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Applications of Computer Simulations to research in Sustainable Energy: what can we learn from computer simulations

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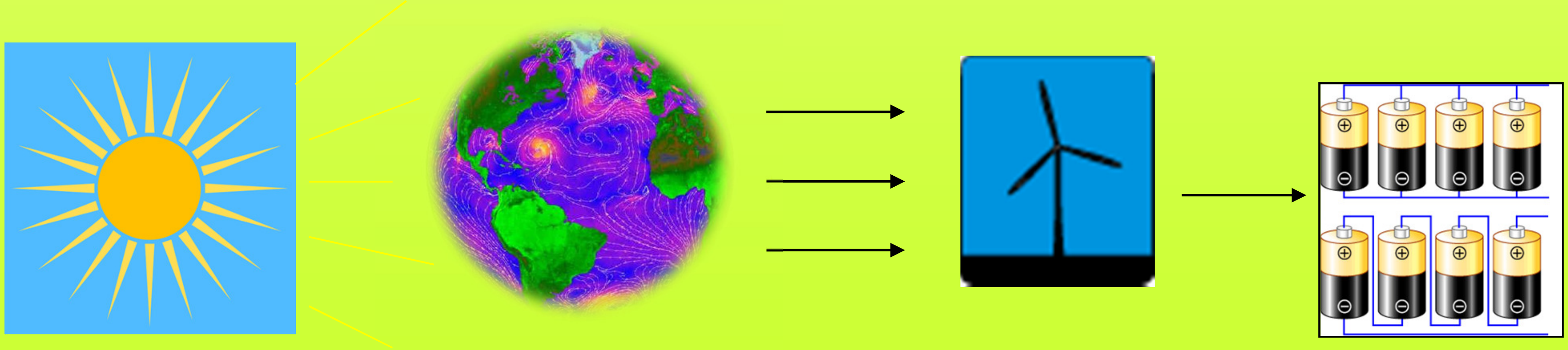
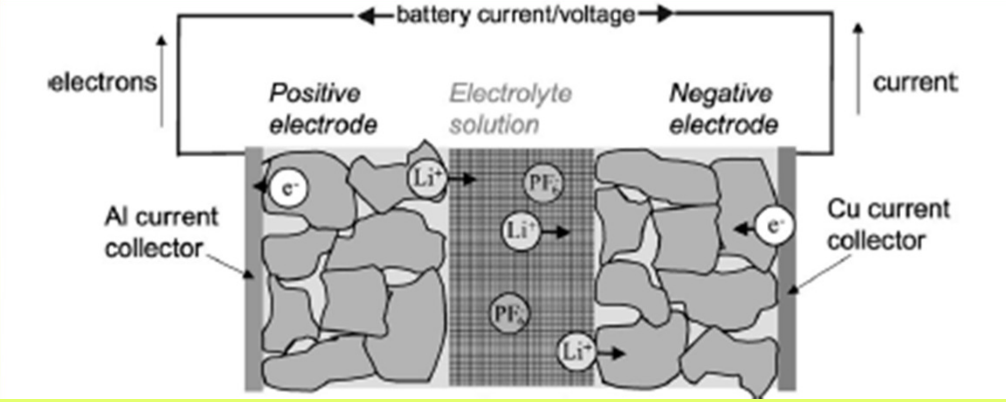
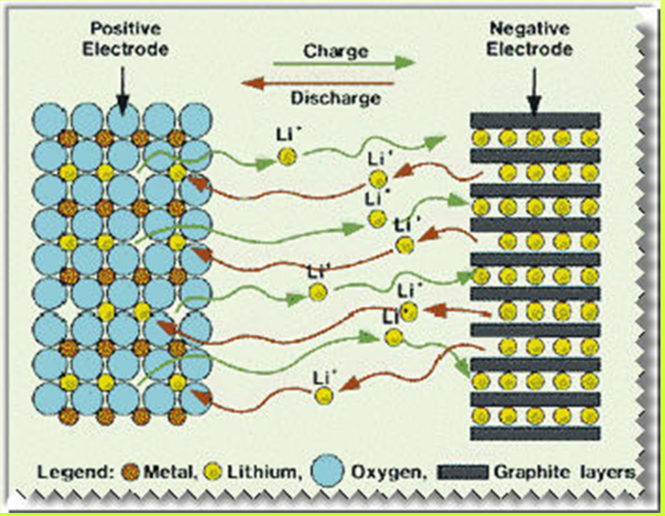
Sustainable Energy Production and Storage

