Ab initio calculations for quantum mechanical simulations

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Ab initio calculations

Computing properties of materials from first principles

- energies
- structures
- relative stabilities of conformers of phases
- mechanical, magnetic and optical properties
- evolution with time
- chemical reactivity
- how different systems interact

First-principles (or *ab initio*) means that we try to compute these properties using the laws of quantum mechanics with no experimental or empirical parameters

Density-functional theory (DFT)

DFT is one of the most popular approaches to study the electronic structure and dynamics of molecules and complex materials

It is widely used in chemistry, condensed matter physics, materials science and engineering

It is usually considered an *ab initio* (or first-principles) method, because it attempts to solve Schrödinger's equation without using empirical parameters

In practice, DFT calculations involve at least one approximation, the exchange-correlation functional

Choosing the correct functional is *the* essential component of all DFT calculations

Overview

1. Introduction to DFT

   Hartree-Fock theory, correlation, Hohenberg-Kohn theorem, orbital-free DFT, the Kohn-Sham equations, the exchange correlation functional, limits of DFT

2. Modelling extended systems

   The crystal lattice, periodic boundary conditions, real and reciprocal space, Bloch's theorem, the Brillouin zone

3. Basis sets and software

   DFT with computers, local and floating basis sets, their strengths and limitations, a practical example

About myself

- PhD in Physical and Theoretical Chemistry (Oxford, UK, 1998-2001)
- Postdoc in Theoretical Chemistry (Cambridge, UK, 2001-2004)
- Postdoc in Theoretical Chemistry (Amsterdam, NL, 2004-2008)
- Principal Scientist (STFC Rutherford-Appleton Lab, UK, 2008-2018)
- Research Assistant Professor in Chemistry and Consultant at CRC (2018-)

Research interests

- *Ab initio* molecular dynamics and chemical reactivity
- Excited states and TD-DFT
- Software development

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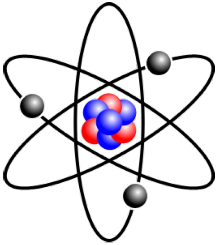
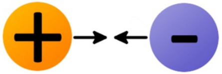
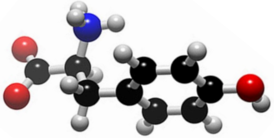
The atomistic description of matter

Atoms, molecules and crystals

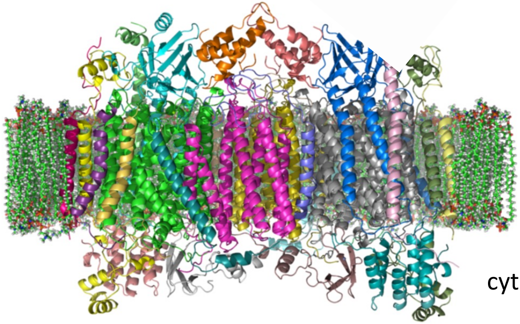


Atom = nucleus + electrons

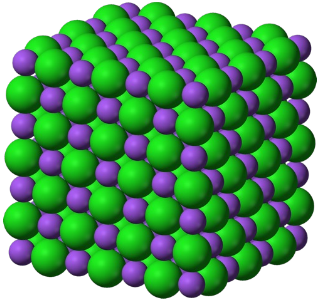




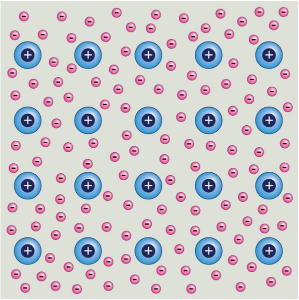
tyrosine



cytochrome c oxidase

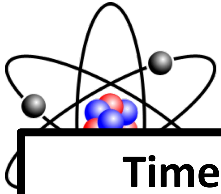


NaCl



a metal

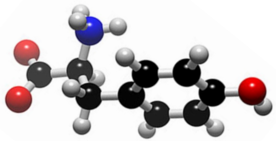
Atoms, molecules and crystals



Atom = r

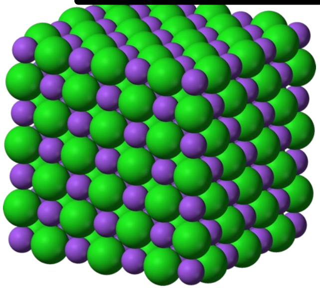
Time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$$

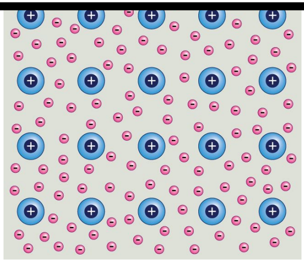


tyrosine

chrome c oxidase



NaCl



a metal

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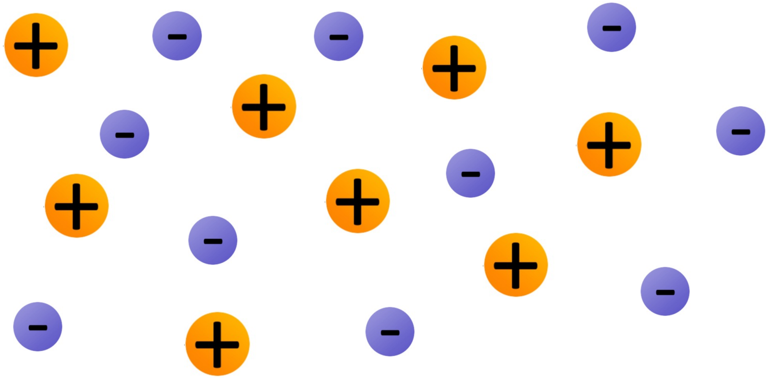
Born-Oppenheimer approximation

The nuclei are generally easy to treat, as they move slowly compared to the electrons and can be considered classical point charges

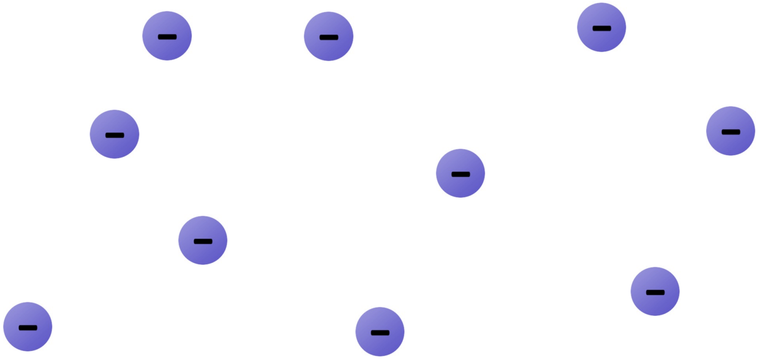


The nuclei are treated as unmovable classical point charges, providing a potential that constrains the motion of the electrons

(BO *versus* adiabatic approximation)

Electron interactions

The nuclei are generally easy to treat, as they move slowly compared to the electrons and can be considered classical point charges

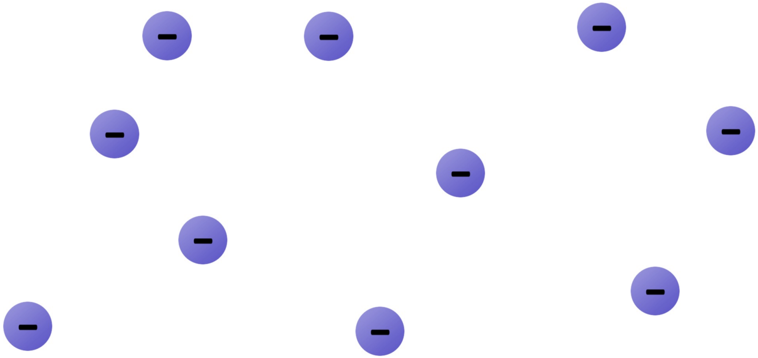


Electrons interact:

- classically (as moving negative point charges)
- quantum mechanically (as fermions)

This leads to the appearance of exchange and correlation effects in their distribution

Schrödinger equation



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

Hartree-Fock

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Hartree-Fock: the quantum nature of the electrons

An ensemble of N interacting electrons is described by a many-body wavefunction

$$\Psi(1, 2, \ldots, N).$$

Electrons obey the Fermi-Dirac statistics (anti-symmetry):

$$\Psi(2, 1, \ldots, N) = -\Psi(1, 2, \ldots, N).$$

The HF method accounts for anti-symmetry exactly using a model approximate wavefunction Φ, called Slater determinant

$$\Phi(1, 2, \ldots, N) = \left(\frac{1}{N!}\right)^{1/2} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \ldots & \phi_N(N) \end{vmatrix}$$

One-electron orbitals

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The Hartree-Fock method

Slater determinant

$$\Phi(1,2,\dots,N) = \left(\frac{1}{N!}\right)^{1/2} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \dots & \phi_N(N) \end{vmatrix}$$

$$\boxed{H\,\Psi = E\,\Psi}$$

Schrödinger’s equation (in BOA)

$$H = -\frac{1}{2}\sum_{i=1}^{N_{\text{elec}}} \nabla_i^2 - \sum_{a=1}^{N_{\text{nuclei}}}\sum_{i=1}^{N_{\text{elec}}} \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} + \sum_{i=1}^{N_{\text{elec}}}\sum_{j>i}^{N_{\text{elec}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{a=1}^{N_{\text{nuclei}}}\sum_{b>a}^{N_{\text{nuclei}}} \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$

Hamiltonian operator

Solution: Vary ϕ_i until E is a minimum

E = total energy

Ψ = wave-function

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Hartree-Fock: total energy

$$E = < \boldsymbol{\Psi} |\ H\ | \boldsymbol{\Psi} >$$

$$\begin{aligned} E = & \sum_{i=1}^{N_{\mathrm{elec}}} \langle \phi_i(1) | h_i | \phi_i(1) \rangle + \\ & \sum_{i=1}^{N_{\mathrm{elec}}} \sum_{j>i}^{N_{\mathrm{elec}}} \langle \phi_i(1)\phi_j(2) | g_{ij} | \phi_i(1)\phi_j(2) \rangle - \langle \phi_i(1)\phi_j(2) | g_{ij} | \phi_j(1)\phi_i(2) \rangle + v_{nn} \\ = & \sum_{i=1}^{N_{\mathrm{elec}}} h_i + \sum_{i=1}^{N_{\mathrm{elec}}} \sum_{j>i}^{N_{\mathrm{elec}}} (J_{ij} - K_{ij}) + v_{nn} \end{aligned}$$

Dirac’s notation

$$\langle \phi \mid \tilde{O} \mid \psi \rangle \equiv \langle \phi \mid \tilde{O}\, \psi \rangle$$

$$\langle \phi \mid \psi \rangle \equiv \int_{-\infty}^{\infty} \overline{\phi}\, \psi \, d\, x,$$

Hartree-Fock: the Coulomb interaction

$$\boxed{\iint d\mathbf{r}\, d\mathbf{r}'\, \rho_i(\mathbf{r})\, \rho_j(\mathbf{r}')}$$

Coulomb repulsion between electron *i* and electron j

$$
\begin{aligned}
E = & \sum_{i=1}^{N_{\text{elec}}} \langle \phi_i(1)|h_i|\phi_i(1)\rangle + \\
& \sum_{i=1}^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} \boxed{\langle \phi_i(1)\phi_j(2)|g_{ij}|\phi_i(1)\phi_j(2)\rangle} - \langle \phi_i(1)\phi_j(2)|g_{ij}|\phi_j(1)\phi_i(2)\rangle + v_{nn} \\
= & \sum_{i=1}^{N_{\text{elec}}} h_i + \sum_{i=1}^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + v_{nn}
\end{aligned}
$$

An electron *i* moves within the average Coulomb field *J* created by the other electrons and within their exchange field *K*

Hartree-Fock = independent electrons moving in a mean field

Hartree-Fock: the exchange interaction

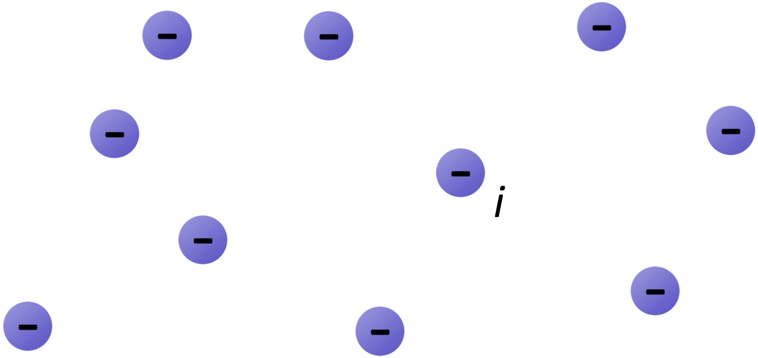
$$
\begin{aligned}
E = & \sum_{i=1}^{N_{\text{elec}}} \langle \phi_i(1) | h_i | \phi_i(1) \rangle + \\
& \sum_{i=1}^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} \langle \phi_i(1)\phi_j(2) | g_{ij} | \phi_i(1)\phi_j(2) \rangle - \boxed{\langle \phi_i(1)\phi_j(2) | g_{ij} | \phi_j(1)\phi_i(2) \rangle} + v_{nn} \\
= & \sum_{i=1}^{N_{\text{elec}}} h_i + \sum_{i=1}^{N_{\text{elec}}} \sum_{j>i}^{N_{\text{elec}}} (J_{ij} - K_{ij}) + v_{nn}
\end{aligned}
$$

