Density Functional Theory Reverse Pedagogy

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- The Schrodïnger equationfor a molecule or a solid is a many-body problem: $\Psi(r_1\ , \ldots, r_N)$
- Extremely time consuming to solve the Schrodïnger equation for large system
- Within Density Functional Theory (DFT), we solve a one-body equation **(the Khon-Sham equation)** and the exchange and correlation effects between electrons are described using an exchange and correlation potential.
- Famous DFT codes:
  - VASP
  - Quantum Espresso
  - SIESTA
  - Gaussian
  - Castep
  - ...

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- There's no way to define analytically the exchange-correlation potential.
- It's only possible to define approximate form of it.
- The two most famous forms are either a direct function of the electronic density, the Local Density Approximation **(LDA)**, or by adding a gradient corection, the Generalized Gradient Approximation **(GGA)**
- None are better! It is mandatory to check several XC for a given system and compare one key quantity with experimental data
- Famous XC:
  - LDA XC: Perdew-Zunger (PZ)
  - GGA XC: Perdew-Burke-Enzerhof (PBE)
  - ...

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- Primarily, DFT is giving us the electronic Ground state of a system
- This ground state is caracterised by an electronic density
- This corresponds to the so called Hohenberg & Kohn theorems
- From the ground state we can compute others physical properties:
  - Electronic properties (effective mass, electronic mobility, conductivity...)
  - Structural properties (Bulk modulus...)
  - Thermal properties (heat capacity, phonon dispersion, thermal conductivity...)

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YES!

- The relaxation time associatied with electrons is several order of magnitude smaller than the relaxation time of atom motions.
- This is the **Borm Oppenheimer approximation**
- At each time step of a MD simulation, we may consider the electronic density at their ground (steady) state.
- The forces between atoms are derived from the total energy:

$$\mathbf{F}_i = \frac{\partial E_{tot}}{\partial \mathbf{R}_i}$$

- Limitation: DFT can only deal with few thousands of atoms.

- Asside from MD, it is mandatory when dealing with a system to relax the atomic structure (minize the forces between atoms) and relax the hydrostatic pressure

What is a pseudopotential?

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- Core electron are (almost) not involved in the electronic properties of molecules or solids
- To reduce the numerical "cost" of dealing with core electrons they are replaced by a pseudo-potential which mimic the interactions with valence electrons.
- They are various technic to build them:
  - Ultra Smooth Pseudo Potential (USPP)
  - Norm Concerving Pseudo Potential
- The separation between core and valence electrons can be tricky
- Ready to use USPP can be found at:

  `https://pseudopotentials.quantum-espresso.org/legacy_tables`

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- Khon-Sham orbitals are the eigenvectors of the Khon-Sham equation
- A basis is used to expand the so called Khon-Sham orbitals
- A basis is mandatory to compute the density matrix
- The most obvious choice is **plane wave**
- Atomic orbitals or gaussian orbitals may also be used
- The size of the basis is a key factor for convergence
- Usually defined by means of an Energy Cut-Off