Intro. to DFT and its planewave–pseudopotential formulation

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- The goal of so-called first principles calculations is to solve the many electron Schrödinger equation:

$$\hat{H}\Psi(r_1, ..., r_N) = E\Psi(r_1, ..., r_N), \qquad (1)$$

where

$$\hat{H} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i V(r_i) + \sum_i \sum_{j>i} \frac{1}{|r_i - r_j|} \qquad (2)$$

in atomic units.

- $V(r)$ is the electrostatic potential generated by a number of positively charged (classical) nuclei with positions R_i.
- This is the fundamental equation of everday matter, with the (good) approximation that the nuclei behave more-or-less classically.

- Unfortunately, this equation is absolutely impossible to solve for all but the smallest systems ($\sim$10 electrons), due to the complexity of the many electron wavefunction Ψ (a complex valued function of 3^N variables).

- Density functional theory (DFT) recasts this problem into one involving the electron density $n(r)$ as the fundamental quantity (a real valued function of 3 variables).

- In principle, this recasting is exact, and one can obtain any property of interest of the system; in practice it involves approximations, and is limited to the ground state.

- The good news is that it is remarkably accurate given the approximations, and you can get lots of interesting information about a material by knowing the ground state.

- Why density "functional" theory?
- A functional is essentially a function of a function; takes a function as input and gives a number as output.
- Example: Expectation value of the energy of a many electron wave function Ψ:

$$E_\Psi[\Psi] = \int \mathrm{d}^{3N}r \, \Psi^* \hat{H} \Psi \tag{3}$$

- In DFT, the energy is instead a functional of the density, which is minimised by the ground state density n_0
- E[n] is unknown, but we know good approximations to it.

- Standard approach to DFT is based on the work of Kohn and Sham, who proposed the following decomposition of the total energy functional:

$$E[n] = T_{KS}[n] + V[n] + E_H[n] + E_{XC}[n] \qquad (4)$$

- $V[n]$ is the energy of the electron density in the external potential $V(r)$.
- $E_{\mathrm{H}}[n]$ is the electrostatic interaction of the density with itself (N.B. includes unphysical self-interaction of each electron with itself)
- $T_{KS}[n]$ is the kinetic energy of a system of non-interacting electrons with the same density as the real system.
- $E_{XC}[n]$, is called the "exchange–correlation" functional. It contains all the extra stuff left over, including corrections to the kinetic energy, and is the thing that is approximate.

- Two basic flavours of $E_{XC}[n]$:
- Local density approximation (LDA): We assume that the inhomogeneous electron density behave locally like a homogeneous electron density (which can be calculated).
- Generalised Gradient Approximation (GGA): Adds terms which depend on the gradient. Numerous forms, but in general improves most properties.

- How to find n_0? Minimise E with respect to n, or equivalently, with respect to the Kohn–Sham orbitals.
- This leads to the Kohn–Sham equations, which is what DFT codes actually solve:

$$\left(-\frac{1}{2}\nabla^2 + V(r) + \int \frac{n(r')}{r - r'} + V(r)\right)\psi(r) = \epsilon\psi(r) \quad (5)$$

  This has the form of a set of one-electron Schrodinger equations, but with an effective potential that depends on the solutions

- These equations much be solved iteratively until self-consistency is reached.
- N.B. $n(r)$ is the sum of the densities of the N lowest energy solutions of these equations (recall the Pauli exclusion principle; no two electrons can occupy the same orbital).

- KS orbitals are solutions of one-electron Schrodinger-like equations; implies that they obey Bloch's theorem in a periodic potential (e.g. a crystal), i.e. they have the form

$$\psi_{nk}(r) = u_{nk}(r)e^{ikr}; u_{nk}(r + R) = u_{nk}(r) \tag{6}$$

where R is a lattice vector.

- This allows us to model the small, periodically repeated bit of the solid instead of the whole thing

- To do calculations on a computer, we need to discretise the KS equations
- Functions are periodic so expand as sums of plane waves (c.f. Fourier analysis)

$$u_{nk} = \sum_G c_{Gnk} e^{iG \cdot x}, \tag{7}$$

  that fit into your simulation box, then solve for co-efficients of the plane waves.
- This equality only holds if an infinite number of planewaves is used; in practice, the series is truncated at some finite value.
- The level of this truncation is specified by the ENCUT keyword in VASP.

- Inert core electrons are localised, and are therefore hard to describe using plane-waves.
- Valence electron wavefunctions oscillate rapidly near the nucleus, to maintain orthogonality with core functions.
- Solve both these problems by replacing core electrons with pseudopotentials.
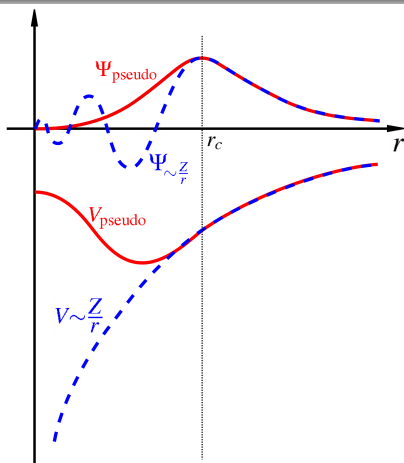
The pseudopotentials in VASP are called PAW potentials, and are contained in the POTCAR file.