Exchange interaction between electron *i* and electron j

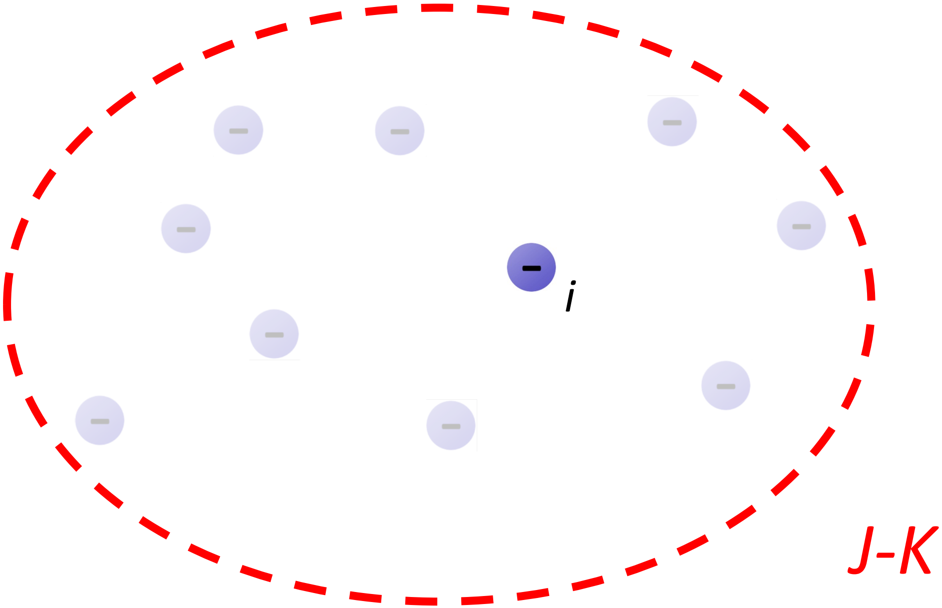
An electron *i* moves within the average Coulomb field *J* created by the other electrons and within their exchange field *K*

Hartree-Fock = independent electrons moving in a mean field

Mean-field approximation



Mean-field approximation



Instantaneous correlation in the motion of the electrons is neglected

Electronic correlation

Correlation in the electron motion: the probability of finding one electron at a given position is not independent of the positions of the other electrons

Dynamical correlation

Electrons tend to avoid each other as they move

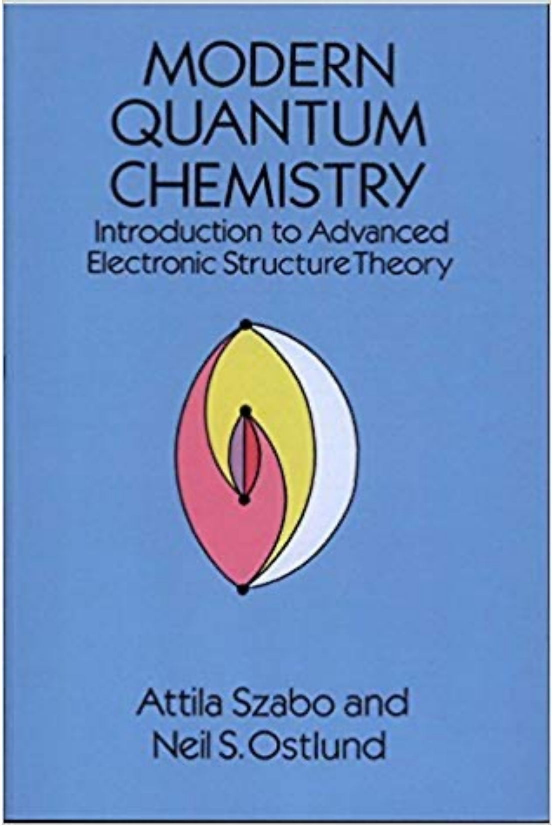
Non-dynamical (static) correlation

Degenerate states influence the motion of the electrons

Hartree-Fock: exchange is exact, but there is no correlation; one needs *post*-Hartree-Fock methods (MP2, CI, CC, *etc.*) to account for correlation

DFT: exchange and (dynamical) correlation are approximated in practice

Hartree-Fock


MODERN QUANTUM CHEMISTRY
Introduction to Advanced Electronic Structure Theory
Attila Szabo and Neil S. Ostlund

Density-functional theory

DFT *versus* wavefunction theory

Unlike Hartree-Fock, DFT does not attempt to propose an *Ansatz* for the wavefunction

There is no many-body wavefunction in DFT

DFT is based on the assumption (justified by a rigorous theorem) that all information about electron interactions can be obtained from the electron density alone

The electron density is a simple and real function of *x, y* and *z* only, and it can be observed experimentally

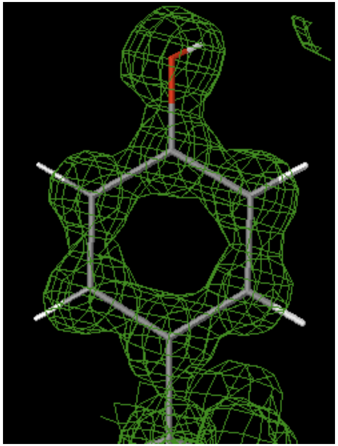
The total energy of a system of nuclei and electrons is a unique functional of the electron density

Density-functional theory

The electron density

In quantum mechanics, the electron density is given by the square modulus of the wavefunction integrated over the coordinates of $N-1$ electrons:

$$\rho(\mathbf{r}) = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N$$



Experimentally, electron density maps can also be obtained using X-ray (or neutron) crystallography

The electron density is a real function in 3D space

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Density-functional theory

The Hohenberg-Kohn theorems

$$H = -\frac{1}{2}\sum_{i=1}^{N_{\text{elec}}}\nabla_i^2 \boxed{-\sum_{a=1}^{N_{\text{nuclei}}}\sum_{i=1}^{N_{\text{elec}}}\frac{Z_a}{|\mathbf{R}_a-\mathbf{r}_i|}} + \sum_{i=1}^{N_{\text{elec}}}\sum_{j>i}^{N_{\text{elec}}}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} \boxed{+\sum_{a=1}^{N_{\text{nuclei}}}\sum_{b>a}^{N_{\text{nuclei}}}\frac{Z_aZ_b}{|\mathbf{R}_a-\mathbf{R}_b|}}$$

External potential: $v_{\text{ext}}(\boldsymbol{r})$

I: For a non-degenerate ground state, the external potential is a unique functional of the electron density; the total energy is therefore a unique functional of the electron density

II: The ground state electron density minimizes the total energy

Note:
A *function* is a rule that, given a *number*, returns a *number*.
A *functional* is a rule that, given a *function*, returns a *number*.

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Density-functional theory

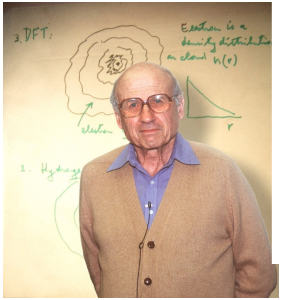
Hohenberg-Kohn theorem I

Assume that two different *external potentials* V_{ext} and V'_{ext} (describing the electron-nuclei interaction plus possibly other perturbations) result in the same electron density ρ.

Since there are two potentials, there are also two different Hamiltonians H and H'. Their respective mimimum-energy wavefunctions are Ψ and Ψ' are also different.

If we now take Ψ' as an approximate wavefunction for H, we obtain, from the variational principle that

Reductio ad absurdum



Walter Kohn (1923-2016)

$$
\begin{aligned}
&\langle \Psi' | H | \Psi' \rangle > E_0 \\
&\langle \Psi' | H | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle > E_0 \\
&E'_0 + \langle \Psi' | V_{\text{ext}} - V'_{\text{ext}} | \Psi' \rangle > E_0 \\
&E'_0 + \int \rho(\mathbf{r})(V_{\text{ext}} - V'_{\text{ext}}) d\mathbf{r} > E_0
\end{aligned}
$$

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Density-functional theory

Hohenberg-Kohn theorem I

Similarly, if we take Ψ as an approximate wavefunction for H', we get

$$E_0 - \int \rho(\mathbf{r})(V_{\text{ext}} - V'_{\text{ext}})d\mathbf{r} > E'_0$$

If we sum the two inequalities, we get that $E'_0 + E_0 > E'_0 + E_0$, which means that the assumption is wrong.

For the ground state, there is a one-to-one correspondence between the electron density and the nuclear potential, and therefore the total energy.

The energy is a *unique functional* of the electron density, $E \equiv E[\rho]$.

Density-functional theory

Hohenberg-Kohn theorem II

Given an approximate electron density ρ' that integrates to the number of electrons,

$$\int \rho(\mathbf{r})d\mathbf{r} = N_{\text{elec}},$$

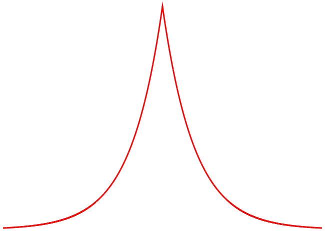
the energy of this density is larger or equal to the exact ground state energy

$$E_0[\rho'] \geq E_0[\rho]$$

This theorem is the DFT version of the variation principle for wavefunctions of quantum mechanics.

Density-functional theory

"Intuitive proof" of DFT (EB Wilson, 1965)

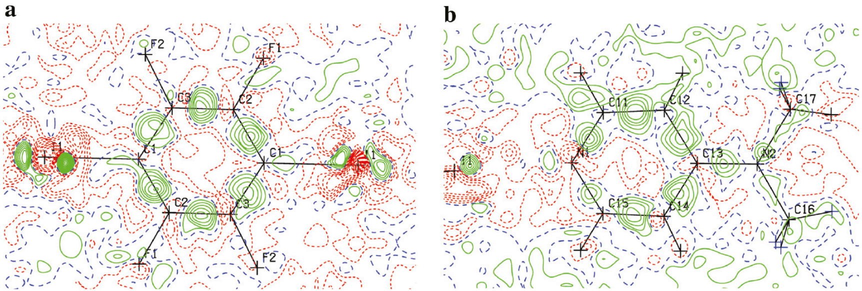


X-ray crystallography

The electron density uniquely determines the positions and charges of the nuclei and therefore the Hamiltonian. This observation is based on the fact that the electron density has a cusp at the nucleus, i.e.

$$Z_a = -\frac{1}{2\overline{\rho}(0)}\left[\frac{\partial\overline{\rho}(r_a)}{\partial r_a}\right]_{r_a=0}$$

where $\overline{\rho}(r)$ is the spherically averaged electron density. A careful examination of the electron density therefore uniquely determines the external potential and the Hamiltonian.



Density-functional theory

The kinetic energy and exchange-correlation problems

In principle, the HK theorem II can be used to determine the ground state electron density. We need to know explicitly $E[\rho]$, then vary ρ until the energy is minimised. In the BO approximation, $E[\rho]$ can be decomposed into kinetic energy, nuclei-electron attraction and electron-electron repulsion terms,

$$E[\rho] = T[\rho] + E_{\text{ne}}[\rho] + E_{\text{ee}}[\rho].$$

The e-e repulsion can be decomposed into a Coulomb ($J[\rho]$) and an exchange ($K[\rho]$) part. We can compute $E_{\text{ne}}[\rho]$ and $J[\rho]$ easily:

$$E_{\text{ne}}[\rho] = -\sum_{a}^{N_{\text{nuclei}}} \int \frac{Z_a \rho(\mathbf{r})}{|\mathbf{R}_a - \mathbf{r}|}\, d\mathbf{r}$$

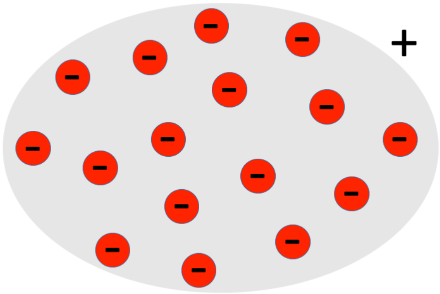
$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$T[\rho]$ and $K[\rho]$ however remain unknown, and they have to be modelled. This is very difficult to do, especially for $T[\rho]$.

$\Longrightarrow$ *“orbital-free”* DFT

Orbital-free DFT

Homogeneous electron gas



Thomas-Fermi kinetic energy functional (1927)

$$T_{TF} = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho(\mathbf{r})^{\frac{5}{3}} d^3r$$

Does not include the exchange-energy, which can be added using a formula derived by Dirac (Thomas-Fermi-Dirac functional). Too inaccurate for most applications.

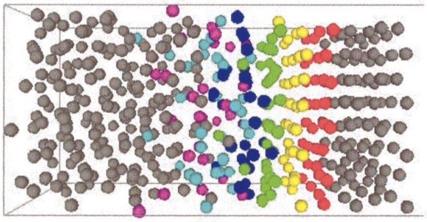
Von Weizsäcker correction (1935)

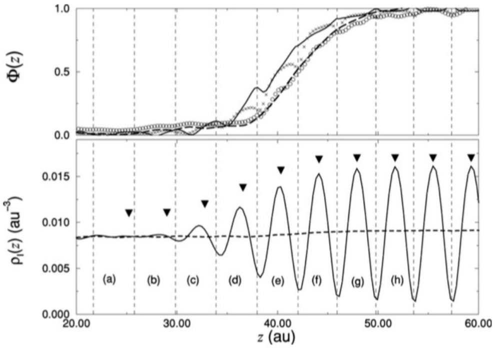
$$T_W = \frac{1}{2} \int [\nabla \rho(\mathbf{r})^{\frac{1}{2}}]^2 d^3r$$

Other corrections can be applied to the TF-W functional.