- Production: solar, bio, wind, tidal, geothermal
- Storage: batteries and hydrogen
- Key : new storage materials



Role of computer simulations



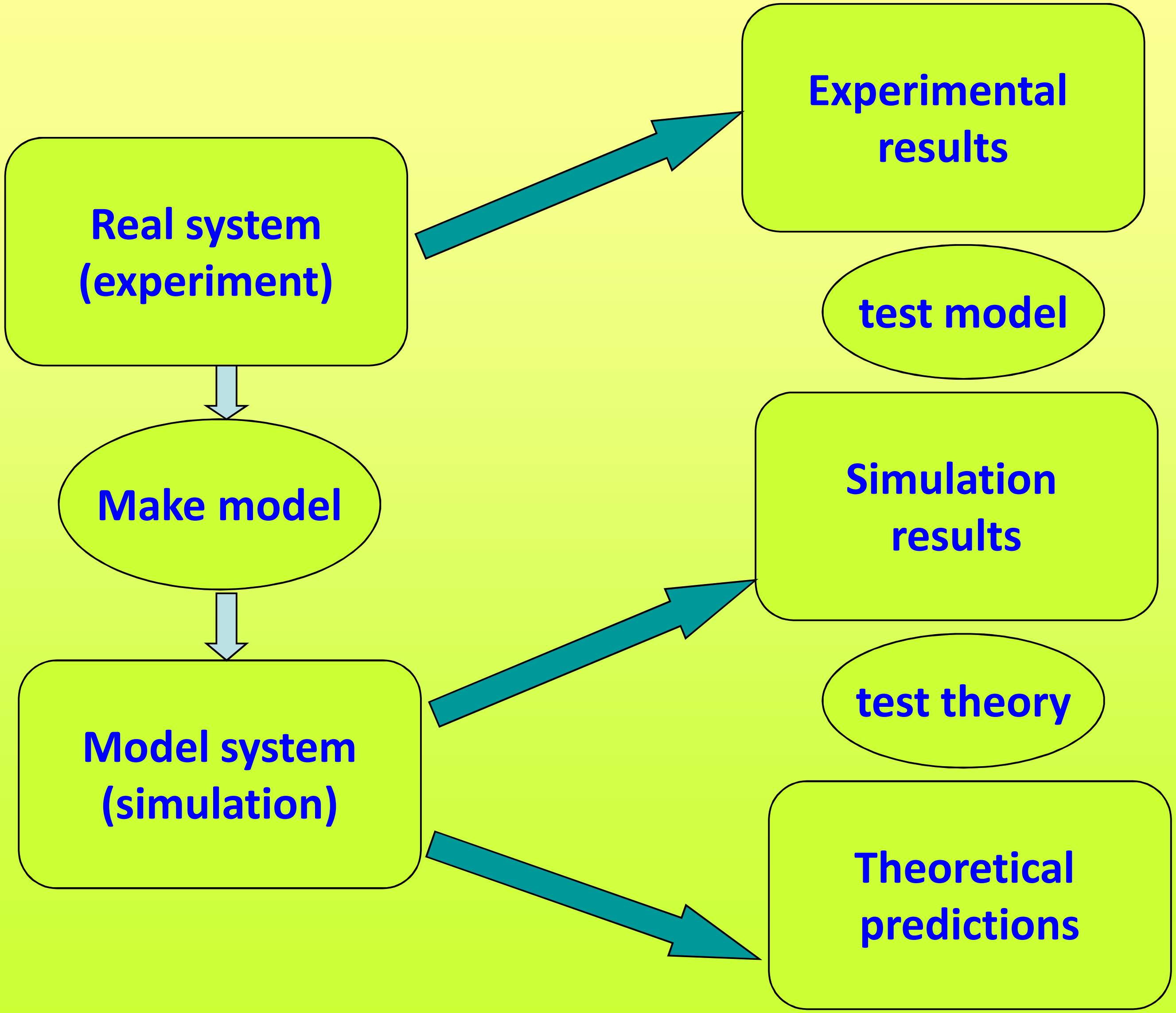


- Provide detailed information on microstructure and electronic structure

- Elucidate fundamental mechanisms underlying functioning of devices

- Suggest criteria for design and optimisation

Relation between theory, experiment and simulation



Real system (experiment)

Make model

Model system (simulation)

Experimental results

test model

Simulation results

test theory

Theoretical predictions

Major computer simulations

- *Classical molecular dynamics*

  Use classical equations of motion to study system composed of N interacting atoms, ions or molecules.

- *Monte-Carlo*

  Statistical behaviour of a system of N interacting particles (atoms, ions, molecules) is investigated using probabilistic techniques

