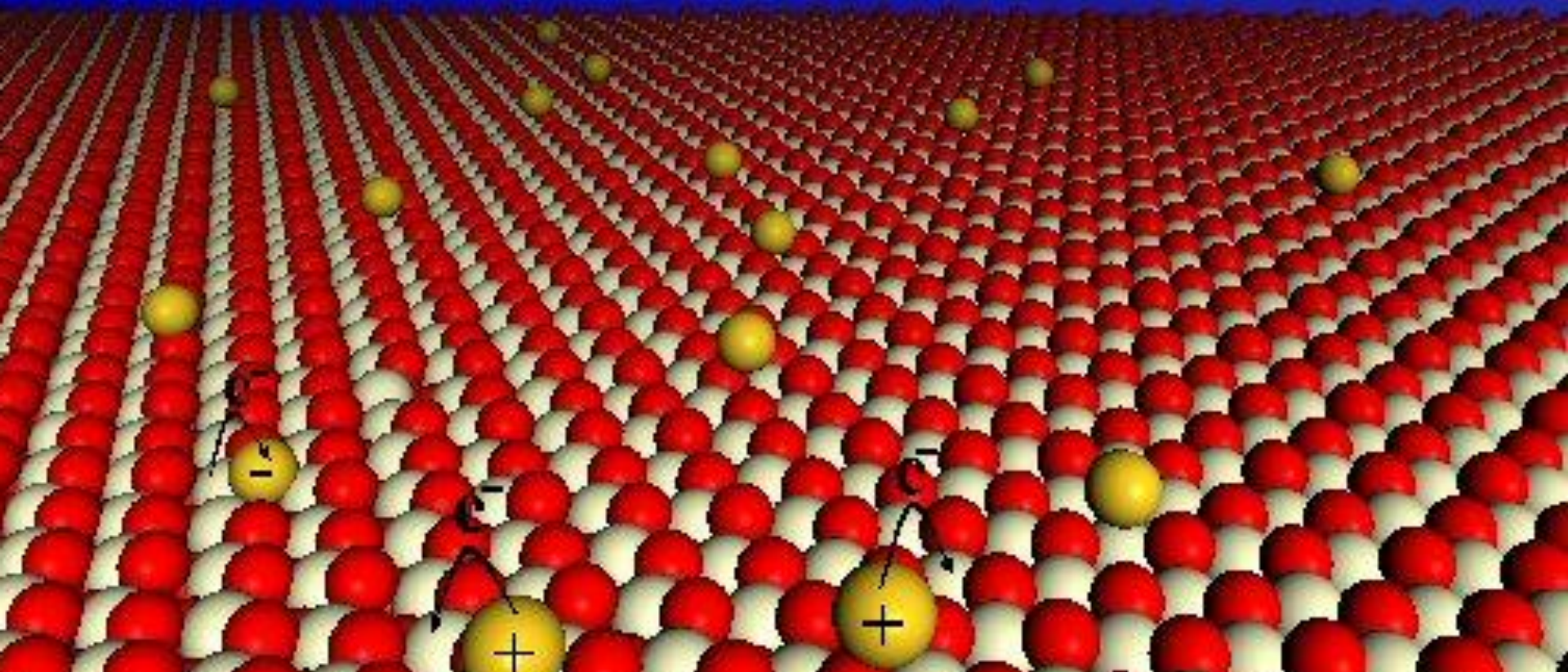# An introduction to atom-level modelling techniques for the not initiated

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Molecular modelling: what is a model?

According to the *Oxford English Dictionary*:

Model: 'Simplified or idealised description of a system or process, often in mathematical terms, devised to facilitate calculations and predictions'.

Use of models in Materials Science:

- Understanding via problem isolation
- Interpretation of experimental data
- Simulation of situations where experiments are difficult to perform
- Rapid screening of properties
- Prediction of new behaviour

Modelling scales (and multi-scale modelling)
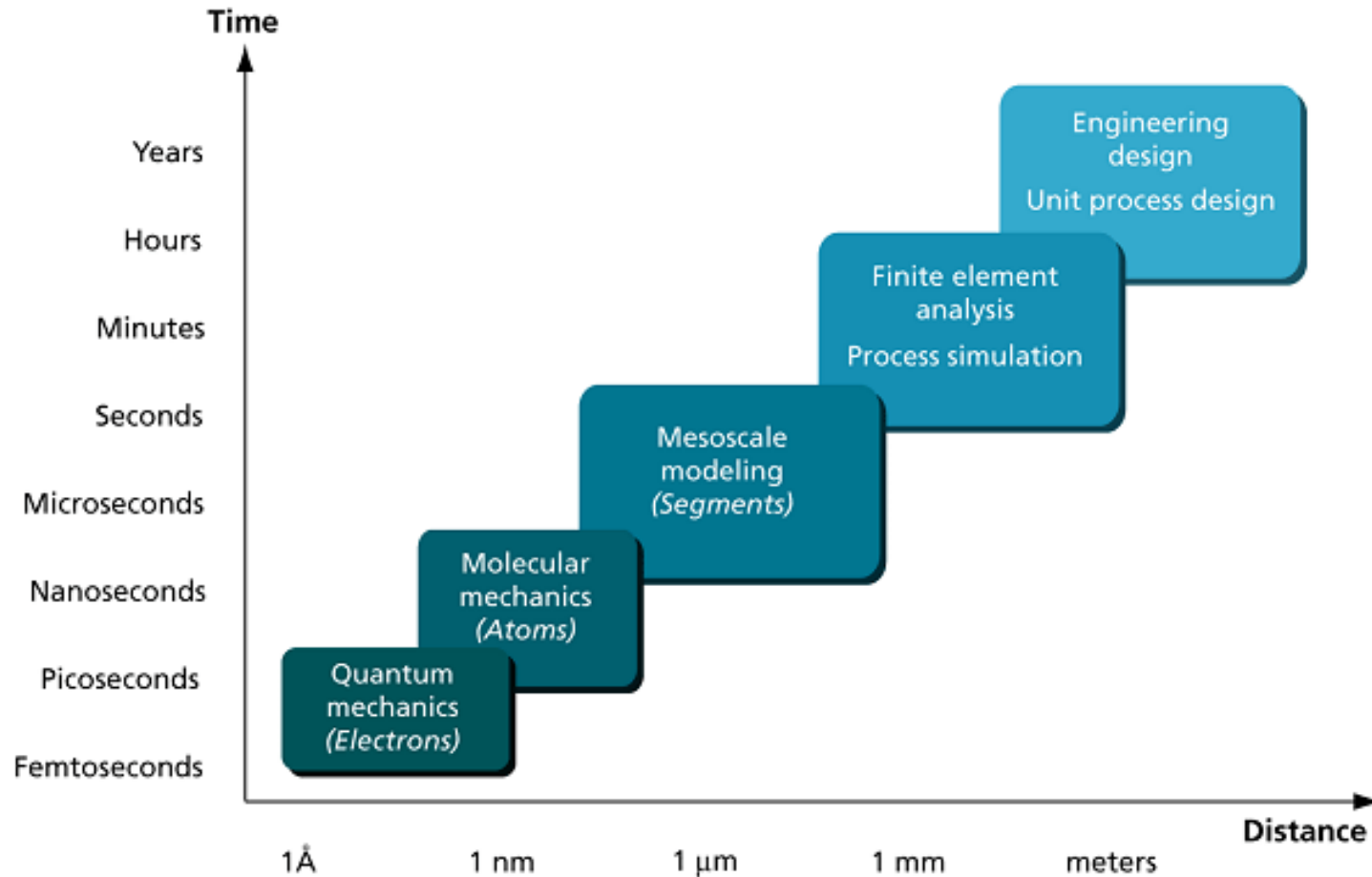
Atom-level modelling methods