Orbital-free DFT

Current KE functionals are typically too inaccurate for general applications. OF DFT can however work well when the deviation of $\rho(\mathbf{r})$ from the HEG is small. It is computationally far less demanding than “standard” DFT.





Al solid-liquid interface

BJ Jesson and PA Madden, JCP 113, 5935 (2000)

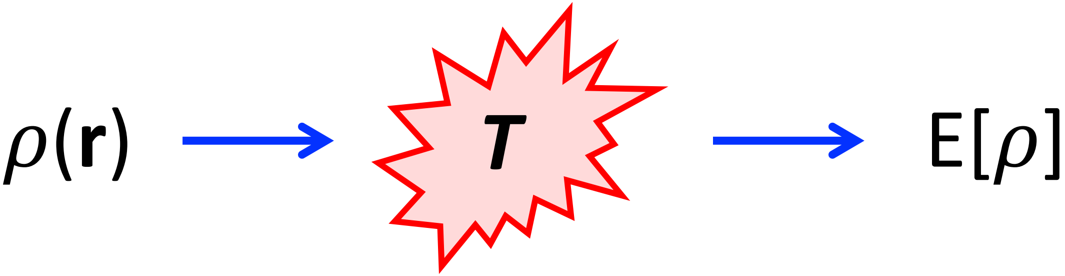
Ab initio molecular dynamics with OF DFT

1062 atoms per cell, 9 ps statistical averages

CONUNDrum: A program for orbital-free density functional theory calculations

P Golub and S Manzhos, Comp. Phys. Comm. 256, 107365 (2020)

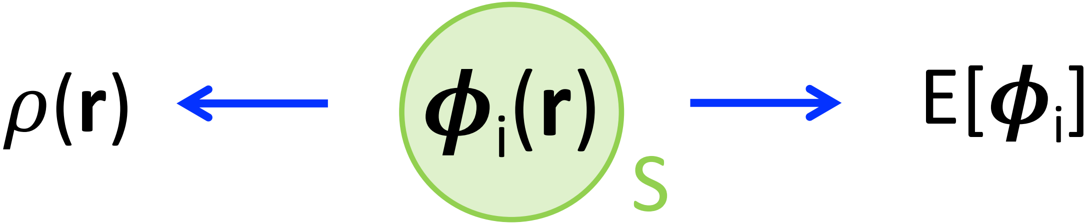
Orbital-free DFT



$$\rho(\mathbf{r}) \longrightarrow T \longrightarrow E[\rho]$$

Interacting electrons

Kohn-Sham DFT



$$\rho(\mathbf{r}) \longleftarrow \phi_i(\mathbf{r})_S \longrightarrow E[\phi_i]$$

Independent electrons

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Density-functional theory

Kohn-Sham theory

The idea of the KS formalism is to split the kinetic energy functional into a part that can be calculated exactly and a small correction term. This is done by introducing a set of orbitals representing a fictitious ensemble of non-interacting electrons.

The kinetic energy can then be computed for the non-interacting electrons

$$T_{\mathrm{S}} = -\frac{1}{2}\sum_{i=1}^{N_{\mathrm{elec}}} \langle \phi_i | \nabla^2 | \phi_i \rangle$$

The orbitals are required to reconstruct the electron density

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_{\mathrm{elec}}} |\phi_i(\mathbf{r})|^2$$

Density-functional theory

The exchange-correlation functional

The *KS energy functional* is then written as

$$E[\rho] = T_{\mathrm{S}} + E_{\mathrm{ne}}[\rho] + E_{\mathrm{ee}}^{c}[\rho] + \boxed{E_{\mathrm{xc}}[\rho]}$$

$E_{\mathrm{xc}}[\rho]$ (the so called *exchange-correlation functional*) contains the component of the kinetic energy not accounted for by T_{S}, $K[\rho]$ and any correlation contribution in the electron dynamics.

$E_{\mathrm{xc}}[\rho]$ is in general unknown and it has to be approximated. The difference between different DFT methods is in the choice of E_{xc}.

It can be proved that E_{xc} is a *universal* functional, valid for all systems.

It is costumary to decompose E_{xc} into an exchange E_{x} and a correlation E_{c} component. However, only E_{xc} has a physical meaning.

Why does Kohn-Sham DFT work?

T_s E^C_{ee} E_{ne} E_{xc}

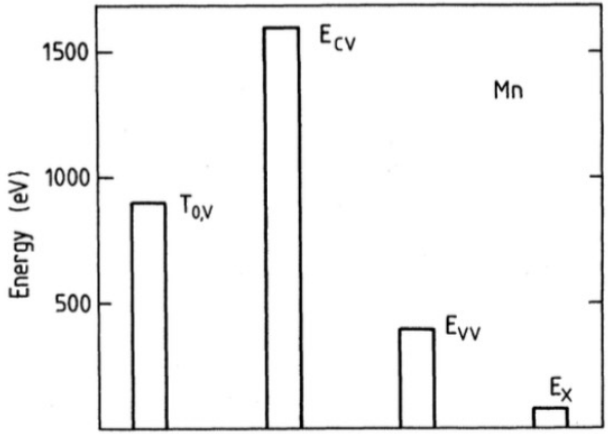

FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).

RO Jones and O Gunnarsson,
Rev. Mod. Phys. 61, 689 (1989)

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The Kohn-Sham equations

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2$$

A set of one-particle eigenvalue equations, with the one-particle wavefunctions giving the total electron density.

These are the equations that all DFT codes solve, a way or another.

However, we still need an expression for E_{xc}.

W Kohn and LJ Sham,
Phys. Rev. 140, A-1133 (1965)

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Density-functional theory

Properties of the exact E_{xc}

➡ (1) Self-interaction free (most commonly used functionals are not SI free - there are ways to correct KS DFT for the self interaction).

(2) For constant densities, the uniform electron gas E_{xc} (which is known) should be recovered. This is especially important in solid state systems.

(3) E_{x} should scale linearly with the density: $\rho \to \lambda\rho \Longrightarrow E_{\mathrm{x}}[\rho] = \lambda E_{\mathrm{x}}[\rho]$.

(4) Scaling ρ by a factor $\lambda > 1$ should increase the correlation component: $-E_{\mathrm{c}}[\rho_\lambda] > -\lambda E_{\mathrm{c}}[\rho]$.

(5) As $\lambda \to \infty$, E_{c} should approach a negative constant.

(6) *Lieb-Oxford condition*: $E_{\mathrm{x}}[\rho] \geq E_{\mathrm{xc}}[\rho] \geq 2.273E_{\mathrm{x}}^{\mathrm{LDA}}[\rho]$ (see below).

➡ (7) The exchange potential should decay as $-r^{-1}$ for $r \to \infty$. Also, the xc potential should change discontinuously as a function of the number of electrons (*"derivative discontinuity"*).

(8) The correlation potential should decay as $-1/2\alpha r^{-4}$, where α is the polarisability of the $N_{\mathrm{elec}} - 1$ system.

Density-functional theory

Approximate density functionals

All xc functionals contain parameters (similar to semi-empirical methods) The parameters can be chosen either

1. by enforcing conditions (1)-(8), or
2. by fitting them to experimental (or quantum mechanical) data.

In practice, the best functional to use depends on the system (e.g. molecule versus solid) and on the properties that are being computed.

There is no absolute reference in DFT, like MP2 or CCSD in quantum chemical methods, although usually *hybrid functionals* (see below) give good performance.

New xc functionals appear very frequently, to address limitations of previous functionals, improve their parameterisation or to address specific properties (e.g. NMR, optical absorption, etc.).

Density-functional theory

Spin polarisation

For a system consisting of α and β spin densities, the total density is given by $\rho = \rho_\alpha + \rho_\beta$. The exchange and correlation components are given by

$$
\begin{aligned}
E_\mathrm{x} &= E_\mathrm{x}^{\alpha}[\rho_\alpha] + E_\mathrm{x}^{\beta}[\rho_\beta] \\
E_\mathrm{c} &= E_\mathrm{c}^{\alpha\alpha}[\rho_\alpha] + E_\mathrm{x}^{\beta\beta}[\rho_\beta] + E_\mathrm{c}^{\alpha\beta}[\rho_\alpha, \rho_\beta]
\end{aligned}
$$

(In E_c the correlation of electrons with parallel spin is different from the one between electrons of opposite spin.)

Functionals can be formulated in terms of ρ_α and ρ_β separately, or in terms of the *spin polarisation* ζ

$$
\zeta = \frac{\rho_\alpha - \rho_\beta}{\rho_\alpha + \rho_\beta}
$$

Density functionals

K Burke, *Perspective on density functional theory,*
J. Chem. Phys. 136, 150901 (2012)

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Density functionals

1) Is there a way to *classify* functionals?

2) Is there a way to say, for a given system, which functional will perform best?

Density functionals

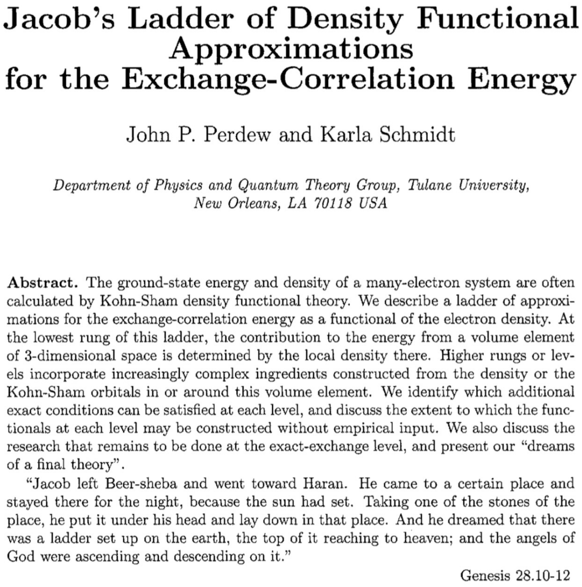
Classification

Quantum chemical methods can be classified according to the level of inclusion of correlation, and their quality can be characterised by a well defined order parameter. This is not possible for DFT methods.

A possible characterisation of functionals can be done based on the variables on which they depend. *"Jacob's ladder"* (JP Perdew) provides one such classification.

Density functionals

Jacob's ladder



Jacob's Ladder of Density Functional Approximations for the Exchange-Correlation Energy

John P. Perdew and Karla Schmidt

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, LA 70118 USA

Abstract. The ground-state energy and density of a many-electron system are often calculated by Kohn-Sham density functional theory. We describe a ladder of approximations for the exchange-correlation energy as a functional of the electron density. At the lowest rung of this ladder, the contribution to the energy from a volume element of 3-dimensional space is determined by the local density there. Higher rungs or levels incorporate increasingly complex ingredients constructed from the density or the Kohn-Sham orbitals in or around this volume element. We identify which additional exact conditions can be satisfied at each level, and discuss the extent to which the functionals at each level may be constructed without empirical input. We also discuss the research that remains to be done at the exact-exchange level, and present our "dreams of a final theory".

> "Jacob left Beer-sheba and went toward Haran. He came to a certain place and stayed there for the night, because the sun had set. Taking one of the stones of the place, he put it under his head and lay down in that place. And he dreamed that there was a ladder set up on the earth, the top of it reaching to heaven; and the angels of God were ascending and descending on it."
>
> Genesis 28.10-12

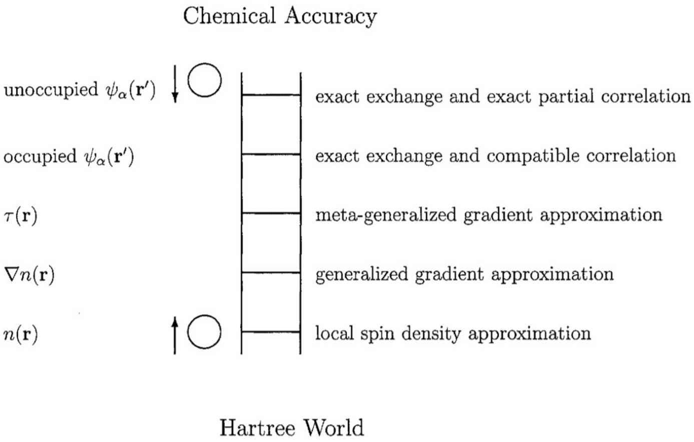
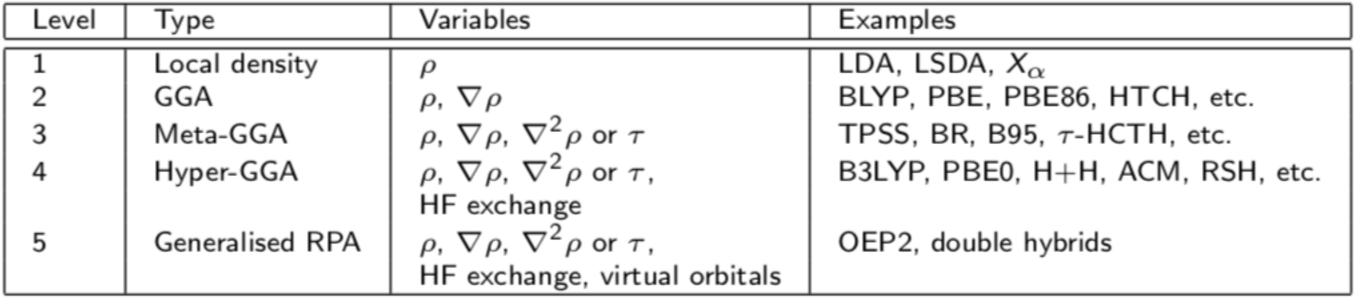


FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

JP Perdew and K Schmidt, AIP Conf. Proc. 577, 1 (2001)