- *Ab initio (total energy) calculations*

  Energy of a system of N interacting particles is computed using a quantum mechanical approach. Density functional theory is the most efficient.

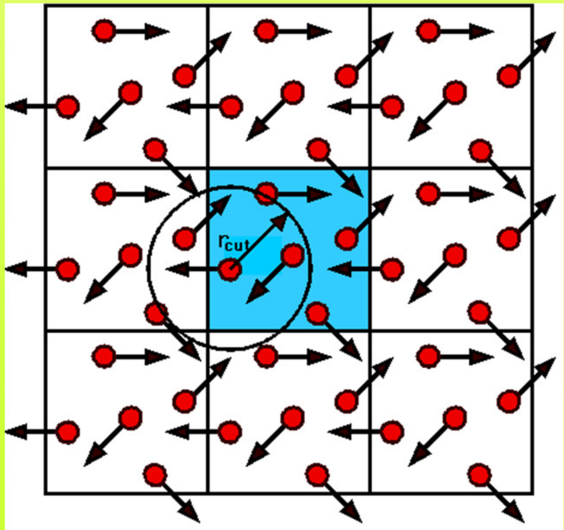
- *Ab initio molecular dynamics.*

  Combine computation of ab initio energy and forces of N interacting atoms or ions with classical equations of motion for the nuclei.

Molecular dynamics

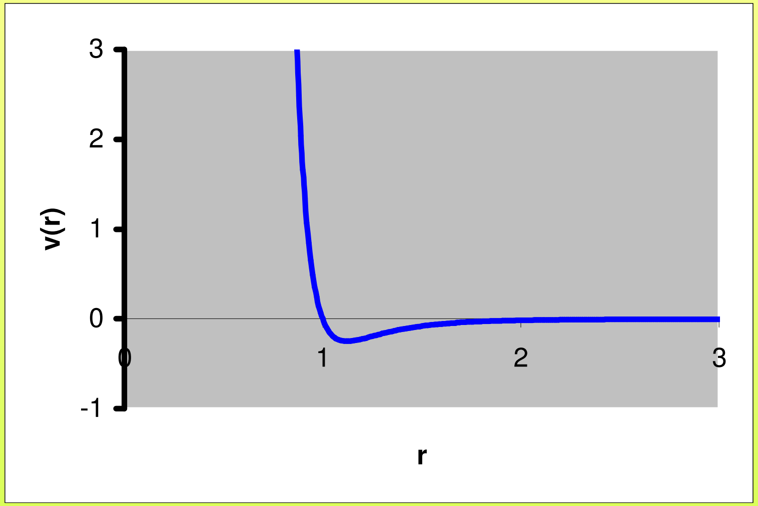
N interacting particles in a (usually cubic) box of side L with positions $\mathbf{r}_i$*, i=1,….,N. The total energy is given by a function* $U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ *of the positions of all particles in the system. In an MD simulation we solve Newton's equation of motion for the N-body system numerically on the computer:*