(Based on the evaluation of the interaction energy for all the atoms in the system)

Energy evaluation
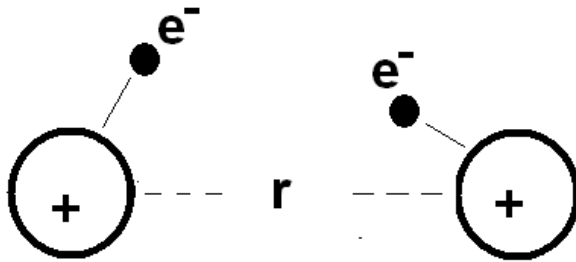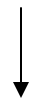
Quantum Mechanical Methods

Molecular Mecanics
or
Force-field Methods

Quantum mechanical methods (QM)

Schrödinger equation for the H_2 molecule:

$$\hat{H}_e \Psi = E_e \Psi$$

$$\Psi, E_e \longrightarrow E(r) = E_{nn}(r) + E_e(r)$$
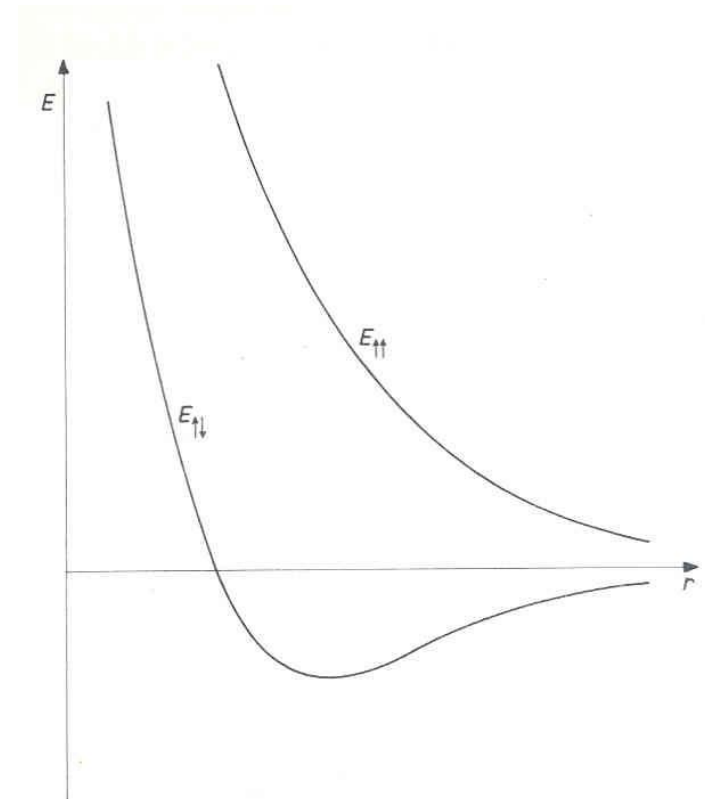
Two merging types of QM methods

Chemistry community

• "Quantum Chemistry",
Hartree-Fock (HF)

• Calculation of atoms and molecules

• **Wavefunction.** Molecular orbitals as linear combination of atomic orbitals (LCAO)

Physics community

•"Band theory",
Density Functional Theory (DFT)

• Calculations of solids

• **Electron density.** Plane waves.
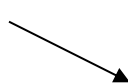
From 1990's

DFT in Chemistry, HF in Physics

Hybrid DFT/HF in Chemistry, Physics, and Materials

Force-field (FF) / Molecular Mechanics (MM) / Interatomic Potentials (IP) methods:

Example:
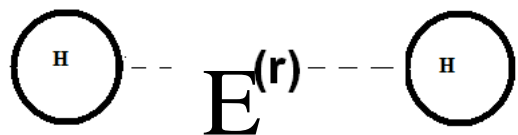
Morse potential:

$$E(r) = D_e(1 - e^{-a(r-r_e)})^2$$
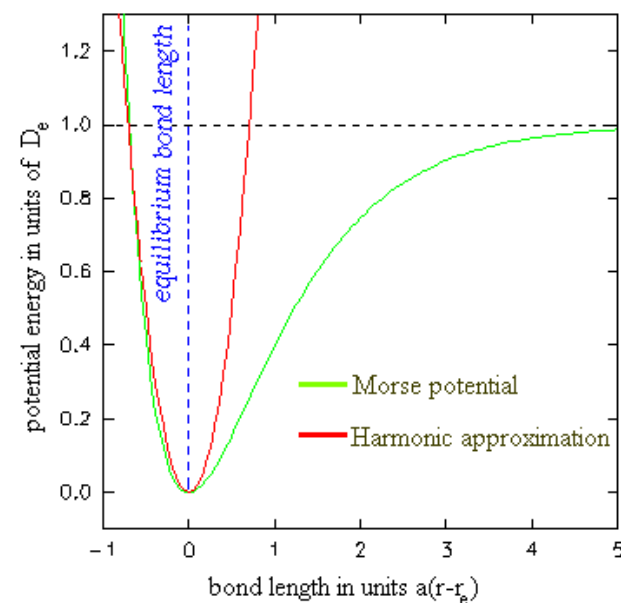
© O. S. Smart, 1995

- Much cheaper (computationally) than QM methods!
- Parameters can be obtained by fitting to experiment or to QM results

What can be done with the energy functions?