Density functionals

Jacob’s ladder



Level	Type	Variables	Examples
1	Local density	ρ	LDA, LSDA, X_α
2	GGA	ρ, $\nabla\rho$	BLYP, PBE, PBE86, HTCH, etc.
3	Meta-GGA	ρ, $\nabla\rho$, $\nabla^2\rho$ or τ	TPSS, BR, B95, τ-HCTH, etc.
4	Hyper-GGA	ρ, $\nabla\rho$, $\nabla^2\rho$ or τ, HF exchange	B3LYP, PBE0, H+H, ACM, RSH, etc.
5	Generalised RPA	ρ, $\nabla\rho$, $\nabla^2\rho$ or τ, HF exchange, virtual orbitals	OEP2, double hybrids

Density functionals

Jacob's ladder

Genesis 28:
10-19

Stained glass, St. Paul Cathedral Pittsburgh

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Density functionals

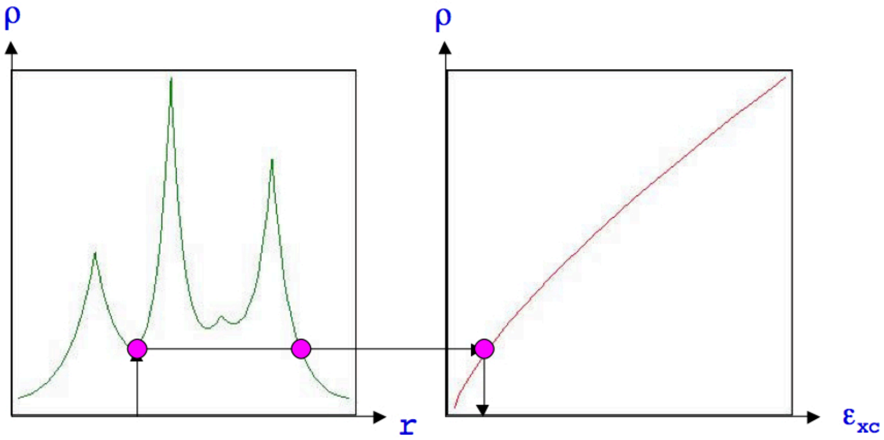
The local density approximation (LDA)

JL rung 1

In LDA, the density is treated locally as a uniform electron gas.

$$E_{\text{xc}}^{\text{LDA}} = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r})) d\mathbf{r}$$

$\epsilon_{\text{xc}}^{\text{LDA}}$ is the xc energy density, which is a function of $\rho(\mathbf{r})$.



(Thanks to Nic Harrison and Andreas Savin for the figure)

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Density functionals

The local density approximation (LDA)

The LDA exchange energy density for the HEG is given by Dirac's formula

$$\epsilon_{\mathrm{x}}^{\mathrm{LDA}} = -C_{\mathrm{x}}\rho^{1/3}$$

For spin-polarised systems, the corresponding LSDA formula is

$$\begin{aligned}\epsilon_{\mathrm{x}}^{\mathrm{LSDA}} &= -C_{\mathrm{x}} f_1(\zeta)\rho^{1/3} \\ f_1(\zeta) &= \frac{1}{2}\left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3}\right]\end{aligned}$$

The correlation energy for the HEG has been derived analytically for the high and low density limits. For intermediate densities, high accuracy data are available from Quantum Monte Carlo. Interpolation formulae have been derived. The most widely used parameterisations are those of *Vosko, Wilk, Nusair (VWN)*(1) and *Perdew-Wang (PW)*(2).

(1) Can. J. Phys. **58**, 1200 (1980); (2) Phys. Rev. B **45**, 13244 (1992)

Density functionals

The local density approximation (LDA)

Performance

LSDA is *exact* for the HEG, apart from the small numerical inaccuracies in the ϵ_c parameterisation.

For molecular systems, LSDA underestimates the exchange energy by $\sim 10\%$. This error is larger than the whole correlation energy. The correlation energy is overestimated and, as a consequence, bond energies are also overestimated, often by ~ 100 kJ/mol.

The accuracy of LSDA is typically considered comparable to Hartree-Fock.

For extended systems, especially metals, in which the density varies slowly, LSDA is usually considered acceptable.

Density functionals

The local density approximation (LDA)

Why does LDA work so well?

The main reason seems to be that LDA (like Hartree-Fock) satisfies a sum rule for the *exchange-correlation hole* P_{xc}. This quantity represents the probability density of finding an electron at $\mathbf{r}_2$ if another electron is located at $\mathbf{r}_1$,

$$P_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{P_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2)$$

P_2 is the pair density, and it determines the total energy.

Physically, P_{xc} describes the hole that the electron at $\mathbf{r}_1$ digs in the surrounding electron density. For LDA (and HF)

$$\int P_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = -1$$

Strictly speaking, in LDA P_{xc} and P_2 are very poorly described, but the *spherical average* of P_{xc} is estimated reasonably.

JL rung 2

Density functionals

Generalised gradient approximations (GGAs)

Improvements of LDA have to address deviations from the HEG limit. This can be done by including in ϵ_{xc} an explicit dependence on the *gradients* of the density (*gradient approximations*). Usually, this does not work, because the resulting functional does not fulfil the P_{xc} sum rule.

In GGAs, the first derivative of the density is included as a variable, and, in addition, sum rules conditions are enforced.

GGAs are parameterised, lighly (1 parameter as in B88) or heavily (15 parameters as in the HTCH series). The parameters are chosen to fit the functional form to either ab initio or experimental data.

Some GGAs have been developed to address specific properties, and they are very strong at predicting those (e.g. Keal-Tozer KT3 for shielding constants).

GGA corrections to LDA can improve the quality of the results, although highly problematic issues in LDA are unlikely cured by GGAs.

B88, B97, OPTX, HCTH93, HCTC147, HCTH497, BLYP, OLYP, OLYP, PW86, PW91, PBE, PBEsol, RPBE, mPW91, KT1, KT2, KT3, etc.

Density functionals

Meta-GGAs

JL rung 3

In addition to the gradient of the density, one can add higher order derivatives, for instance the Laplacian $\nabla^2\rho$. Alternatively, a dependence on the *orbital kinetic energy density* τ can be used, with the kinetic energy of each KS orbital described by the von Weizsäcker functional τ_{W},

$$\tau_{\mathrm{W}}(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|^2}{8\rho(\mathbf{r})}$$

Examples:
BR, B95, τ-HTCH, VSXC (21 empirical parameters),
TPSS and PKZB (non empirical)

These functionals can improve substantially some properties compared to LDA.

RMS atomisation energy errors (kJ/mol) for G3 data set:
HF 649, LSDA 439, PBE 87, τ-HTCH 31.

Density functionals

Hybrid or hyper-GGA functionals

JL rung 4

Mix wavefunction theory (HF) and DFT using the *adiabatic connection formula*

$$E_{\mathrm{xc}} = \int_0^1 \langle \Psi_\lambda | V_{\mathrm{xc}}^{\mathrm{hole}}(\lambda) | \Psi_\lambda \rangle d\lambda \simeq \frac{1}{2}\left(\langle \Psi_0 | V_{\mathrm{xc}}^{\mathrm{hole}}(0) | \Psi_0 \rangle + \langle \Psi_1 | V_{\mathrm{xc}}^{\mathrm{hole}}(1) | \Psi_1 \rangle\right)$$

$\lambda = 0$: non-interacting electrons → no correlation, only exchange; the exact wavefunction is a single Slater determinant: we can compute $\langle \Psi_0 | V_{\mathrm{xc}}^{\mathrm{hole}}(0) | \Psi_0 \rangle$

$\langle \Psi_1 | V_{\mathrm{xc}}^{\mathrm{hole}}(1) | \Psi_1 \rangle$ is unknown. Approximating it using LSDA gives the *half-and-half* (H+H) functional

$$E_{\mathrm{xc}}^{\mathrm{H+H}} = \frac{1}{2} E_{\mathrm{x}}^{\mathrm{HF}} + \frac{1}{2}\left(E_{\mathrm{x}}^{\mathrm{LSDA}} + E_{\mathrm{c}}^{\mathrm{LSDA}}\right)$$

Using GGAs gives hybrid functionals like B3LYP

$$E_{\mathrm{xc}}^{\mathrm{B3LYP}} = (1-a)E_{\mathrm{x}}^{\mathrm{LSDA}} + aE_{\mathrm{x}}^{\mathrm{HF}} + b\Delta E_{\mathrm{x}}^{\mathrm{B88}} + (1-c)E_{\mathrm{c}}^{\mathrm{LSDA}} + cE_{\mathrm{c}}^{\mathrm{LYP}}$$

with $a = 0.2$, $b = 0.7$, $c = 0.8$, and PBE0 with $a = 0.25$.

Density functionals

Hybrid or hyper-GGA functionals

Hybrids usually give better accuracy than LDA and GGAs.

RMS atomisation energy errors (kJ/mol) for G3 data set:
HF 649, LSDA 439, PBE 87, B3LYP 39, τ-HTCH 31.

Energies, geometries, vibrational and magnetic properties are usually more accurate than LDA/GGAs, both in molecules and in the condensed phase.

Treating the non-local HF part of the functional may be very demanding depending on the basis set used.

➡ Localized basis sets versus plane-waves

➡ Self-consistent hybrid functionals for solids

Density functionals

JL rung 5

Generalised random phase methods

These functionals use information from both occupied and virtual KS orbitals. Examples include *Optimised Effective Potential* (OEP) methods. In these approaches, one requires that the density derived from a KS calculation using a single-determinant wavefunction exactly matches the density derived from a correlated wavefunction (e.g. from MBPT). This in turn defines the exchange-correlation potential.

In *OEP1* the reference density does not include correlation: it is an exchange-only potential. *OEP2* uses a reference density from MP2 theory, and therefore contains both exchange (exactly) and correlation (to second order of PT).

Other example include *double hybrids* (DH), mixing HF exchange and MP2 correlation:

$$E_{\mathrm{xc}}^{\mathrm{DH}} = (1-a)E_{\mathrm{x}}^{\mathrm{DFT}} + aE_{\mathrm{x}}^{\mathrm{HF}} + (1-b)E_{\mathrm{c}}^{\mathrm{DFT}} + bE_{\mathrm{c}}^{\mathrm{MP2}}$$

Little is known about their performance, especially in the solid state.

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Density functionals

Summary

There is a huge number of functionals available. Their performance depends on the system and the properties under study. One may assume that climbing Jacob's ladder leads to better accuracy, but this may not always be the case.

Density functionals

Limitations of DFT

Irrespective of the functional there are issues that DFT is currently unable to address, for instance:

(1) Dispersion forces (van der Waals interactions)
(2) Loosely bound electrons in anions (SI problem)
(3) Some kind of bonds (e.g. two-centre one-electron) predicted to be too stable
(4) Direct description of excited states is problematic (although some excited state properties can be computed in TD-DFT)
(5) Relative energies of states with different spin multiplicities can be poorly described

Density functionals

Limitations of DFT

Irrespective of the functional there are issues that DFT is currently unable to address, for instance:

➡ (1) Dispersion forces (van der Waals interactions) Grimme's correction *(D2, D3)*

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Density functionals

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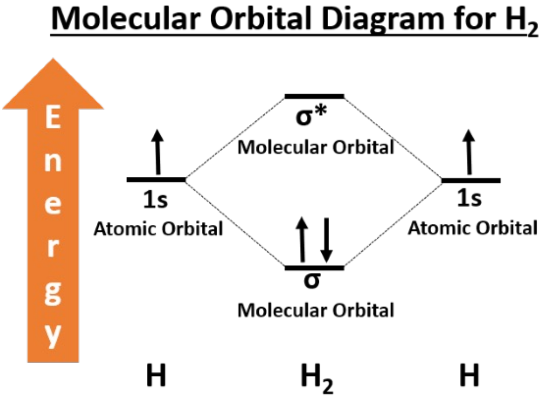
(4) Direct description of excited states is problematic (although some excited state properties can be computed in TD-DFT)

➡ (5) Relative energies of states with different spin multiplicities can be poorly described "Broken-symmetry DFT"

A fundamental limitation of DFT

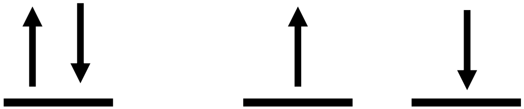
Static correlation aka non-dynamical correlation aka left-right correlation



Molecular Orbital Diagram for H_2

H_2 dissociation

CA Coulson and I Fischer, *Philos. Mag.* 40, 386 (1949)



singlet

open-shell singlet

Open-shell singlets

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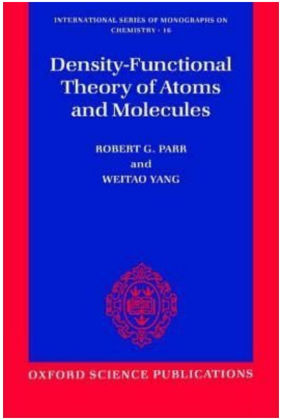
Density-functional theory

Summary

1. Hohenberg-Kohn theorem
2. Exchange-correlation energy
3. Kohn-Sham equations
4. Exchange-correlation functionals
5. Limitations of DFT

Density-functional theory

References



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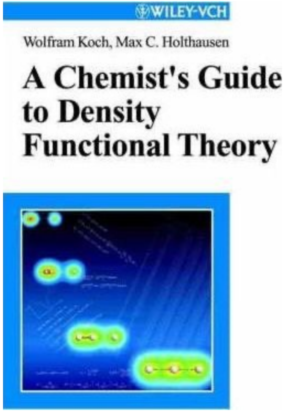

