Density Functional Theory

The plane wave pseudopotential method

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Outline

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A brief digression on units...

I will be using atomic units throughout this presentation.

Atomic units

$$\hbar = 1$$
$$m_e = 1$$
$$e = 1$$

length	Bohr	0.529 Å
energy	Hartree	27.2 eV = 627 kcal/mol

Why wavefunctions are awkward

Schrödinger's equation is essentially exact for chemical systems with moderate atomic number:

$$\mathcal{H} = -\frac{\nabla^2}{2} + \sum_{N<M} \frac{Z_N Z_M}{\left|\vec{R_N} - \vec{R_M}\right|} - \sum_{Ni} \frac{Z_N}{\left|\vec{r_i} - \vec{R_N}\right|} + \sum_{i<j} \frac{1}{|\vec{r_i} - \vec{r_j}|}$$

$$E_{tot} = \int \psi^*(\vec{r_1}, \vec{r_2}...\vec{r_n})\mathcal{H}\psi(\vec{r_1}, \vec{r_2}...\vec{r_n})d\vec{r_1}d\vec{r_2}...d\vec{r_n}$$

Alas, ψ is a function in $3n$ dimensions, which makes wavefunction-based approaches impractical for large numbers of electrons—we can't even *store* the many-body wavefunction.

Hohenberg-Kohn Theorem

Hohenberg and Kohn proved that the *ground state* energy of a system of electrons in an external potential $V(\vec{r})$ is the minimum of a universal functional of the electron density

$$E_{ground} = \min_{n(\vec{r})} \left\{ F[n(\vec{r})] + \int V(\vec{r}) n(\vec{r}) d\vec{r} \right\}$$

Thus if we had a decent approximation to $F[n(\vec{r})]$ we'd never again have to worry about those pesky wavefunctions, and could just work with the electron density.

The Kohn-Sham approach

$$\begin{aligned} F_{KS}[n(\vec{r})] &= T + E_{Hartree}[n(\vec{r})] + E_{xc}[n(\vec{r})] \\ n(\vec{r}) &= \sum_i |\psi_i(\vec{r})|^2 \\ T &\equiv \sum_i \int \psi_i^*(\vec{r}) \left(-\frac{\nabla^2}{2}\right) \psi_i(\vec{r}) d\vec{r} \\ E_{Hartree}[n(\vec{r})] &\equiv \int\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}' \\ E_{xc}[n(\vec{r})] &\equiv \text{everything else} \end{aligned}$$

Note: This is still exact. The approximation will be in E_{xc}.

Eigenvalue equation

Minimizing the Kohn-Sham functional leads to solution having the form of a self-consistent single-partical eigenproblem.

$$\mathcal{H}_{sp}\psi_i = \epsilon_i\psi_i$$

$$\mathcal{H}_{sp} \equiv -\frac{\nabla^2}{2} + V_{Hartree}(\vec{r}) + V_{xc}(\vec{r})$$

$$V_{xc}(\vec{r}) \equiv \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$$

Note: V_{xc} is a functional of $n(\vec{r})$, so this requires self-consistency.

Meaning of eigenvalues

$$\mathcal{H}_{sp}\psi_i = \epsilon_i\psi_i$$

- Eigenvalues ϵ_i is not the energy of an excited state.
- Eigenfunctions ψ_i are not actual wavefunctions.
- "Electron kinetic energy" T is not the total electron kinetic energy. (Some is hidden in E_{xc})

Spin-density functionals

One can alternatively split the total electron density into two parts an "spin up" density $n_\uparrow(\vec{r})$ and a "spin down" density $n_\downarrow(\vec{r})$.

$$F_{KS}[n_\uparrow(\vec{r}), n_\downarrow(\vec{r})] = T + E_{Hartree}[n(\vec{r})] + E_{xc}[n_\uparrow(\vec{r}), n_\downarrow(\vec{r})]$$

$$n_\uparrow(\vec{r}) = \sum_i |\psi_{i\uparrow}(\vec{r})|^2 \qquad n_\downarrow(\vec{r}) = \sum_i |\psi_{i\downarrow}(\vec{r})|^2$$

- In *principle* no more exact than ordinary DFT.
- In *practice* necesary for magnetic systems, or insulating systems with an odd number of electrons.