1. Geometry search:

Equilibrium geometry is the one that minimises the potential energy.
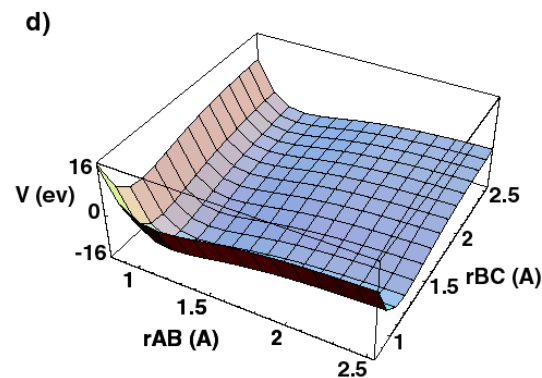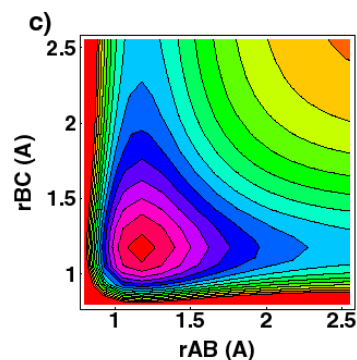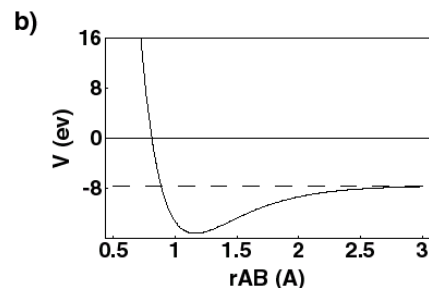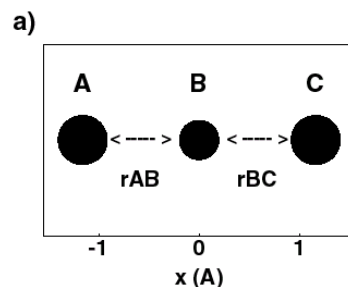
What can be done with the energy functions?

2. **Vibrational properties:**

Frequencies depend on the curvature of U(r)
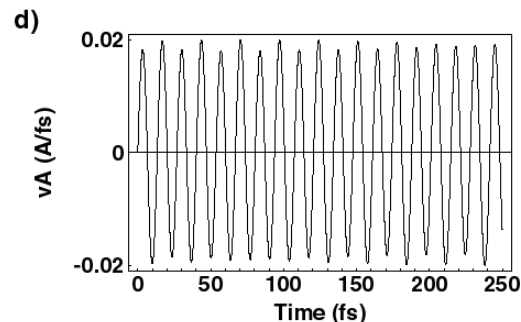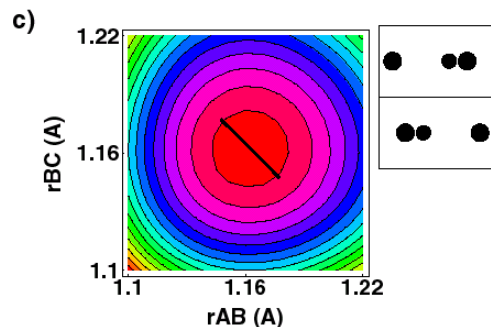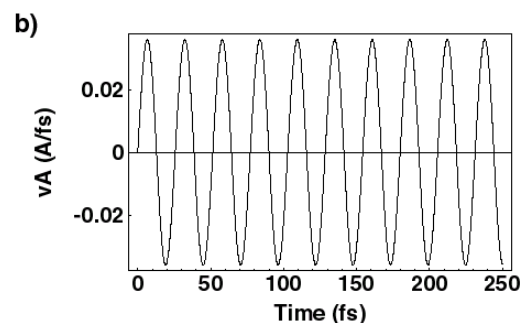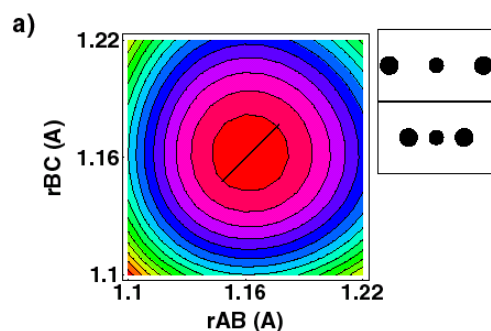
What can be done with the energy functions?

3. Molecular dynamics:

Ions are (typically) heavy enough to follow Newton's second law of motion:

$$F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2}$$

$$F_i = -\frac{dU}{dr_i} \quad \longrightarrow \quad \begin{cases} r_i(t) \\ v_i(t) \end{cases}$$

U

F

r
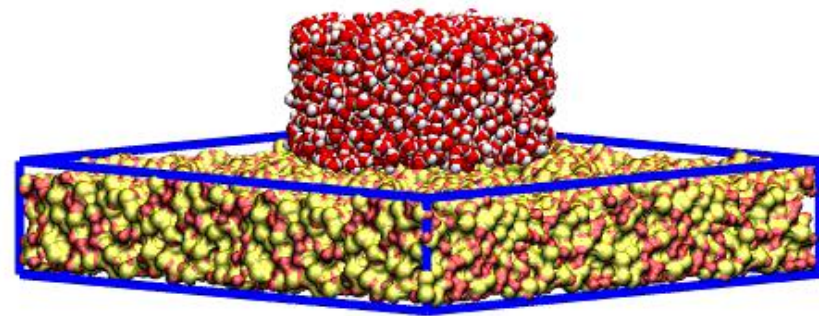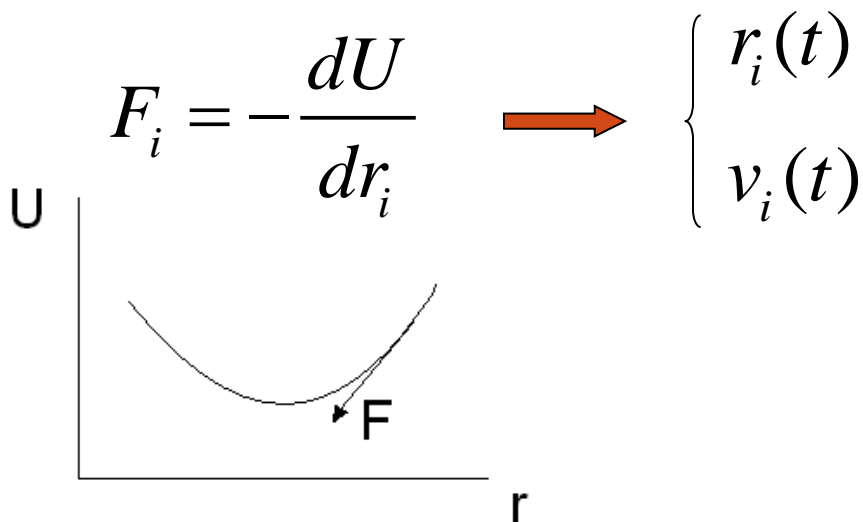
MD simulation of water droplet on a silica surface
http://www.ks.uiuc.edu/Gallery/Movies/

Quantum (QM) vs. Classical (FF) simulations

• QM calculations are much more computationally expensive than FF calculations.

• Van der Waals interactions are easy to include within FF methods, but require sophisticated (and more expensive) approaches within QM.

• QM methods give access to the electronic properties of the system (via the calculation of one-electron spectra).

• QM methods allow the investigation of bond breaking and formation, and of metallic behaviour in solids. These properties are generally beyond the reach of FF methods.

• In principle, QM methods require no adjustable parameters, and are completely transferable.

Quantum mechanical approaches

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble."