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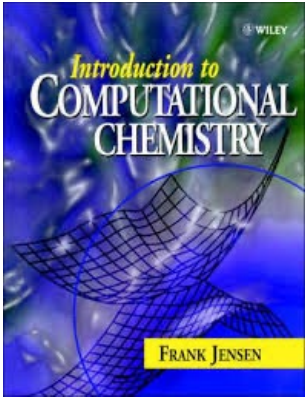

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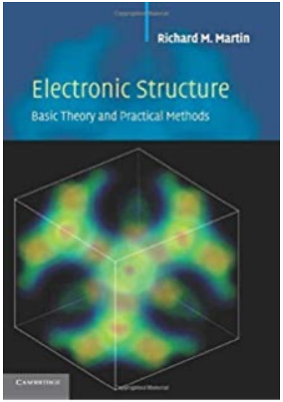

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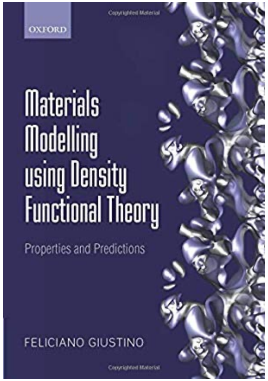

OXFORD

Materials Modelling using Density Functional Theory

Properties and Predictions

FELICIANO GIUSTINO

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$$\boxed{H\,\Psi = E\,\Psi}$$

Slater determinant

$$\Phi(1,2,\ldots,N) = \left(\frac{1}{N!}\right)^{1/2} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \ldots & \phi_N(N) \end{vmatrix}$$

Wave-function methods

Hartree-Fock and *post* Hartree-Fock

Density-functional theory

$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \rightarrow \rho(\mathbf{r})$

$E = E[\rho(\mathbf{r})]$

$E[\rho(\mathbf{r})] = E_K + E_{ne} + E_C + E_{xc}$

Electron density replaces the wfn

The energy is a *functional* of $\rho(\mathbf{r})$

E_{xc}

Exchange-correlation functional

Notation:
$n(\mathbf{r}) \equiv \rho(\mathbf{r})$

Easy to code

Can be used on large and extended systems

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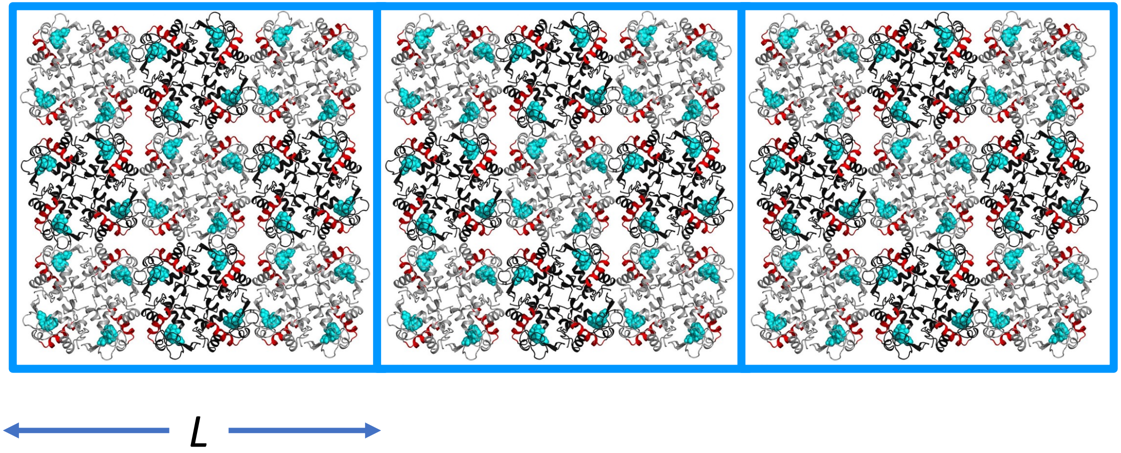
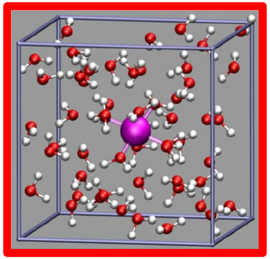
Simulation of extended systems

What do we mean by an “extended system”?



Periodic boundary conditions

$F(x + nL) = F(x)$



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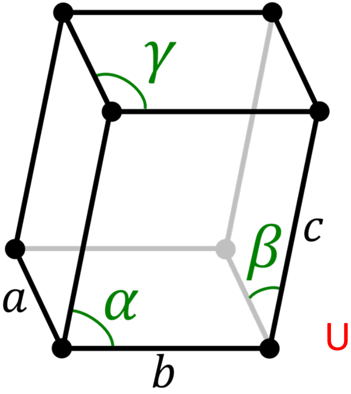
Perfect crystals: the direct lattice **R**

Infinite (3D) arrays of atoms (or groups of atoms) placed on a set of discrete points.

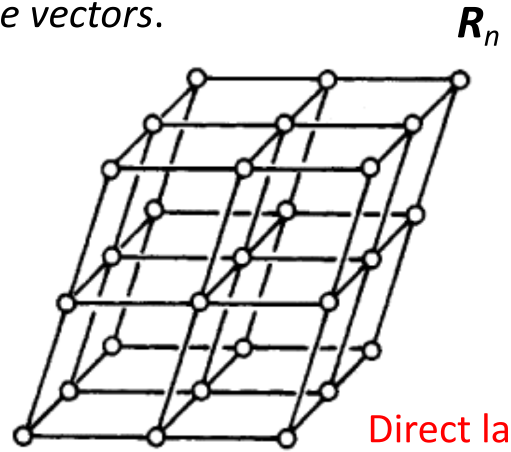
$\boldsymbol{R}_n = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}$ where $n = (n_1, n_2, n_3)$ are sets of integers

n_i are integers and ***a*, *b*** and **c** are *primitive vectors*.



$\boldsymbol{a} = \boldsymbol{a}_1$
$\boldsymbol{b} = \boldsymbol{a}_2$
$\boldsymbol{c} = \boldsymbol{a}_3$

Unit cell



Direct lattice

The full lattice is created by translations.
n = (1, 1, 1) defines the unit cell.

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Unit cell: primitive and conventional cell

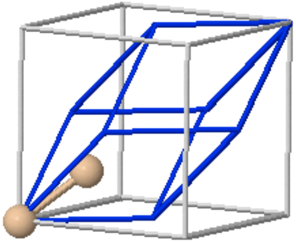
Primitive cell

It contains only one lattice point and the whole crystal can be constructed by translating it

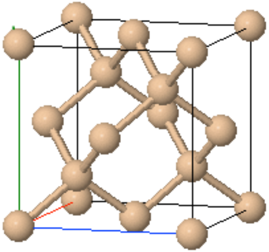
Conventional cell

The smallest unit cells whose axes follow the symmetry axes of the crystal structure; it may or may not be primitive and its volume is an integer multiple of the primitive cell volume

Silicon



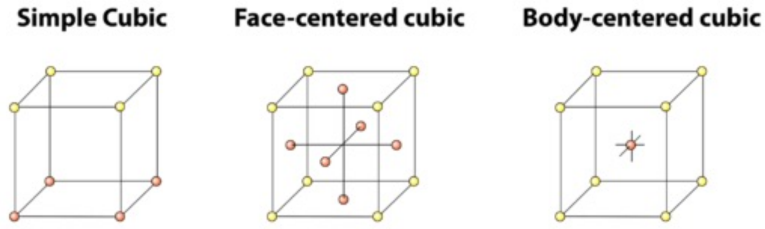
Primitive



Conventional

Conventional cells

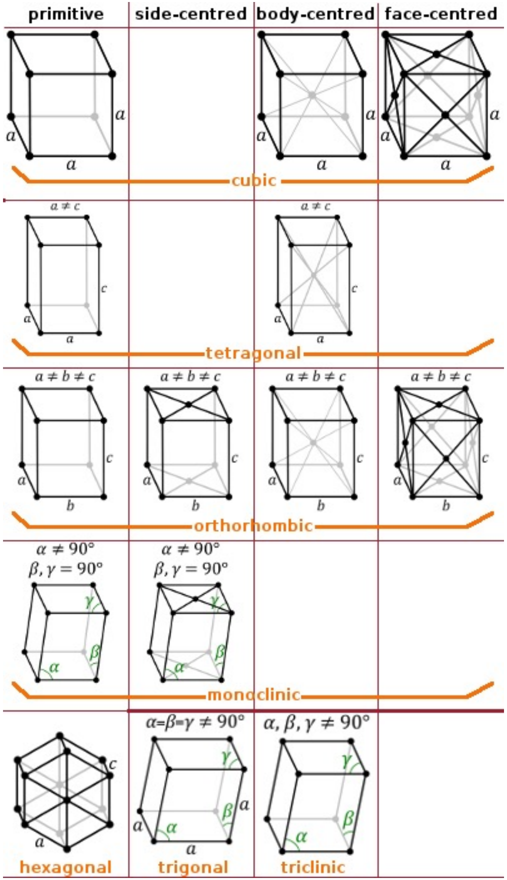
Cubic



N=1 N=4 N=2

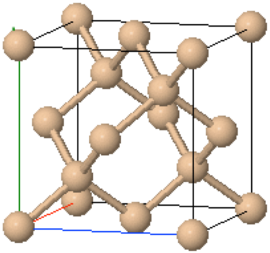
Rhombohedral, hexagonal, triclinic: one unique form each
Tetragonal: simple and body-centered
Monoclinic: simple and side-centered
Orthorhombic: simple, face-centered, body-centered, side-centered

Bravais lattices



Crystallographic point groups

Sets of symmetry operations that
leave the structure of
a crystal unchanged



14 Bravais lattices x 32 MPGs
= 130 space groups

(MPGs = molecular point groups)

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Atoms in the crystal lattice

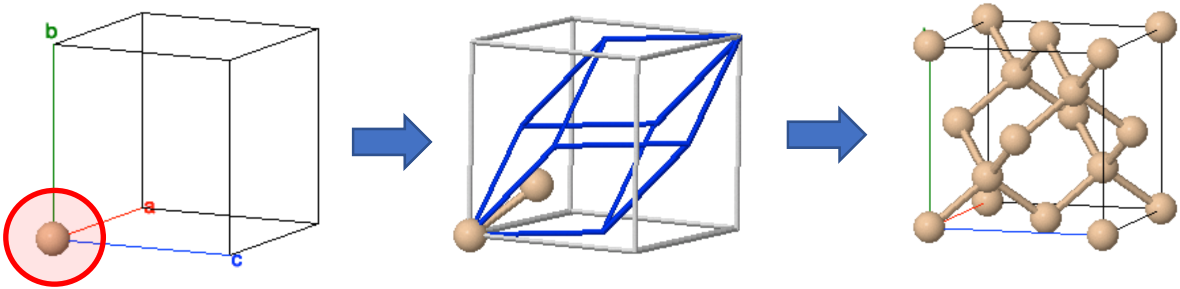
Asymmetric unit

Smallest fraction of a unit cell that, rotated and translated (according to the space group), generates the full unit cell

Silicon

Bravais lattice: face centered cubic
Point group: m3m
Space group: 227 (F d -3 m)
Lattice constant: a=0.543 nm

Asymmetric unit   Primitive cell   Conventional cell

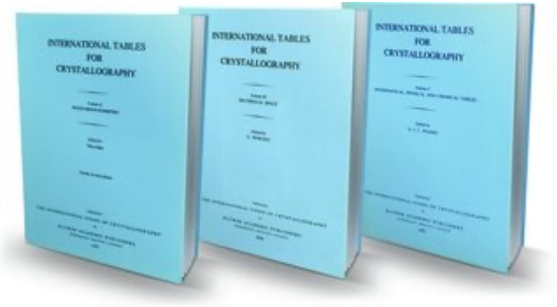


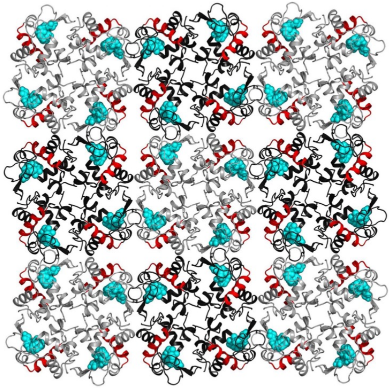
Special position

NB: most *ab initio* codes require a primitive cell

X-ray diffraction

Cell parameters,
space group,
special positions





Lysozyme crystal
G. Katona *et al.* [DOI: 10.1063/1.4931825](https://doi.org/10.1063/1.4931825)

The reciprocal lattice **G**

Set of vectors $\mathbf{G}_m = n_1\boldsymbol{b}_1 + n_2\boldsymbol{b}_2 + n_3\boldsymbol{b}_3$ that are Fourier transforms of the real lattice vectors $\mathbf{R}_n$:

$$e^{i\mathbf{G}_m\cdot\mathbf{R}_n} = 1 \Rightarrow \mathbf{G}_m \cdot \mathbf{R}_n = 2\pi N$$

$\boldsymbol{b}_1 = \boldsymbol{a}^*$
$\boldsymbol{b}_2 = \boldsymbol{b}^*$
$\boldsymbol{b}_3 = \boldsymbol{c}^*$

For instance, for a simple cubic direct lattice:

$\mathbf{G}_m = n_1(2\pi/a) + n_2(2\pi/b) + n_3(2\pi/c)$, with $a = b = c$.

The space in which **G** is defined is called reciprocal space (or G-space).

NOTE

A plane wave e^{ikx} is a function of both k and x: it oscillates with periodicity $\frac{2\pi}{k}$ in real (direct) space and with periodicity $\frac{2\pi}{x}$ in its reciprocal space.

