June-15 July

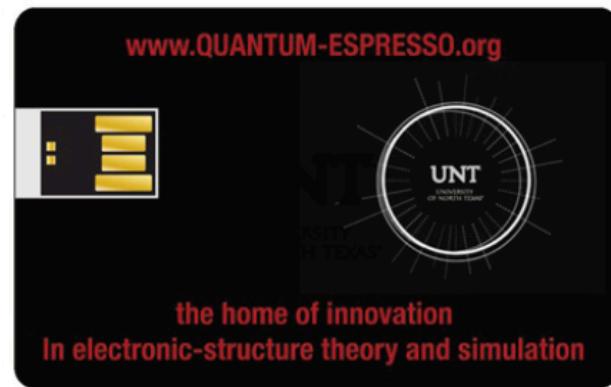

Spatially Extended Kondo State in Magnetic Molecules Induced by Interfacial Charge Transfer.
Phys. Rev. Lett. 105 106601 (2010). Courtesy of H. Kulik.

QUANTUM ESPRESSO

is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

QE-Box

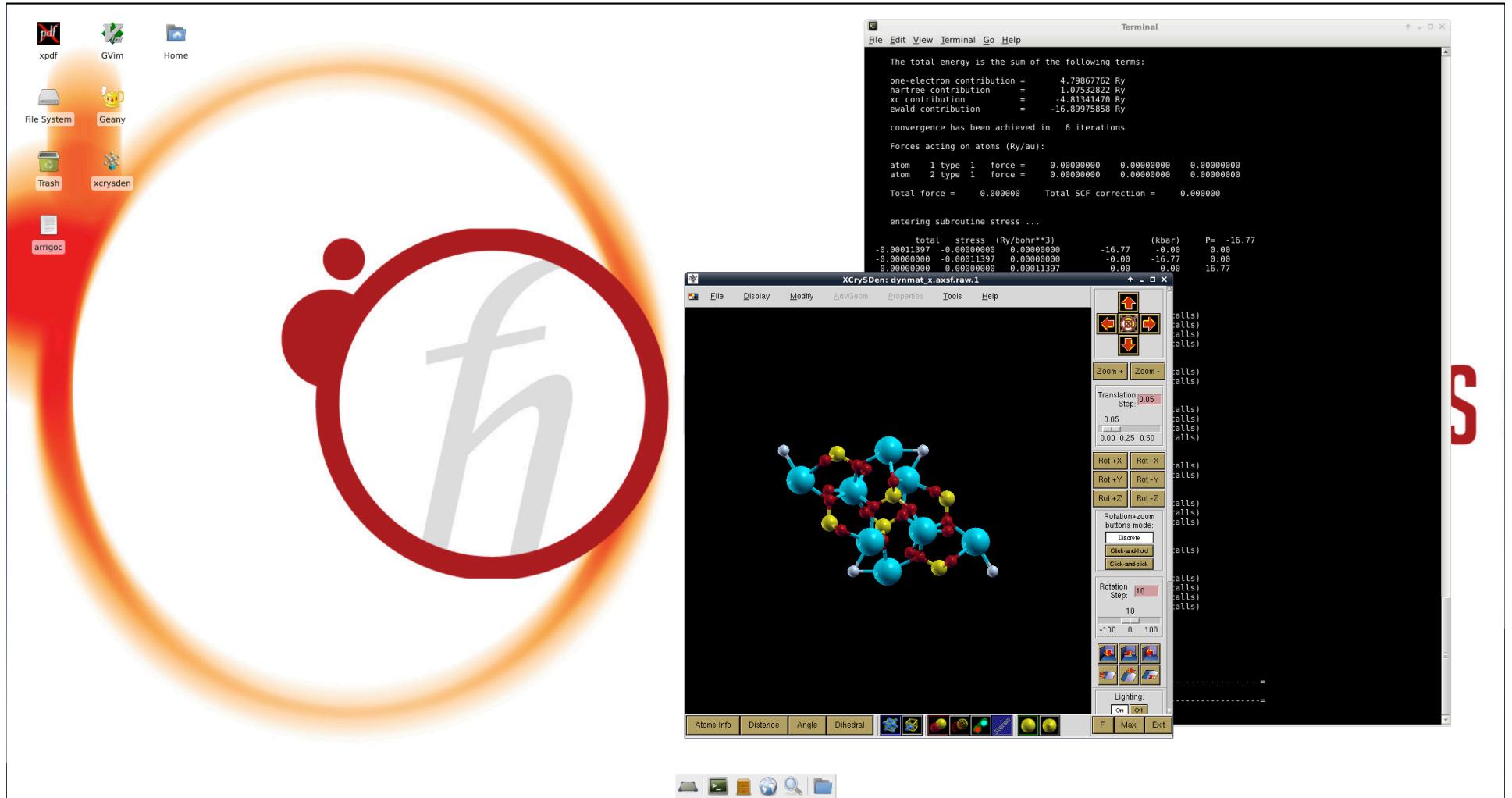
- portable solution for Quantum ESPRESSO on any machine with hardware virtualization
- Light Linux (Debian) Virtual Machine built for Oracle's VM VirtualBox
- Bootable USB card with a full installation of Quantum ESPRESSO, WanT, and XCrysDen visualization software



Try for yourself !!!

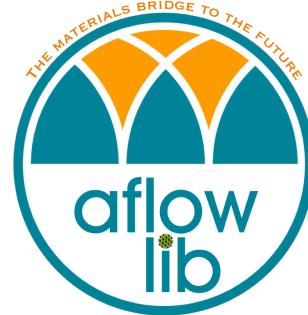


QE-Box





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