$$m\ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

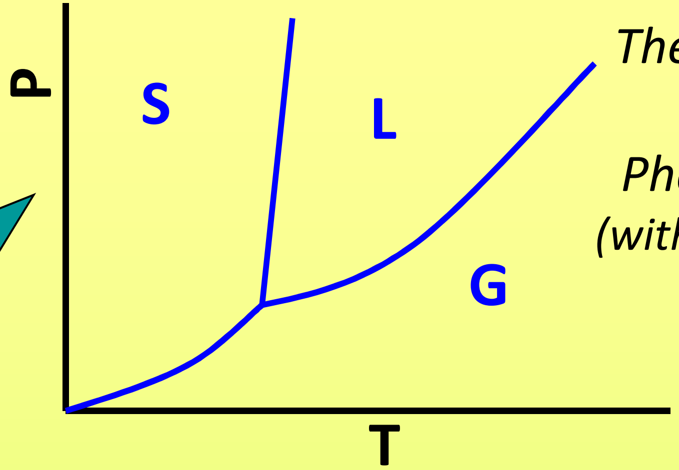


Typically N~100-10,000 (although much larger systems have been simulated.
Finite size effects due to the nearness of surfaces are avoided by using periodic boundary conditions.

What can you compute?



Intermolecular potential

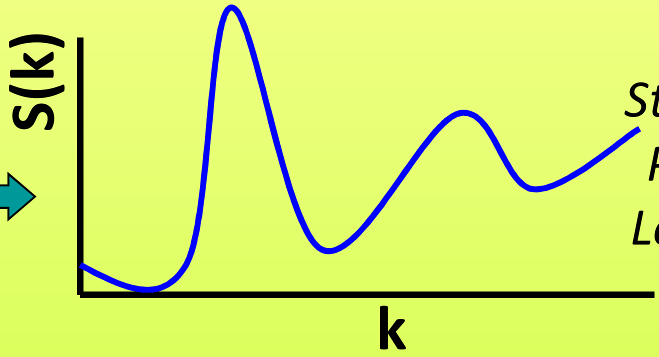


Thermodynamics

P,T,E

Phase behaviour

(with some difficulty)

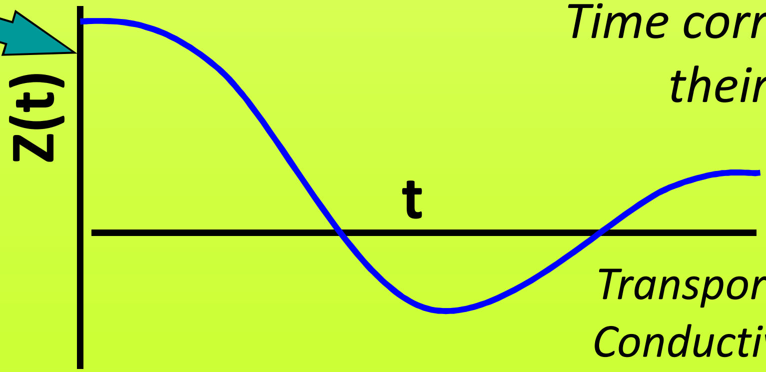


Structure:

Structure functions

Pair distributions

Local coordination



Dynamics:

Time correlations and their spectra

Transport coefficients

Conductivity Diffusion

Viscosity

Monte Carlo Simulation

Helmholtz free energy F=E-TS for a system of N (rigid) molecules with positions $\mathbf{r}_i$ *and orientations* Ω_i *in a volume V interacting through a potential function* $U(\mathbf{r}_1,\ldots,\mathbf{r}_N,\Omega_1,\ldots,\Omega_N)$ **is, apart from trivial factors, given by:**

$$F(N,V,T) = -k_B T \ln Q(N,V,T)$$

T is the temperature and k_B is Boltzman's constant

$Q(N,V,T)$ is the configurational integral:

$$Q(N,V,T) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \int d\mathbf{\Omega}_1 \cdots d\mathbf{\Omega}_N e^{-\beta U}$$

$\beta=(k_B T)^{-1}$

Monte Carlo Simulation

Configurations of the system are distributed according the Boltzman factor:

$$P\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)\propto\exp\left(-\beta U\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)\right)$$

Thermodynamic quantities are averages over the Boltzman distribution, e.g.

$$\left\langle U\right\rangle=\int d\mathbf{r}_1\cdots d\mathbf{r}_N\int d\mathbf{\Omega}_1\cdots d\mathbf{\Omega}_N U\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)P\left(\mathbf{r}_1,\cdots,\mathbf{r}_N;\mathbf{\Omega}_1,\cdots,\mathbf{\Omega}_N\right)$$

In a Monte Carlo simulation a chain of configurations is generated on the computer with the probability of a configuration given by the Boltzman distribution. Thermodynamic quantitie are computed as averages over this chain of configurations.

Monte Carlo Simulation

Metropolis algorithm:

- Choose a particle at random, say particle *l*.
- Change its position by a small random amount $\delta\mathbf{r}_l$ and it is orientation by a small random change in the orientational angles. Let ΔU be change in energy.
- Choose random number λ, uniformly distributed on [0,1].
- If λ>min(1,exp(-$\beta\Delta\boldsymbol{U}$)) accept new configuration
- Otherwise reject new configuration and retain old one.
- Repeat

Generates a change of configurations distributed according to the Boltzman distribution

Ab initio simulations

- Many electron Schrödinger equation.
- Variational principle.
- Hartree-Fock theory.
- The pair density and the correlation hole.
- Basic ideas of DFT.
- The non-interacting reference system: Kohn-Sham equations.
- Local density approximation
- Beyond the LDA
- Pseudopotentials

Many electron Schrödinger equation

Consider a system of N electrons in an external potential **$V_{ext}(\mathbf{r})$.**
The energy E of the system is obtained as the solution
of the time-independent Schrödinger equation:

$$H\Psi\left(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N\right)=E\Psi\left(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N\right)$$

This is a linear equation for the wave function $\Psi\left(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N\right)$
a function of the 3N coordinates of the electrons.

*The Hamiltonian **H** is a sum of three terms: the **kinetic energy**, the **external potential** and the **electron-electron interaction**:*

$$H=-\frac{1}{2}\sum_{i=1}^{N}\nabla^2+V_{ext}+\sum_{i>j}^{N}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

We use atomic units, i.e. $m=e=\hbar=1$

Many electron Schrödinger equation

In materials simulations the external potential **V_{ext}** *is usually the interaction of the electrons with the nuclei. Thus:*

$$V_{ext}(\mathbf{r}) = \sum_{\alpha=1}^{N_\alpha} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

The separation of electron and nuclear degrees of freedom is valid under the ***Born-Oppenheimer approximation****. Relativistic effects are neglected.*

The external potential and the number of electrons therefore completely determine the Hamiltonian ***H****.*

We assume for simplicity a nondegenerate ground state. Then the wave function $\Psi(\mathbf{r}_1, \ldots\ldots, \mathbf{r}_N)$ *must be* ***anti-symmetric*** *under exchange of its arguments (Pauli-principle) and we assume* $\Psi(\mathbf{r}_1, \ldots\ldots, \mathbf{r}_N)$ *is* ***normalized****.*