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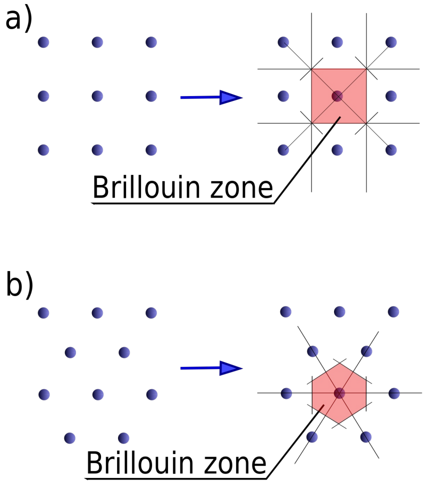
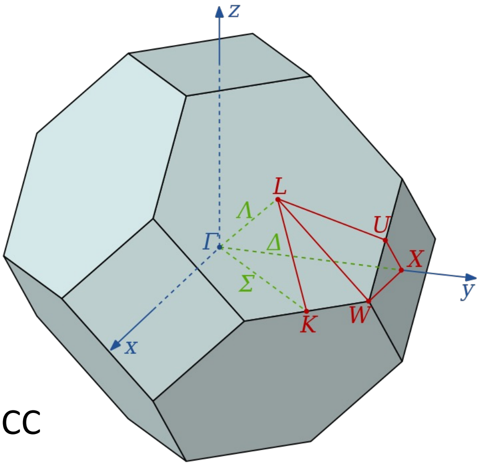
The Brillouin zone

A uniquely defined primitive cell in **G** space: volume in **G** space that is closer to the origin than to any other lattice point



2D sc

2D hex

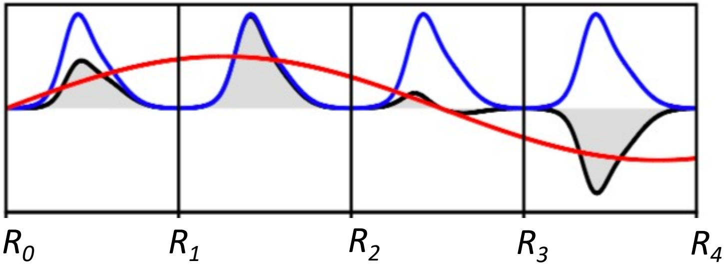


3D FCC

The Brillouin zone in direct space is called Wigner-Seitz cell.

Electrons in crystals: Bloch waves

In a periodically repeated environment, the wavefunctions of the electrons have the Bloch wave form (Bloch theorem):



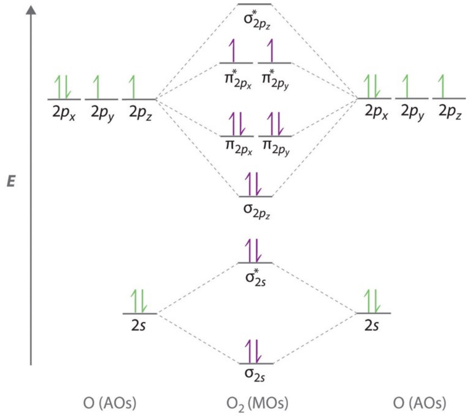
$$\psi_{\vec{k}n}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}n}(\vec{r})$$

n is the band index and the reciprocal lattice vector **k** is called the crystal wave vector. $u_{\boldsymbol{k}n}(\boldsymbol{r})$ has the same periodicity of the lattice.

For any vector **G**, $\psi_{kn}(\boldsymbol{r}) = \psi_{(\boldsymbol{k}+\boldsymbol{G})n}(\boldsymbol{r})$. Therefore, we can restrict the calculations to only those vectors ***k*** contained in the Brillouin Zone.

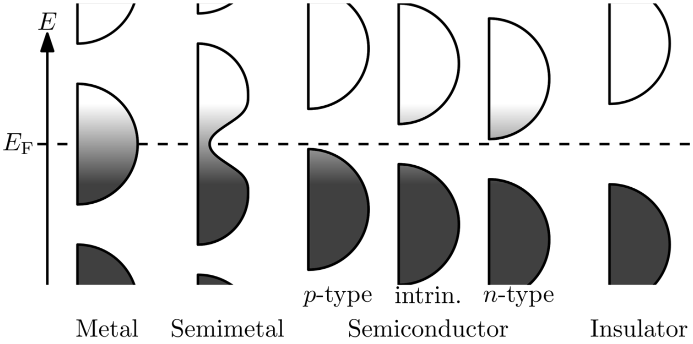
We can describe the properties of an infinite crystal in terms of a finite volume in reciprocal space.

Energy levels in molecules and in solids



Molecules

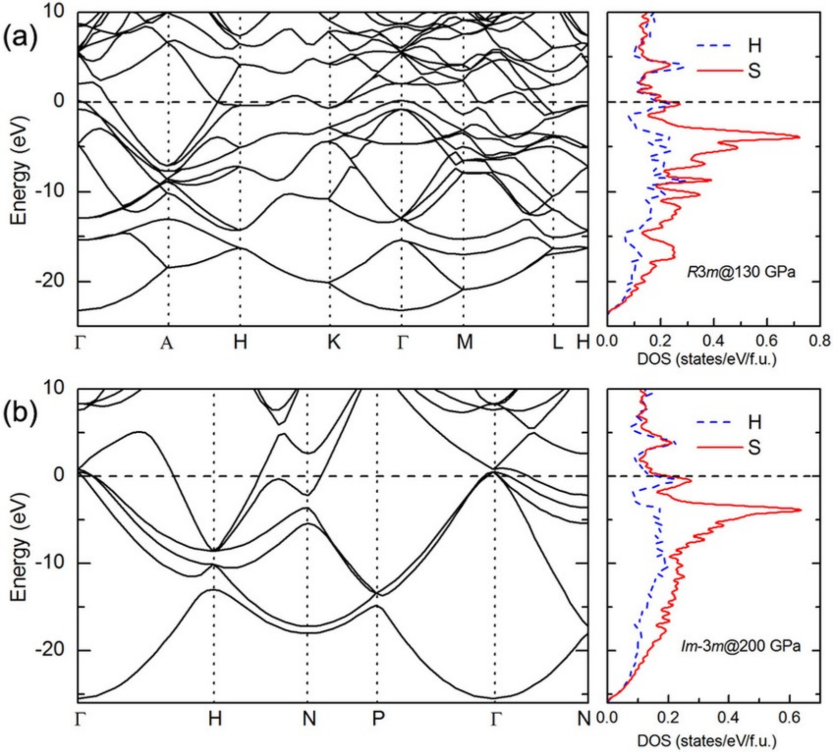
Discrete energy levels (MO energies)



Solids

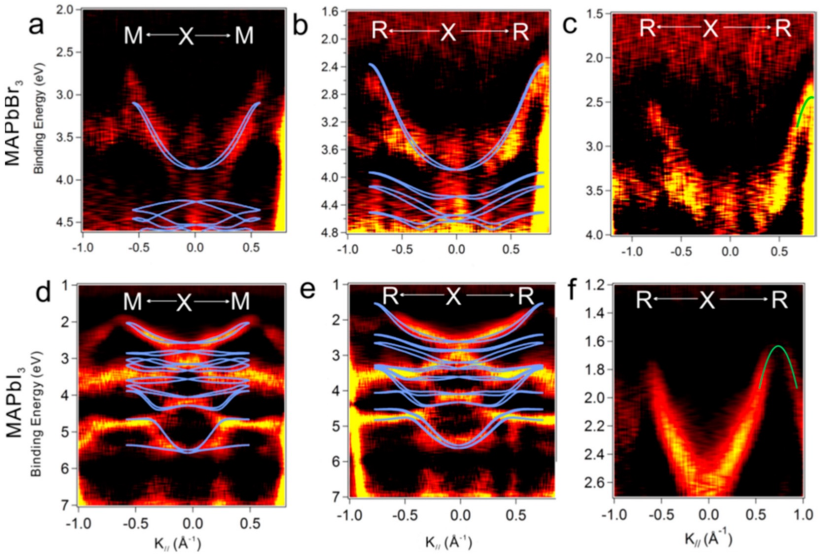
Energy bands

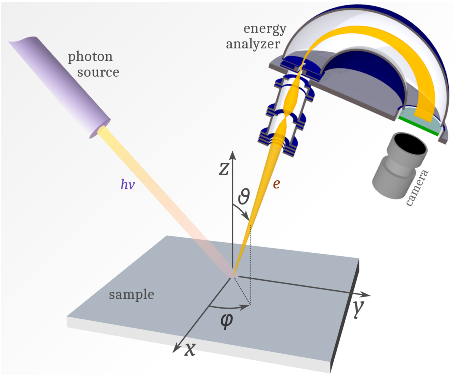
Band structures and electronic densities of states



D. Duan *et al.*, *Scientific Reports* 4, 6968 (2014)

Angle-resolved photoemission spectroscopy (ARPES)





K. Wang *et al.*, *Crystals* 10, 773 (2020)

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Summary

- Real space lattice **R**
- Add atoms: crystal structure
- Reciprocal lattice
- Brillouin zone
- Calculations are restricted to **k** vectors in the Brillouin zone

DFT software

Two approaches

1) **Code your own DFT software**

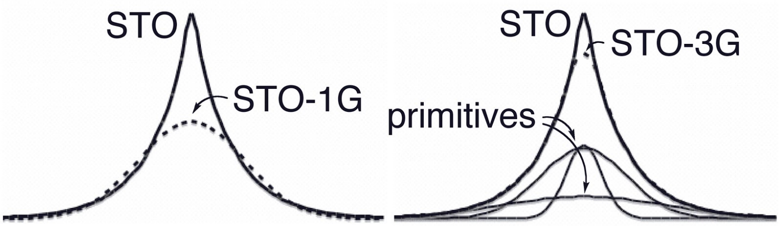
2) **Use existing academic/commercial or open-source packages:**

ABINIT, ACES, ADF, Atomistix, BigDFT, CADPAC, CASTEP, CFOUR, COLUMBUS, CONQUEST, COSMOS, CP2K, CPMD, CRYSTAL, DACAPO, DALTON, DFTB+, DFT++, DIRAC, DMol3, EXCITING, FLEUR, FHI-aims, FreeON, Firefly, GAMESS (UK), GAMESS (US), GAUSSIAN, GPAW, hBar Lab, JAGUAR, Materials Studio, MOLCAS, MOLPRO, MOPAC, MPQC, NWChem, OCTOPUS, ONETEP, OpenAtom, OpenMX, ORCA, PLATO, PQS, Priroda-06, PSI, PWscf, Q-Chem, Quantum ESPRESSO, SPARTAN, SIESTA, TURBOMOLE, VASP, WIEN2k, ...

How do DFT codes differ from each other?

Largely in the **basis sets** they use and in whether they work for molecules (*e.g.,* Gaussian), for extended systems (*e.g.,* VASP) or for both *(e.g.*, CRYSTAL, CP2K).

Basis set functions are used to represent continuous functions (like the electron densities and KS orbitals) in **discrete** form. In this way, operations can be expressed in **matrix form** and handed by a computer.



A computer only stores and manipulates basis set **coefficients**, not the basis set functions themselves.

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Kohn-Sham equations in matrix form

$$\boxed{h_{\mathrm{KS}}\phi_i = \epsilon_i \phi_i}$$

Kohn-Sham equations

$$\phi_i = \sum_{\alpha}^{M_{\mathrm{basis}}} c_{\alpha i} \chi_\alpha$$

Basis set expansion

$$\boldsymbol{h}_{\mathrm{KS}} \boldsymbol{C} = \boldsymbol{S} \boldsymbol{C} \boldsymbol{\epsilon}$$

$$h_{\alpha\beta} = \langle \chi_\alpha | h_{\mathrm{KS}} | \chi_\beta \rangle$$

$$S_{\alpha\beta} = \langle \chi_\alpha | \chi_\beta \rangle$$

Matrix representation

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Basis set functions

The choice of basis set depends on the system. Local basis sets (like Gaussian functions or Slater orbitals) are mostly suitable for molecular systems.

Gaussian, ADF, …

However, they can also be used for periodic systems.

CRYSTAL

Floating basis sets, like plane-waves, are ideal for infinite systems.

VASP, ABINIT, …

Different basis sets can be used together, to speed up specific parts of the calculations.

CP2K

Plane-waves

CPMD

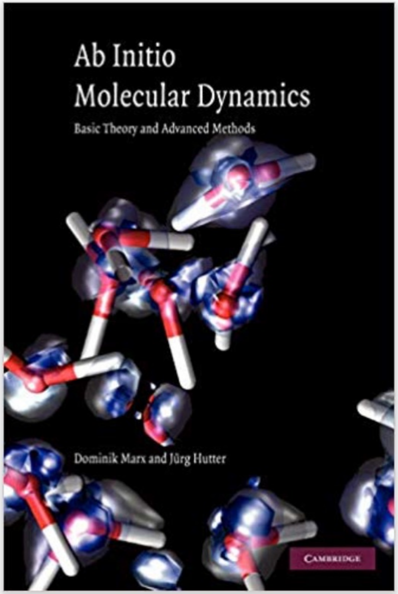
CASTEP

VASP

QUANTUM ESPRESSO

Abinit

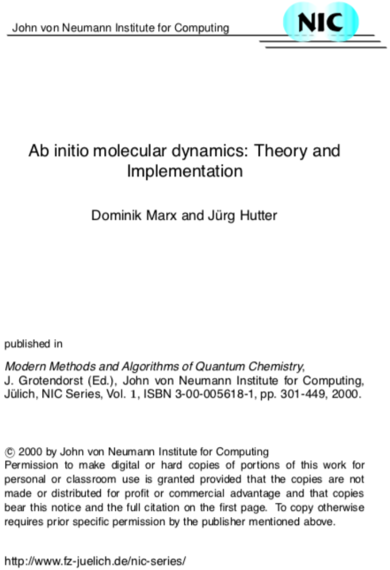
Plane-wave codes



Ab Initio
Molecular Dynamics
Basic Theory and Advanced Methods

Dominik Marx and Jürg Hutter

CAMBRIDGE



John von Neumann Institute for Computing NIC

Ab initio molecular dynamics: Theory and Implementation

Dominik Marx and Jürg Hutter

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000.