Paul Dirac (1902-1984), British physicist.

Schrödinger equation for *M* nuclei and *N* electrons:

$$\left[-\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2 - \sum_{A=1}^{M}\frac{\hbar^2}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A e^2}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{e^2}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B e^2}{R_{AB}} \right]\Phi = E\Phi$$

Atomic units: $\hbar = 1; \quad m_e = 1; \quad e = 1$

(lengths in *Bohrs*, energies in *Hartrees*)

$$\left[-\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \right]\Phi = E\Phi$$

1. Born-Oppenheimer approximation:

Nuclei are much heavier and move much slower than electrons, so we can study the movement of electrons considering fixed nuclei positions:

$$\left[-\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} \right] \Psi = E\Psi$$

$$\mathbf{T_e} \qquad\qquad \mathbf{U_{en}} \qquad\qquad \mathbf{U_{ee}}$$

2. Introduction of spin: $\mathbf{x}=\{\mathbf{r},\sigma\}$ are the generalised coordinates of one electron.

We impose the **antisymmetry principle (Pauli exclusion):**

$$\Psi(\mathbf{x}_1,...,\mathbf{x}_i,....,\mathbf{x}_j,...,\mathbf{x}_N) = -\Psi(\mathbf{x}_1,...,\mathbf{x}_j,....,\mathbf{x}_i,...,\mathbf{x}_N)$$

Further approximations

• Solving the non-relativistic electronic problem, even after the BO approximation, is a formidable task!

• Other approximations are required. They include:

- Approximations for the electron – electron interaction (e.g. Hartree-Fock).

- Approximations for dealing with core electrons (e.g. Pseudopotentials)

The Hartree – Fock approximation

The multielectron wavefunction is built as a *Slater determinant*:

$$\Psi(\mathbf{x}_1,...,\mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{pmatrix}$$

Simplest form that holds the antisymmetry principle.
N is the number of electrons in the system.

The variational principle

Any state defined by an approximate wave function Ψ_{approx} has an average energy that is above or equal to the true groundstate energy.

$$\left\langle \Psi_{approx} \mid \hat{H} \mid \Psi_{approx} \right\rangle \geq E$$

The equality holds only if the wave function is exact.

Therefore, the lower the energy of the approximate wavefunction, the closer this is to the real wavefunction.

Application: We can find the best wavefunction within a certain class of functions by choosing the one for which the energy is the lowest. We say that we "*minimise the energy*".

Minimising the HF electronic energy:

$$E_{\mathrm{HF}} = <\Psi_{\mathrm{HF}} \mid \hat{H} \mid \Psi_{\mathrm{HF}}>$$

Its value depends on the selection of the electronic orbitals ψ_i in the Slater determinant.

After some maths, it is found that the energy is minimised when:

$$\hat{h}_i^{\mathrm{HF}} \psi_i = \varepsilon_i \psi_i$$

where

$$\hat{h}_i^{\mathrm{HF}} = -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|} + \hat{v}_i^{\mathrm{HF}}$$

Again, one-electron problem!

$\hat{v}_i^{HF}$ represents the e-e interaction in the HF approximation: average potential experienced by the ith electron due to the presence of the other electrons.

The one-electron Hamiltonian operator

$$\hat{h}_i^{\mathrm{HF}} = -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|} + \hat{v}_i^{\mathrm{HF}}$$

also depends on the orbitals of the other electrons!

But now $\hat{v}_i^{HF}$ contains two terms:

$$\hat{v}_i^{\mathrm{HF}}\psi_i(\mathbf{x}) = \left[\sum_{j\neq i}\int d\mathbf{x}'\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x}')r_{ij}^{-1}\right]\psi_i(\mathbf{x}) - \left[\sum_{j\neq i}\int d\mathbf{x}'\psi_j^*(\mathbf{x}')\psi_i(\mathbf{x}')r_{ij}^{-1}\right]\psi_j(\mathbf{x})$$

Coulomb term:

Classical interaction of the electron with the cloud of all the other electrons

Exchange term:

No classical equivalent. Creates repulsion between electrons of like spin. Consequence of antisymmetry (or Pauli principle)

Egg-and-chicken problem:

We need the effective potential to find the electron orbitals, but we need the electron orbitals to find the effective potential!

Solution: The self-consistent field method

Initial guess of orbitals

↓

Effective potential ←——————

↓   No

Hartree-Fock equation

↓

New set of orbitals ——→ Convergence? ——Yes——→ End

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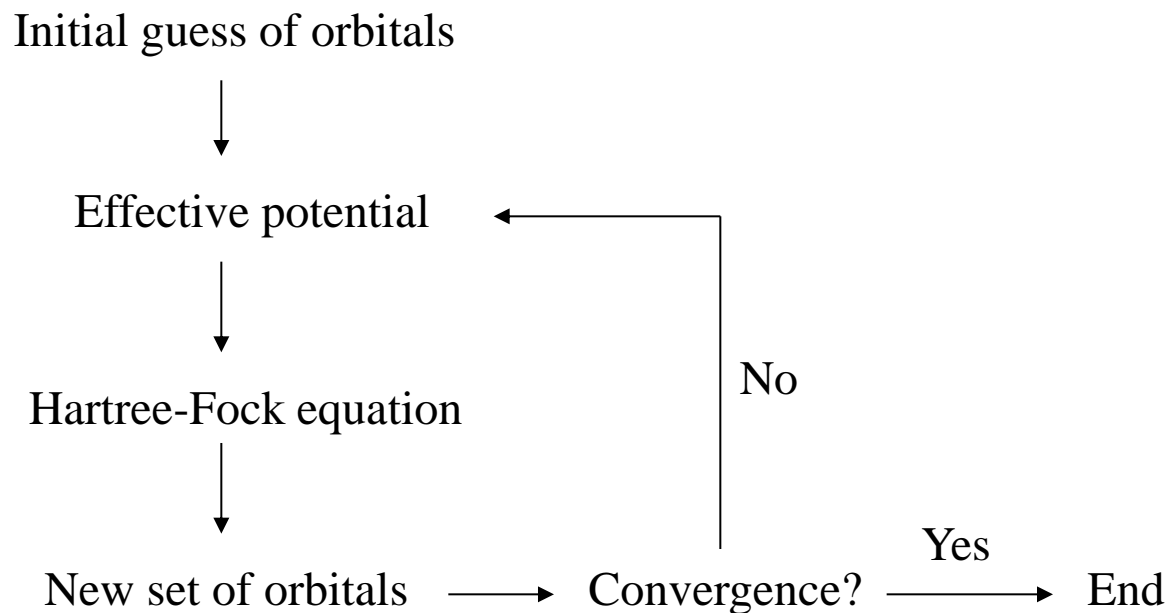
Orbitals and orbital energies

(number of calculated spatial orbitals = number of **basis functions** = K)

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu(\mathbf{r}) \qquad i=1, K$$

Orbitals for N electrons
(assuming closed shells)