Exchange-correlation functionals

LDA	“Local Density Approximation” This functional is uniquely determined by the properties of the uniform electron gas. Usually overbinds by a few percent.
LSDA	“Local Spin Density Approximation”
GGA	“Generalized Gradient Approximation” Actually a class of functionals, which depend on both the density and its gradient. They tend to correct the overbinding of LDA, but sometimes overcorrect.
PBE	“Perdue-Burke-Ernzerhof” The most commonly use GGA by physicists, based on an interpolation between analytically solvable regimes.

Chemists more commonly use empirical functionals such as those by Becke (e.g. B3LYP—which is actually a hybrid functional), but don’t tend to work well for solids.

Metals

When working with metals, one needs to add a “filling factor” f_i to the computation of the density.

$$n(\vec{r}) = \sum_i f_i \left|\psi_i(\vec{r})^2\right|$$

For efficiency reasons, when handling metals one generally introduces an artificial finite electronic “temperature”, with the result that the filling factor can take intermediate values between 0 and 1.

What DFT can and cannot predict

Fundamentally, DFT can only predict the density and total energy of a set of electrons under an external potential.

DFT can predict

- Total energy
- Forces
- Lattice constants
- Bond lengths
- Vibrational frequencies
- Phonon frequencies
- Electron density
- Static dielectric response

DFT cannot predict

- Excited state energies
- Band gap
- Band structures
- Wave functions
- Fermi surface
- Superconductivity
- Excitons
- Electronic transport

What DFT can predict accurately

Accuracies I expect from LDA calculations (ballpark estimates)

bond length	∼3% too small
bulk modulus	∼10% too high
phonon frequency	∼10% too high
energy difference	> 1 mHartree
cohesive energy	very poor (much too high)

Accuracies for properties that DFT technically does not predict

band gap	∼50% too small
band structure	qualitatively reasonable
fermi surface	qualitatively reasonable

A bit of solid state terminology

Bravais lattice	A periodic array of points, defined by three vectors, which are referred to as "lattice vectors" $\vec{R}$.
Reciprocal lattice	A bravais lattice that is related to the real space bravais lattice by $\vec{G} \cdot \vec{R} = 2\pi n$
Reciprocal space	Also known as "k-space", the space in which wave vectors live.
k-vector or k-point or "crystal momentum"	A quantum number in periodic systems (see Bloch's theorem).
Brillouin zone	Portion of k-space in which the k-vectors live.
Irreducible Brillouin zone	Portion of the BZ which cannot be mapped onto itself by symmetry operations.
Cutoff energy	Plane waves having a kinetic energy less than the cutoff energy are included in the basis. $G^2/2 < E_{cut}$

Approches for representing Kohn-Sham orbitals numerically

Basis set methods

- A linear combination of basis functions.
- Integrals and derivatives may be computed exactly.
- The energy is variational.

Finite difference methods

- Store the actual value of the orbitals at grid points.
- Both integrals and derivatives are approximate—not variational in grid spacing.
- Usually easier to parallelize.
- Easy to systematically improve.

Hybrid methods

See the next presentation.

Advantages and disadvantages of a plane wave basis

Advantages

- It is simple.
- All necesary matrix elements can be efficiently computed.
- The basis doesn't prefer one location over another, so there are no "Pulay forces".
- A single parameter controls convergence of the basis.