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http://www.fz-juelich.de/nic-series/

Plane-wave basis set

$$f_{\mathbf{G}}^{\mathrm{PW}}(\mathbf{r}) = N \exp\left[i\mathbf{G}\mathbf{r}\right]$$

$$N = 1/\sqrt{\Omega}$$

- PWs form an orthonormal set
- They do not depend on the atomic coordinates: they have no origin
- They represent all space in the same “unbiased” way
- Computing forces is much easier than with atom centered basis sets
- The quality of a calculation can be improved by simply adding more PWs
- They do not suffer from BSSE and linear dependence issues

Plane-wave expansion

Orbitals

$$\phi_i(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_i(\mathbf{G},\mathbf{k}) \exp[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}]$$

Density

$$n(\mathbf{r}) = \frac{1}{\Omega} \sum_i \int d\mathbf{k}\; f_i(\mathbf{k}) \sum_{\mathbf{G},\mathbf{G}'} c_i^\star(\mathbf{G}',\mathbf{k}) c_i(\mathbf{G},\mathbf{k}) \exp[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}]$$

$$= \sum_{\mathbf{G}} n(\mathbf{G}) \exp[i\,\mathbf{G}\cdot\mathbf{r}]$$

$c_i(\mathbf{G},\mathbf{k})$ (Complex) PW coefficients

This is the data stored on a computer;
the PW coefficients change during the SCF

Fourier transform: $n(\mathbf{r}) \Leftrightarrow n(\mathbf{G})$

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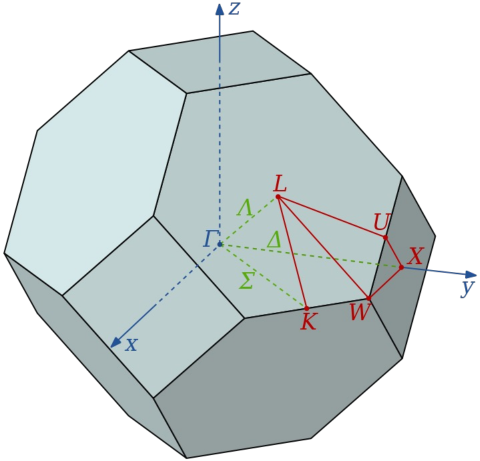
Brillouin zone sampling

$$n(\mathbf{r}) = \frac{1}{\Omega}\sum_i \int d\mathbf{k}\, f_i(\mathbf{k}) \sum_{\mathbf{G},\mathbf{G}'} c_i^\star(\mathbf{G}',\mathbf{k}) c_i(\mathbf{G},\mathbf{k}) \exp[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}]$$
$$= \sum_{\mathbf{G}} n(\mathbf{G}) \exp[i\,\mathbf{G}\cdot\mathbf{r}]$$

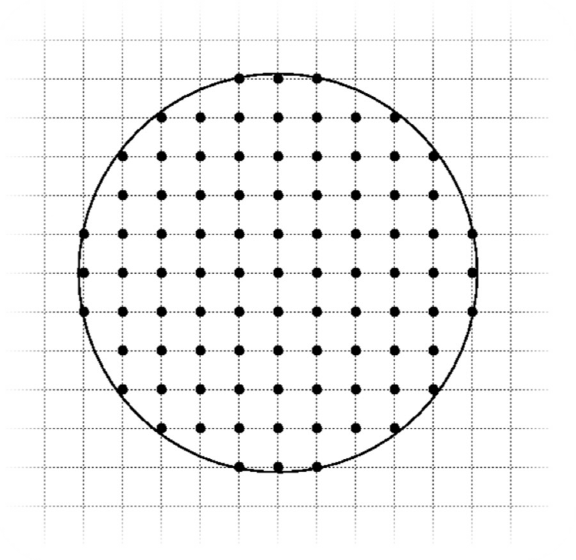
$$\int d\mathbf{k} \rightarrow \sum_{\mathbf{k}} w_{\mathrm{k}}$$



(1) Monkhorst-Pack mesh (1976)
(2) Γ-point approximation

Truncation: the kinetic energy cutoff

The accuracy of a PW calculation depends on a single parameter, E_{cut}



Truncate the PW expansion at each ***k***-point to keep only those PWs whose kinetic energy is lower than E_{cut}

$$\frac{1}{2}\,|\mathbf{k}+\mathbf{G}|^2 \leq E_{\mathrm{cut}}$$

$$N_{\mathrm{PW}} = \frac{1}{2\pi^2}\,\Omega\,E_{\mathrm{cut}}^{3/2}$$

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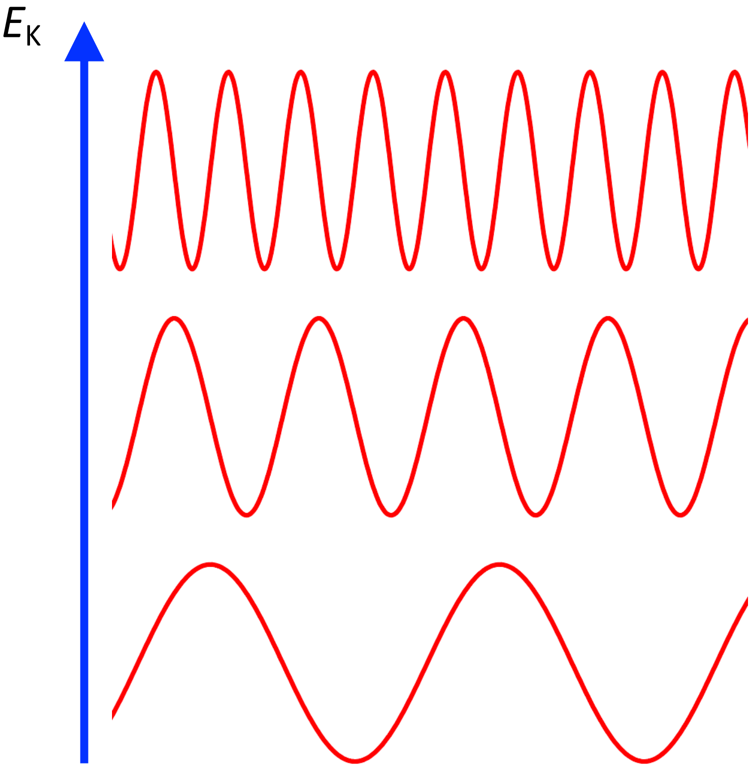
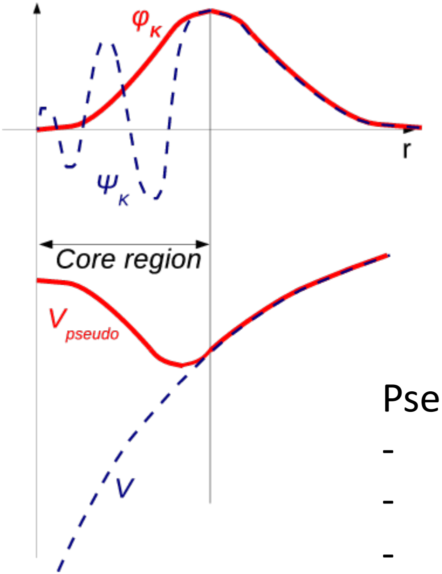
Truncation: the kinetic energy cutoff



Increasing the PW kinetic energy allows one to describe finer details in direct space

Functions oscillating rapidly in space require PWs with very high kinetic energies

Pseudopotentials and PAW



Gaussian basis sets, in contrast to PWs, treat the Coulomb singularity analytically

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-t^2(\mathbf{r}-\mathbf{r}')^2} dt.$$

(Singer, 1960)

Pseudopotentials
- remove the singularity
- remove wavefunction oscillations
- reduce the number of electrons

- Local versus non-local pps
- Norm-conserving versus *ultra-soft* pps
- Projector augmented wave (PAW) method

The Hartree (or Coulomb) potential

- *n(**r**)* and *n(***G***)* contain the same information
- We can convert one into the other using Fast Fourier Transforms (FFTs), which scale as $N_{pw}\log(N_{pw})$
- Some components of the Hamiltonian are easy to compute in real space (*e.g.,* xc potential), others in **G**-space (*e.g.,* kinetic energy)

$$\frac{1}{2}\int\int d\vec{r}d\vec{r}'\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} = 2\pi\Omega_{cell}\sum_{\vec{G}}\frac{n(\vec{G})^2}{G^2}$$

R space **G** space

If we include the nuclear charge in *n*(***r***), *n*(***G=0***) is the total charge

G=0 term !!! → charge neutrality and background charge

Unfortunately, this technique cannot be used efficiently with the non-local exchange operator

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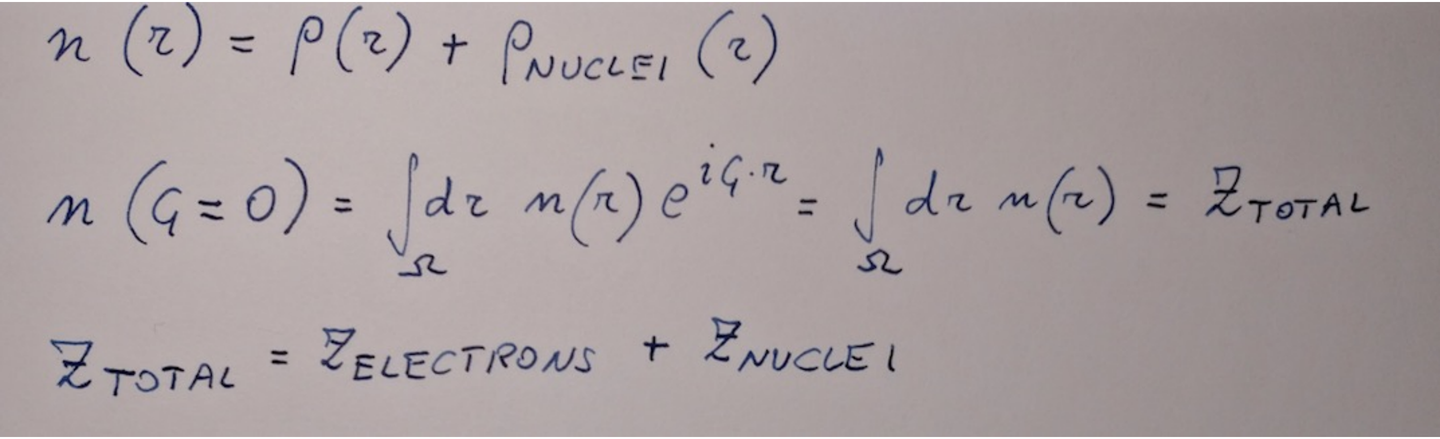
The Hartree (or Coulomb) potential



$$n(r) = \rho(r) + \rho_{NUCLEI}(r)$$

$$n(G=0) = \int_{\Omega} dr\, n(r)\, e^{iG\cdot r} = \int_{\Omega} dr\, n(r) = Z_{TOTAL}$$

$$Z_{TOTAL} = Z_{ELECTRONS} + Z_{NUCLEI}$$

Molecular calculations with plane-waves

First method (for neutral molecules): supercell approach

This method can be applied to surfaces as well.

Extremely inefficient, because a large number of PWs are used to describe the empty volume of the supercell, and large cut-offs are required to describe the electron density distribution in the molecular region.

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Molecular calculations with plane-waves

Second method (for charged molecules too):
cluster boundary conditions

Separation of short- and long-range Coulomb interactions.