ψ_K ———

⋮

$\psi_{N/2+1}$ ———

$\left.\rule{0pt}{3em}\right\}$ K-$N/2$ virtual orbitals

$\psi_{N/2}$ ——— ↑↓

⋮

ψ_3 ——— ↑↓

ψ_2 ——— ↑↓

ψ_1 ——— ↑↓

$\left.\rule{0pt}{5em}\right\}$ $N/2$ occupied orbitals

We always need $K > N/2$ basis functions!
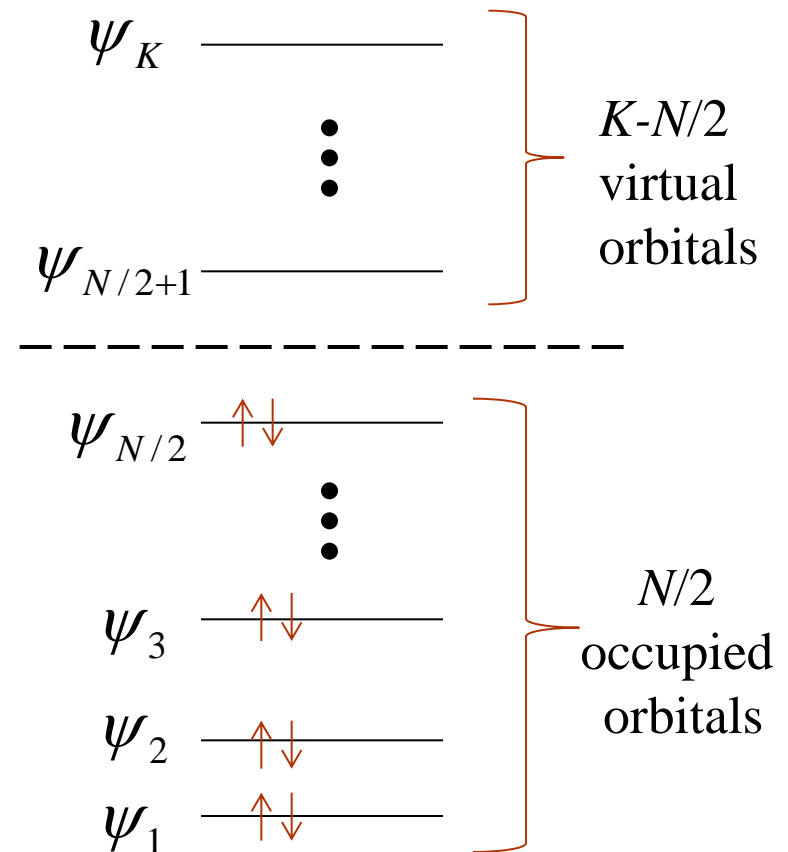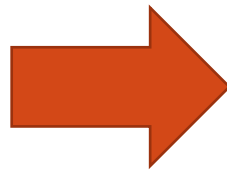
Sources of errors in the Hartree-Fock approach

1. Incompleteness of the basis set

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu(\mathbf{r})$$ only exact when $K \rightarrow \infty$ (impossible in practice)

2. Intrinsic HF error

Even in the limit of a complete basis set, there is a remaining error in the solution, because we have forced the Slater determinant shape for the all-electron wavefunction!

HF energy _____   ⬆

Correlation energy

Exact energy _____

Quality of the HF solutions

- Reasonable values for total energies of atoms and molecules

- Good description of exchange effects

- Excitation energies too large

- Fails to reproduce metallic state in solids

Further reading on HF and related methods:

• Ostlund and Szabo: *Modern quantum chemistry: introduction to advanced electronic structure calculations.* (rigorous maths)

• Levine: *Quantum Chemistry* (more intuitive introduction to topics)

Density Functional Theory
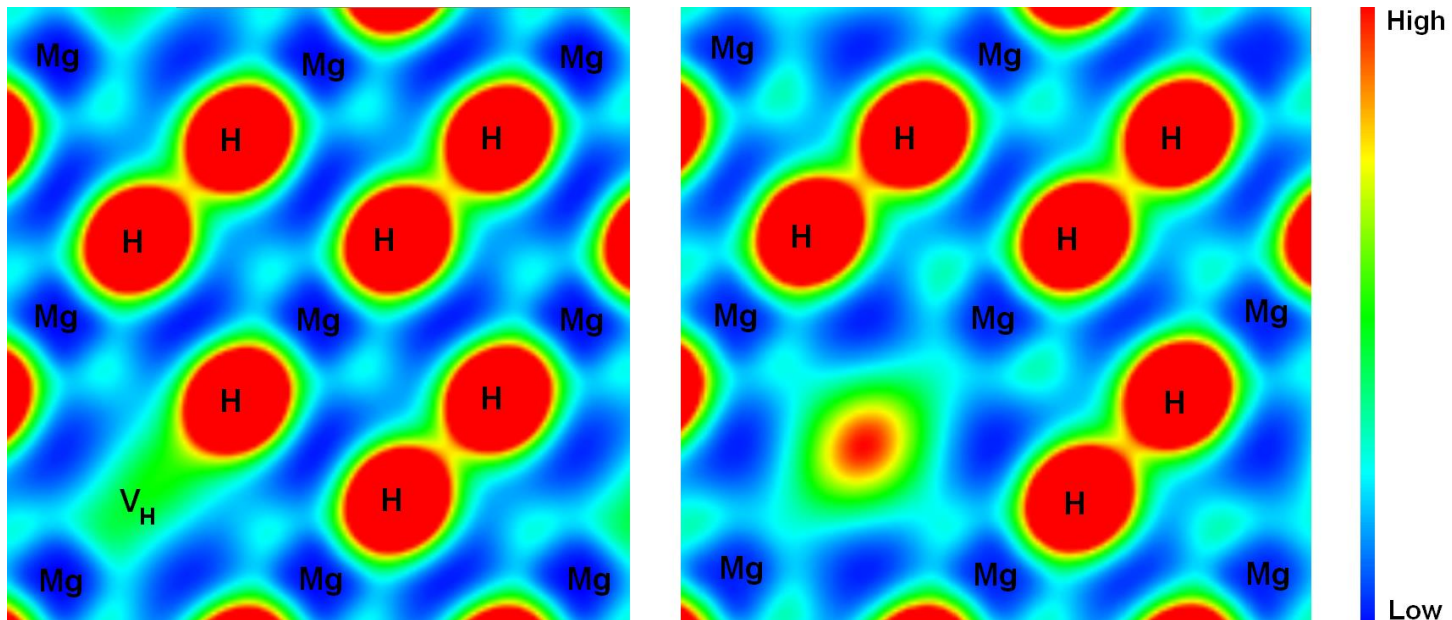
Motivation behind the Density Functional Theory (DFT)

Multi-electronic wavefunction Ψ contains too much irrelevant information:

Example: How many variables does the multielectron wavefunction have in a methane molecule, CH_4?