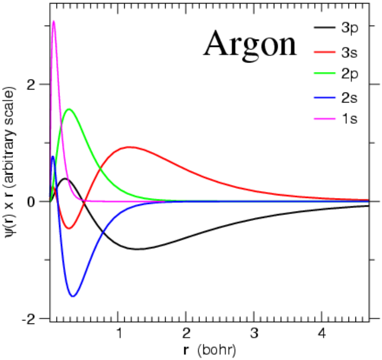
Disadvantages

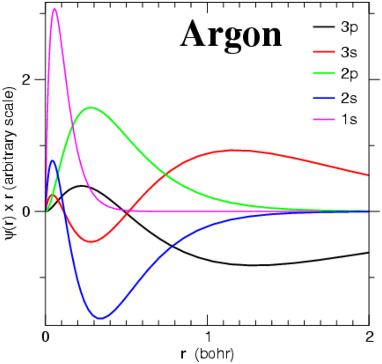
- Nonlocalized basis functions are hard to parallelize efficiently.
- Cannot take advantage of vacuum to reduce the basis size.
- Representing atomic wavefunctions requires a prohibitively large number of planewaves ($k_{max} \propto Z$).

Pseudopotential approach

The pseudopotential approach addresses two problems:

1. Atomic orbitals require a very high cutoff energy.
2. There are lots of boring core states.

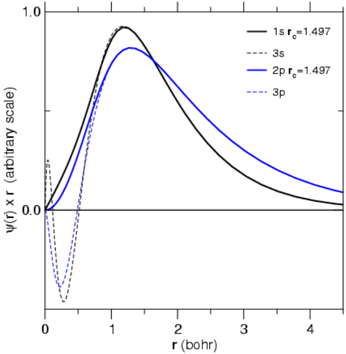


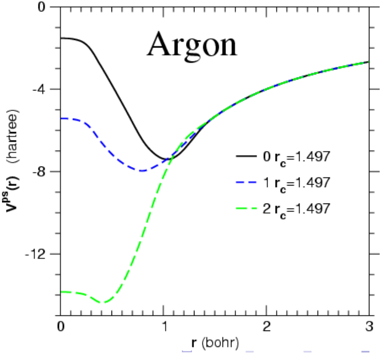


Norm-conserving pseudopotentials

An effective potential that

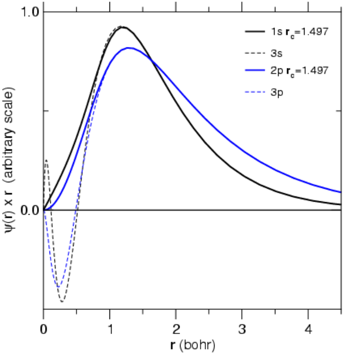
- Is generally non-local (one potential per angular momentum *l*)
- Reproduces valence orbital eigenvalues exactly
- Reproduces all-electron potential outside some cutoff radius
- Creates orbitals that integrate to the same “norm” within the cutoff radius.

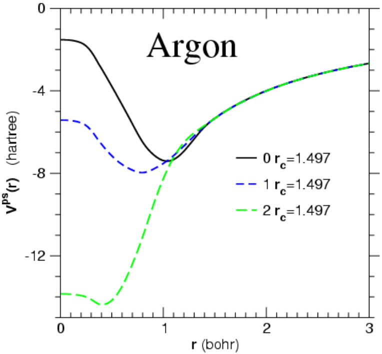




Norm-conserving pseudopotentials

- “Pauli repulsion” represented by a repulsion in the core region.
- Additional smoothing for angular momentum channels for which there are no core electrons (and thus no Pauli repulsion).





Pseudopotential flavors

Flavors

- Norm conserving:
    - Troullier-Martins
    - Rappe
    - Hamann
- Vanderbilt ultrasoft pseudopotentials
- Projector Augmented Wave (PAW)

Codes

- FHI pseudopotential generating code: fhi98PP
- OPIUM

Transferability of pseudopotentials

A transferable pseudopotential gives correct results in a wide variety of environments.

Factors affecting transferability

- Cutoff radii
- Partial core correction
- Reference configuration
- Cutoff energy used for actual planewave calculation

The only solution is to test your pseudopotentials!