The contribution to the Coulomb energy from the second term are

$$\frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}'\, \frac{n_{\text{tot}}(\mathbf{r})n_{\text{tot}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{2}\int d\mathbf{r}\, V_{\text{H}}(\mathbf{r})n_{\text{tot}}(\mathbf{r})$$

which can be computed by solving a Poisson's equation

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

with boundary conditions

$$V_{\text{H}}(\mathbf{r}) \to 0 \text{ for } \mathbf{r} \to \infty$$

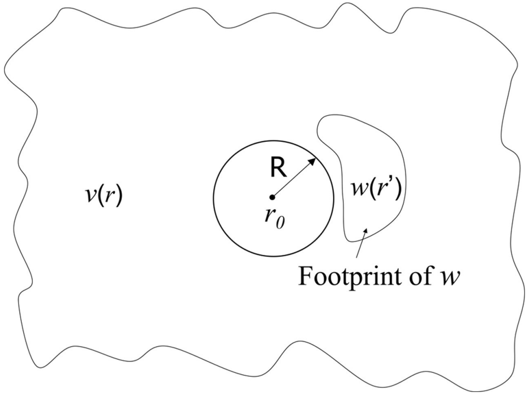
Plane-waves

- ✓ The most popular approach to solid state calculations
- ✓ Accuracy controlled by a single parameter (E_{cut})
- ✓ Relatively easy to code and parallelize
- ✓ Atomic forces for AIMD are easy to compute
- ✓ Extensive libraries of pseudopotentials and PAW projectors available
- ✓ Scales reasonably well with PW number: $N_{pw} \log (N_{pw})$

- ✗ Advanced DFT functionals (e.g. hybrids) are expensive
- ✗ Simulations on non-periodic systems (molecules, surfaces, etc.) are extremely inefficient
- ✗ System sizes are limited to a few hundred atoms

Real space methods:
Local basis sets

Nearsightedness of electronic matter (NEM)



Prodan & Kohn, 2005

For a many-electron system, the density change induced by *w(r')* at r_0 decays monotonically (exponentially or polynomially) with *R*

NEM provides a rigorous justification for local-basis set and "linear scaling" electronic structure methods

Walter Kohn

W Kohn, Phys Rev Lett 76, 3168 (1996)
W Kohn, Phys Rev 113, A171 (1964)

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Real space DFT codes (a few)

Numeric atom-centered orbitals

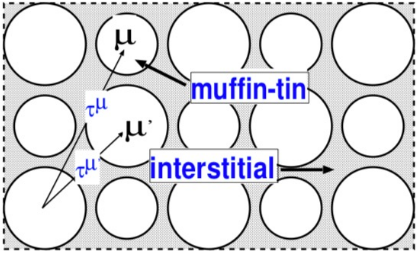
FHI-aims, SIESTA*, ADF-BAND, CONQUEST*, ONETEP*

Gaussian basis sets

AIMPRO, CRYSTAL

Linearized augmented plane-wave (LAPW)

Wien-2k, FLEUR, exciting, Elk



Real space grids and wavelets

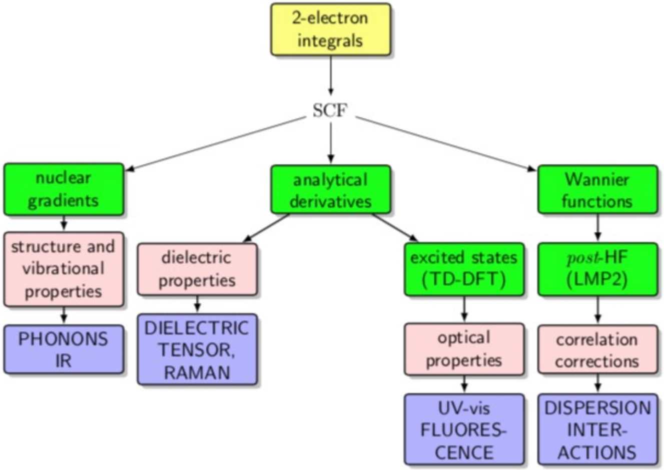
octopus, GPAW, BigDFT*

(* Linear scaling codes)

CRYSTAL: a quantum-chemical code for periodic systems

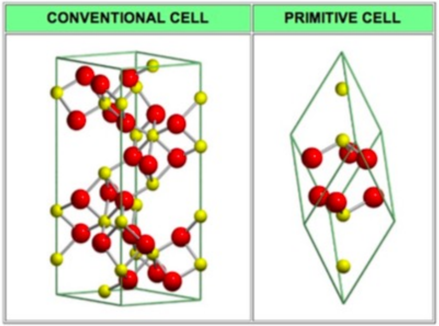
$$\phi_{abc}^{GTO}(x,y,z) = N x^a y^b z^c e^{-\zeta r^2}$$

(Contracted) Gaussian-Type Orbitals (GTOs)


2-electron integrals
SCF
nuclear gradients
analytical derivatives
Wannier functions
structure and vibrational properties
dielectric properties
excited states (TD-DFT)
post-HF (LMP2)
PHONONS IR
DIELECTRIC TENSOR, RAMAN
optical properties
correlation corrections
UV-vis FLUORESCENCE
DISPERSION INTERACTIONS

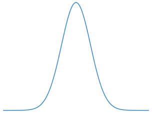
$$(\mu\nu||\rho\tau)$$

- screening
- symmetry



- insulators, semiconductors
- metals
- surfaces, polymers, molecules

http://www.crystal.unito.it/



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Crystal orbitals and SCF

Self-consistent field equation

$$\boldsymbol{F}^k \boldsymbol{C}^k = \boldsymbol{S}^k \boldsymbol{C}^k \boldsymbol{E}^k$$

Each *crystal orbital* $\psi_i(\mathbf{r}, \mathbf{k})$ is a combination of N Bloch functions $\phi_\mu(\mathbf{r}, \mathbf{k})$,

$$\psi_i(\mathbf{r}, \mathbf{k}) = \sum_{\mu}^{N} C_{\mu j}^{\mathbf{k}} \phi_\mu(\mathbf{r}, \mathbf{k}).$$

The BFs are properly symmetrised linear combinations of *atomic orbitals*, each of which is expressed in terms of a set of atom centred *Gaussian basis set functions* $\chi_\mu(\mathbf{r} - \mathbf{R})$,

$$\phi_\mu(\mathbf{r}, \mathbf{k}) = N^{-\frac{1}{2}} \sum_{\mathbf{R}}^{N} e^{i\mathbf{k}\cdot\mathbf{r}} \chi_\mu(\mathbf{r} - \mathbf{R}),$$

where the sum is over the real-lattice vectors $\mathbf{R}$, and $N \to \infty$.

Scales (theoretically) as $N_{AO}{}^3$

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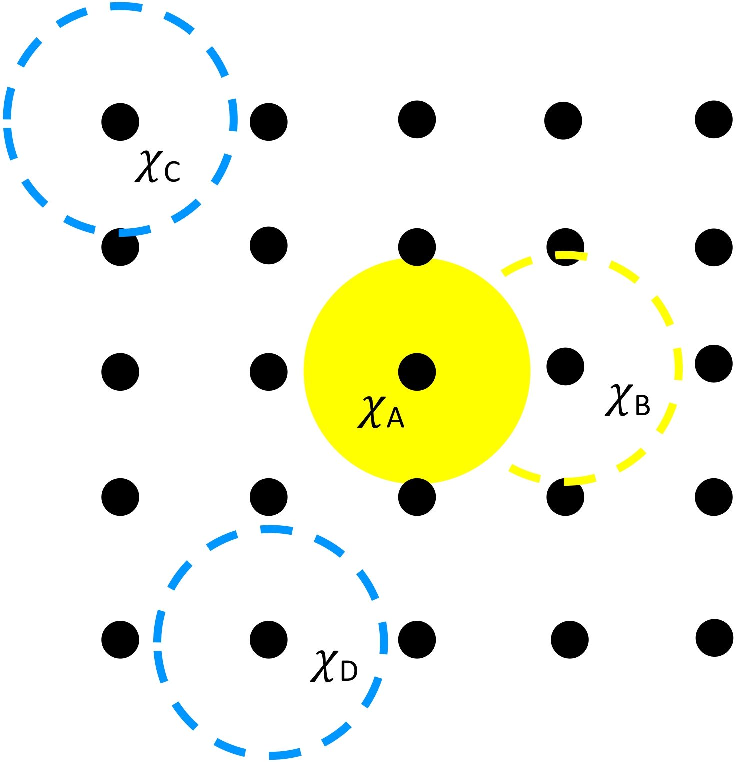
Crystal orbitals and SCF



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Gaussian basis sets

The quality of a CRYSTAL calculation depends crucially on the choice of the basis set $\{\chi_\mu\}$.

Standard Gaussian basis sets (Gaussian, NWChem, GAMESS, etc) can be used with CRYSTAL.

Usually very diffuse basis functions are not required in solids, unless one is interested in excited state calculations, for instance.

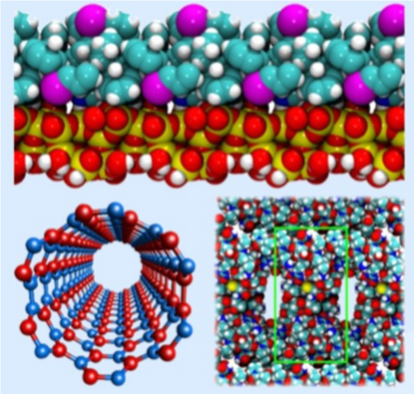
Basis sets can be *optimised* for solids: this usually involves varying the number of *contracted Gaussians* per shell (*s, p, sp, d, etc*).

The energy is *variational* with the basis set size.

Possible problems:

1. Linear dependence
2. Basis set superposition error (BSSE)

Gaussian basis sets



Calculation (*)	Full geometry optimization		
XC functional	**HSE06 (PWs)**	**B3LYP**	**HSE06**
Lattice parameter	4.2530 (+0.38%)	4.2853 (+0.37%)	4.2603 (+0.22%)
Dispersion	D3	D3	D3
K-mesh	7x7x7	7x7x7	7x7x7
Time (hours)	**13.5**	0.09 (~5 min)	**0.29** (~17 min)
Band gap	2.052	2.149	1.926

Good for accurate all-electron calculations on periodic systems, surfaces and polymers. Can treat easily non-local density functionals.

(*) Cu_2O data from Aleks Živković (Utrecht University)

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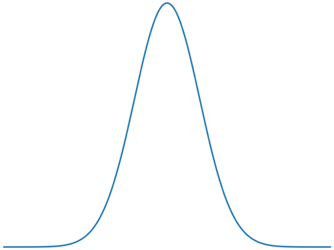
Two extremes

Plane-waves

- Floating
- Delocalized in real space
- FFTs
- Need pseudopotentials
- Easy to code
- Easy to parallelize
- $N_{pw}\log(N_{pw})$ scaling



Gaussian functions

- Atom centered
- Localized in real space
- Recursive integral calculation
- All-electron calculations possible
- Difficult to code in periodic systems
- Parallelization is highly non-trivial
- N_{AO}^3-N scaling

The Gaussian/plane-wave method

The Gaussian and plane-wave method (GPW)

Atoms centered Gaussians are used to represent the wavefunction and the Kohn-Sham matrix. PWs are used to represent the electron density and to compute efficiently the Hartree potential.

The representation of the wavefunction is compact, which allows for efficient algorithms with a relatively small memory footprint.

For large systems, this method scales linearly, because the Kohn-Sham matrix and the density matrix are sparse.

https://www.cp2k.org/about

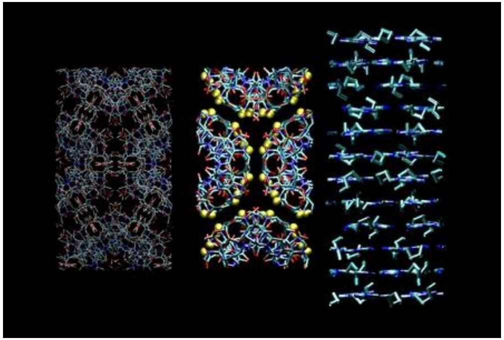
The Gaussian and plane-wave method (GPW)

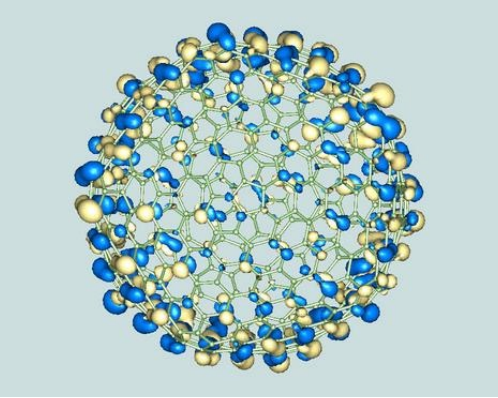
CP2K is well suited for large-scale AIMD simulations

It requires specifying both a Gaussian basis set and a set of pseudopotentials

For finite systems, cluster boundary conditions can be used

Wide variety of xc functionals available, but hybrids remain computationally very expensive





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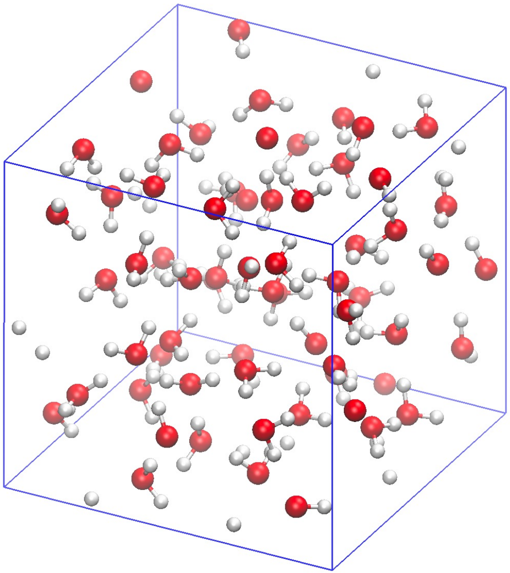
Example

/xhome/crc/leb140/WorkshopFall2024

Total energy calculation (DFT/BLYP with van der Waals corrections) of a periodic box of 64 water molecules (192 atoms); DZVP basis set, E_{cut}=280 Ry



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Software: Summary

- Plane-wave codes are widespread and generally easy to use
- A single parameter E_{cut} determines the accuracy of the calculations
- They work well on medium size systems
- All of them can do AIMD

- Real-space codes are more complex to use
- They can be better for specific tasks (*e.g.,* modelling surfaces)
- Some of them can treat advances functionals, like hybrids
- AIMD with atom-centered basis set code may be complicated to do

- The GPW method attempts to exploit the benefits of both

Talk summary

This talk:

1. Density-functional theory
2. Simulating infinitely large systems
3. Software: Plane-waves, Gaussians, GPW

A (possible) future talk:

1. Ab initio molecular dynamics
2. Modelling excited states and photochemistry
3. Machine learning in electronic structure theory