Answer: There are 6+4=10 electrons. Each electron has three spatial coordinate and one spin coordinate, therefore the wavefunction is a function of 40 variables!

$$\Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2, x_3, y_3, z_3, \sigma_3, x_4, y_4, z_4, \sigma_4, x_5, y_5, z_5, \sigma_5,$$

$$x_6, y_6, z_6, \sigma_6, x_7, y_7, z_7, \sigma_7, x_8, y_8, z_8, \sigma_8, x_9, y_9, z_9, \sigma_9, x_{10}, y_{10}, z_{10}, \sigma_{10})$$

… and in gets much worse for bigger molecules!

DFT focuses on the electronic density, rather than on the wavefunction.

Ignoring spin, the electron density is a function of only three variables, **regardless of the number of electrons**:

$$\rho(\vec{r}) = \rho(x, y, z)$$

Point of space

Hohenberg-Kohn theorems

• Theorem by Hohenberg and Kohn (1964): All the properties of the system are determined by the electronic density ρ(*r*).

• There is a universal *functional* $F[\rho(\mathbf{r})]$ that allows calculation of the energy of a system of electrons from its electronic density. For a given potential $V(\mathbf{r})$ the energy of the fundamental state is written as:

$$E[\rho(\mathbf{r})] = \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})]$$

• Unfortunately, we don't know the form of this functional!

Kohn-Sham method

Real system replaced by a fictitious system of non-interacting electrons that has the same density

$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})]$$

$$E[\rho(\mathbf{r})] = \sum_{i=1}^{N} \left\langle \psi_i \mid -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{|\mathbf{r}-R_A|} + \frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \mid \psi_i \right\rangle + E_{xc}[\rho(\mathbf{r})]$$

Density for the non-interacting electrons:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i|^2$$

Kohn-Sham Hamiltonian

Minimisation of the energy functional leads to the one-electron problem:

$$h^{KS}\psi_i = \varepsilon_i\psi_i$$

with

$$h^{KS} = -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M}\frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|} + \int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}(\mathbf{r})$$

Kinetic energy of one electron

Coulomb interaction of the electron with the nuclei

Coulomb (classical) interaction of the electron with all the other electrons

Non-classical interactions with other electrons: **exchange** and **correlation**. Also kinetic energy corrections.

Comparison between Hartree-Fock and Kohn-Sham DFT

• The KS equation should be solved iteratively like the HF equation, since the KS operator itself depends on the orbitals of the solution

• Although Kohn-Sham DFT uses a Hamiltonian similar to the one in HF theory, no claim is made here about the form of the wavefunction. The method would be exact if we knew the exact form of E_{xc} (we don't!)

• While the HF method gives exact exchange and no correlation (by definition), the KS-DFT method gives approximate values for both exchange and correlation contribution to the energy.

The local density approximation (LDA)

Considers the general inhomogeneous electronic system as *locally homogeneous*:

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

$$\varepsilon_{\text{xc}}^{\text{LDA}}(\rho) = \quad \text{exchange} - \text{correlation energy per particle of a uniform electron gas (jellium).}$$

• Well known from accurate calculations (Quantum Monte Carlo) [Ceperley and Alder (1980)]

• Has been fitted to analytic representations [Vosko, Wilk and Nusair (1980); Perdew and Zunger (1981)]

• In general, it should be a *functional* of the density, and not a function.

The General Gradient Approximation (GGA)

Incorporates gradient corrections to $\varepsilon_{xc}^{LDA}(\rho(\mathbf{r}))$

$$E_{\text{xc}}^{\text{GGA}}[\rho(\mathbf{r})] = \int d^3\mathbf{r}\,\rho(\mathbf{r})\,\varepsilon_{\text{xc}}^{\text{LDA}}(\rho(\mathbf{r}))F(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}))$$

In the LDA the exchange-correlation energy per electron is a function of the electron density, while in the GGA it is a function of both the electron density and of its gradient.

Different expressions have been given for the gradient corrections, e.g:

• **BLYP**: a combination of an exchange functional developed by Becke (1988) and a correlation functional by Lee, Yang and Parr (1988). Contains parameters fitted to experimental molecular data.

• **PBE:** developed by Perdew, Burke and Ernzerhof in 1996. No fitting parameters!

Comparison between Hartree-Fock and Kohn-Sham DFT

• The KS equation should be solved iteratively like the HF equation, since the KS operator itself depends on the orbitals of the solution

• Although Kohn-Sham DFT uses a Hamiltonian similar to the one in HF theory, no claim is made here about the form of the wavefunction. The method would be exact if we knew the exact form of E_{xc} (we don't!)

• While the HF method gives exact exchange and no correlation (by definition), the KS-DFT method gives approximate values for both exchange and correlation contribution to the energy.

	Hartree-Fock	**DFT (Kohn-Sham)**
State Description	$\Psi(\mathbf{x}_1,...,\mathbf{x}_N) = \dfrac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{pmatrix}$	$\rho(\mathbf{r}) = \sum_{i=1}^{N} \left| \psi_i \right|^2$
Total energy	$E = <\Psi \mid \hat{H} \mid \Psi>$	$E[\rho(\mathbf{r})] = \sum_{i=1}^{N} \left\langle \psi_i \mid -\dfrac{1}{2}\nabla^2 - \sum_{A=1}^{M} \dfrac{Z_A}{\mid \mathbf{r} - R_A \mid} + \dfrac{1}{2}\int \dfrac{\rho(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} d\mathbf{r}' \mid \psi_i \right\rangle$ $+ E_{xc}[\rho(\mathbf{r})]$
One-electron energies	$h_i^{HF} \psi_i = \varepsilon_i \psi_i$ $h_i^{HF} = -\dfrac{1}{2}\nabla^2 - \sum_{A=1}^{M} \dfrac{Z_A}{\mid \mathbf{r} - \mathbf{R}_A \mid} + \hat{v}_i^{HF}$ Coulomb + Exchange $\hat{v}_i^{HF} \psi_i(\mathbf{x}) = \left[\sum_j \int d\mathbf{x}' \psi_j^*(\mathbf{x}') \psi_j(\mathbf{x}') r_{ij}^{-1} \right] \psi_i(\mathbf{x})$ $- \left[\sum_j \int d\mathbf{x}' \psi_j^*(\mathbf{x}') \psi_i(\mathbf{x}') r_{ij}^{-1} \right] \psi_j(\mathbf{x})$	$h_i^{KS} \psi_i = \varepsilon_i \psi_i$ $h^{KS} = -\dfrac{1}{2}\nabla^2 - \sum_{A=1}^{M} \dfrac{Z_A}{\mid \mathbf{r} - \mathbf{R}_A \mid} + \int \dfrac{\rho(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} d\mathbf{r}' + v_{xc}(\mathbf{r})$ Coulomb Exchange + Correlation + Kinetic energy corrections
Electron-electron interactions	• Exact **Coulomb** and **Exchange** • No **Correlation** (by definition)	• **Coulomb** including *self-interaction* (error) • Approximate **Exchange** • Approximate **Correlation**

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Electron self-interaction problem

- In local and semi-local DFT each density region of one electron interacts with other density regions of the **same** electron – this is incorrect.

- Origin: The exchange contribution is given by a density functional, and does not cancel the Coulomb interaction of the electron with itself.

- This problem is not present in HF:

$$\hat{v}_i^{HF}\psi_i(\mathbf{x}) = \left[\sum_j \int d\mathbf{x}'\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x}')r_{ij}^{-1}\right]\psi_i(\mathbf{x}) - \left[\sum_j \int d\mathbf{x}'\psi_j^*(\mathbf{x}')\psi_i(\mathbf{x}')r_{ij}^{-1}\right]\psi_j(\mathbf{x})$$

$$= \left[\sum_{j\neq i} \int d\mathbf{x}'\psi_j^*(\mathbf{x}')\psi_j(\mathbf{x}')r_{ij}^{-1}\right]\psi_i(\mathbf{x}) - \left[\sum_{j\neq i} \int d\mathbf{x}'\psi_j^*(\mathbf{x}')\psi_i(\mathbf{x}')r_{ij}^{-1}\right]\psi_j(\mathbf{x})$$

$j=i$ terms are the same but with opposite sign for Coulomb and exchange contribution, and cancel out!

Consequences of the self-interaction problem

• DFT tends to favour delocalised solutions where electrons do not interact strongly with themselves.

• This is a problem in the description of strongly localised d or f states in transition metal or rare earth compounds.

• The covalent character in the bonding of ionic and semi-ionic compounds is typically exaggerated within DFT, and band gaps are underestimated.

• Delocalised metallic states can be artificially preferred over the real localised state in semiconductors.

• Two widely used approaches to correct self-interaction problems: hybrid functionals and DFT+U methods.

Correcting self-interaction in DFT: Hybrid functionals

Exchange contribution is given partially by the HF expression and partially by the DFT functional, for example:

$$E_{xc} = (1-a)E_x^{DFT} + aE_x^{HF} + E_c^{DFT}$$

where $0 < a < 1$ is the proportion of HF exchange
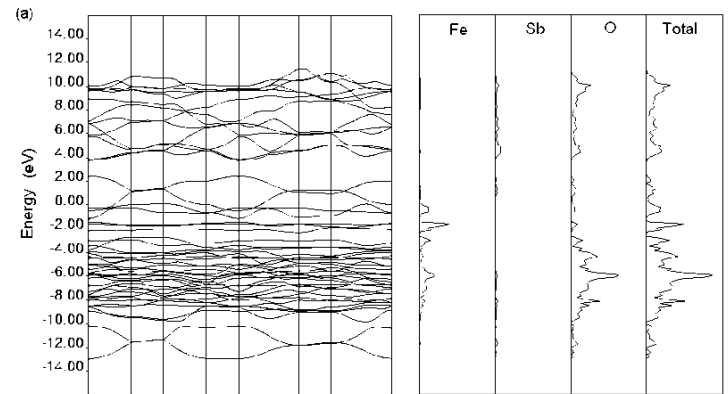
Example: B3LYP

Exchange: Becke(1988)/LDA + HF(20%)
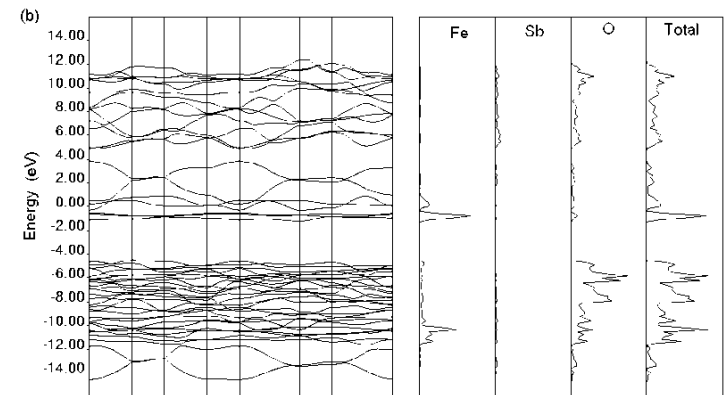Correlation: LYP/LDA

Values of parameters fitted against binding energy of molecules.
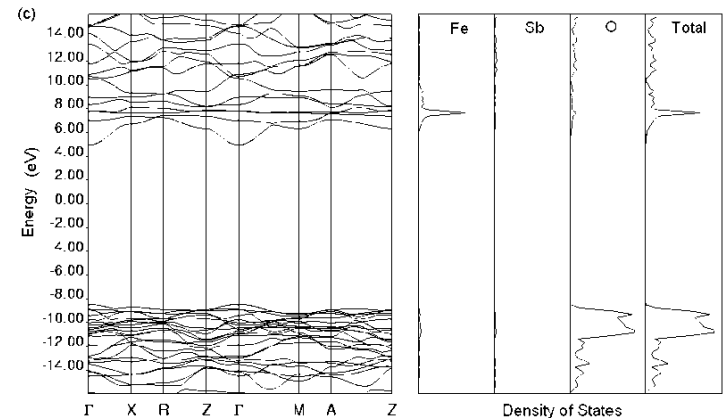
Example: Band gap in $FeSbO_4$

DFT (too narrow) ⟶

HF/DFT hybrid (correct)
(B3LYP, 20% HF) ⟶

HF (too wide) ⟶

Grau-Crespo R et al. *Phys. Rev. B* (2006)

Correcting self-interaction in DFT: The DFT+U method

- One of the consequences of the artificial delocalization in DFT is more overlapping between the orbitals.

- Problem can be partially corrected by introducing a penalty energy against the hybridisation of the *d* or *f* orbitals:

$$E_{DFT+U} = E_{DFT} + U \times \text{Hybridisation}$$

Penalty term proportional to overlap of *d* orbitals with ligands' *p* orbitals.

- Whenever the orbitals of one atom attempt to hybridise with those of the neighbouring atoms, a penalty applies with some positive energy (proportional to U). Therefore, DFT+U tends to avoid the wrong delocalized solution.

- Typically, the U parameter is fitted to reproduce experimental data (e.g. band gaps), but there are ways to obtain the value ab initio.

Solving the Schrödinger equation in crystalline solids

- **Main idea**: crystals are *periodic*, therefore the potential exerted by the nuclei on the electrons, and any observable property (e.g. electron density) must be periodic too.
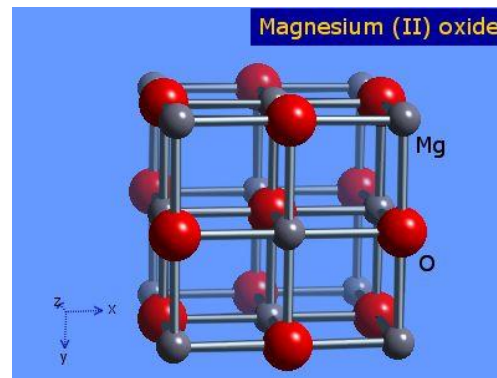
- In a periodic calculation, we focus on a ***unit cell*** of the crystal. Periodicity means that all other cells within the crystal will behave in the same way.

- **Mind:** Some types of solids are non-crystalline (non-periodic), e.g. glasses. But non-periodic solids can be approximately described using a ***very large*** unit cell, and therefore calculated in the same way.
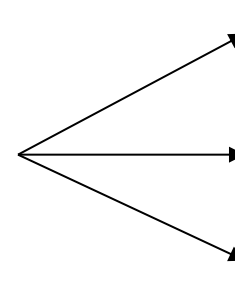
The simplest periodic potential: the zero potential

Electron in a *zero* potential: wavefunction of the free electron:

$$\psi_{\mathbf{k}}(\mathbf{r}) = A \exp[i\mathbf{k} \cdot \mathbf{r}]$$

plane wave

The condition

$$\mathbf{k} \cdot \mathbf{r} = \text{constant}$$

defines a plane

It satisfies the equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \varepsilon \psi$$

Energy (kinetic): $\quad \varepsilon_{\mathbf{k}} = \dfrac{\hbar^2 \mathbf{k}^2}{2m}$

Well-defined momentum: $\quad \mathbf{p} = \hbar \mathbf{k}$

(and completely uncertain position)

Electron in a periodic potential (Bloch's theorem, 1928):

The wavefunction of an electron in a periodic crystal can be written as a **product** of a periodic function and a planewave:

$$\psi_{\mathbf{k}}(\mathbf{r}) = f_{\mathbf{k}}(\mathbf{r})\exp[i\mathbf{k}\cdot\mathbf{r}]$$

periodic function: Plane wave

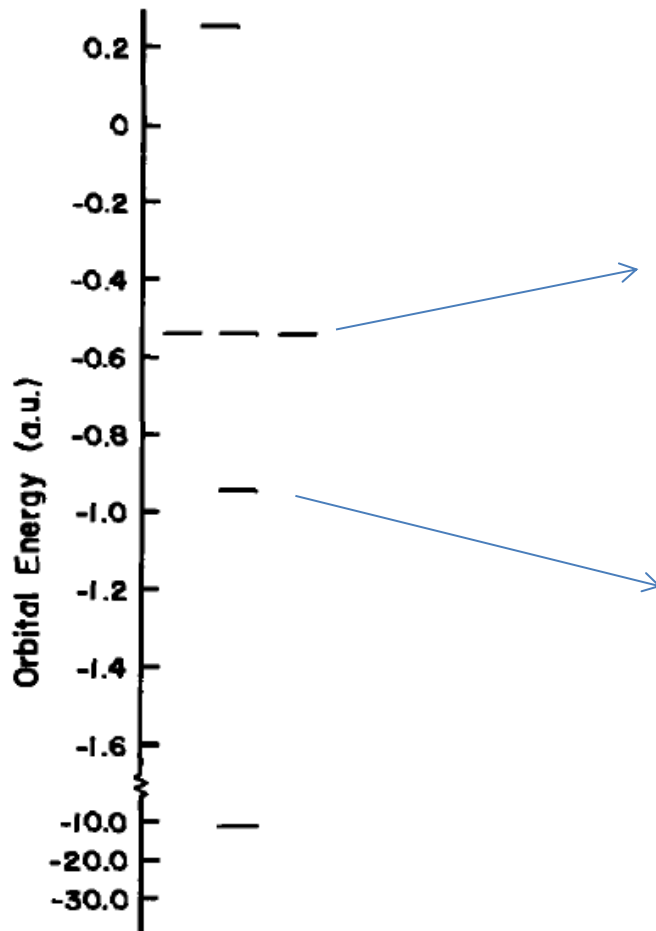$$f_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = f_{\mathbf{k}}(\mathbf{r})$$

where **T** is a translation vector of the lattice

The continuous index **k** is called the **wave vector**.
The one-electron Schrodinger equation (from HF or from DFT)
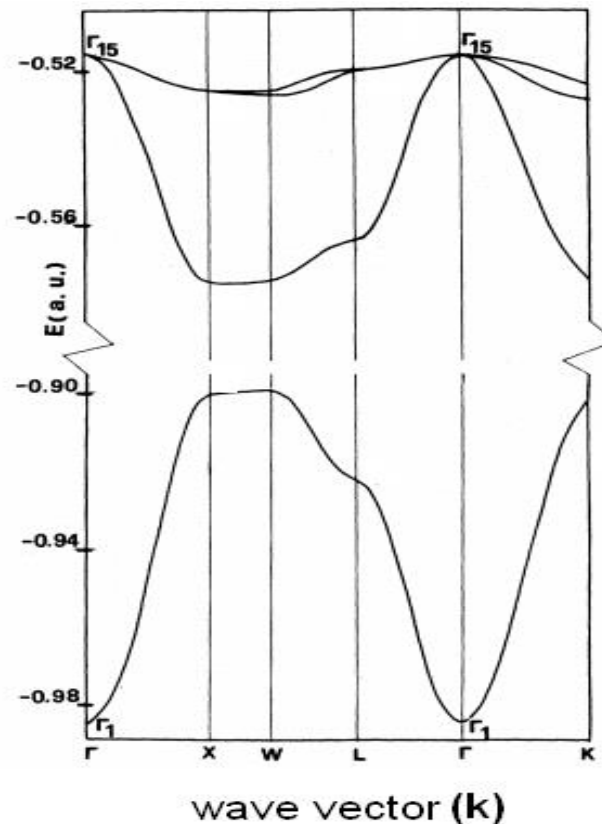has to be solved for each wave vector **k**.

Indexes for electronic levels: molecules vs solids

$$\psi_n \to \varepsilon_n \qquad\qquad \psi_{n,\mathbf{k}} \to \varepsilon_{n,\mathbf{k}}$$

CH_4 molecule
(HF calculation)

Valence bands in CH_4 crystal
(periodic HF calculation)

Some molecular HF/DFT codes

Program	Licence	Basis set
Gaussian	Commercial	Gaussian
Gamess US/ Gamess UK	Free academic licences	Gaussian
NWChem	Free educational licence	Gaussian
DMol	Commercial	Numerical atomic orbitals

Some periodic DFT codes

Program	Licence	Basis set
VASP	Commercial. Incorporated in MedeA.	Plane waves
Quantum Espresso	Free	Plane waves
CASTEP	Commercial, incorporated in Materials Studio (free for UK academics)	Plane waves
WIEN2k	Commercial	Plane waves + atomic local orbitals
SIESTA	Commercial (free for UK academics)	Numerical atomic orbitals
DMol	Commercial	Numerical atomic orbitals
CRYSTAL	Commercial (free for UK academics)	Gaussian