Variational principle

For any allowed wave function $\Psi(\mathbf{r}_1, \ldots\ldots, \mathbf{r}_N)$ *the energy E can be calculated as:*

$$E = \int \Psi^* H \Psi d\mathbf{r}_1 \ldots . d\mathbf{r}_N = \langle \Psi | H | \Psi \rangle$$

We can regard the energy as a ***functional*** *of the wave function*

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

The ***variational principle*** *states that the ground state wave function minimizes the energy. Thus for all wave functions we have that:*

$$E[\Psi] \geq E_0$$

where E_0 *is the ground state energy. This leads to a well known strategy for determining the wave function. We search all possible permissible* $\Psi(\mathbf{r}_1, \ldots\ldots, \mathbf{r}_N)$ *and minimize* ***E*** *to get the ground state energy. Unfortunately this is generally not feasible. It is possible only for certain classes of functions.*

Hartree-Fock equations

*In **Hartree-Fock** theory the wave function is approximated as a **Slater determinant** of single particle wave functions:*

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \cdots & \varphi_1(\mathbf{r}_N) \\ \vdots & & \vdots \\ \varphi_N(\mathbf{r}_1) & \cdots & \varphi_N(\mathbf{r}_N) \end{vmatrix}$$

*Hence the **anti-symmetry** requirement is automatically fulfilled. This leads to the following expression for the energy of a system:*

Hartree-Fock equations

$$E_{HF}=\sum_{i=1}^{N}\int\varphi_i^*(\mathbf{r})\left[-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})\right]\varphi_i(\mathbf{r})\,d\mathbf{r}+$$

$$\frac{1}{2}\sum_{i,j=1}^{N}\int\int\frac{\varphi_i^*(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2-$$

$$\frac{1}{2}\sum_{i,j=1}^{N}\int\int\frac{\varphi_i^*(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)\varphi_j(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2$$

The first line is a single particle energy, the ***kinetic energy*** *and the* ***interaction of the electrons with the nuclei****. The second line is the* ***Coulomb interaction*** *between charge distributions corresponding to electrons in wave functions* φ_i *and* φ_j *respectectively. The last term is the* ***exchange integral****, which has no classical equivalent.*

Hartree-Fock equations

Minimizing the energy with respect to all single particle wave functions leads to the ***Hartree-Fock equations*** *for the wave-function*

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\right]\varphi_i(\mathbf{r}) - \int v_X(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')\,d\mathbf{r}' = \varepsilon_i\varphi_i(\mathbf{r})$$

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

$$\int v_X(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')\,d\mathbf{r}' = \sum_{j=1}^{N}\int \frac{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\varphi_i(\mathbf{r}')\,d\mathbf{r}'$$

Clearly ρ*, the total electron density alongside the third term describes the interaction of the electron in orbital* φ_i *due to all electrons in the system. The last term is the* ***nonlocal exchange potential****. The Hartree-Fock approximation corresponds to a set of* ***non-interacting electrons*** *moving under the influence of the* ***mean electrostatic field*** *due to all electrons and a* ***nonlocal exchange potential****. Correlations are neglected.*

Selfconsistent field equations have to be solved ***iteratively****.*

Beyond Hartree-Fock

Hartree-Fock neglects correlation in the electronic motion and the difference between the Hartree-Fock energy and the true ground state energy is usually referred to as the ***correlation energy****.*

Quantum chemistry has developed many approximations for the ***correlation energy****.*

For small systems these methods are quite accurate and satisfactory. For large systems these calculations become impossible because of the bad scaling with problem size.

Examples:

MP2, MP3, MP4: ~ N^5, N^6, N^7
CISD ~ N^6
CCSD ~ N^6
CCSD(T) ~ N^7

The pair density

The ***two-particle density matrix*** *is defined as*

$$\rho_2\left(\mathbf{r}_1',\mathbf{r}_2';\mathbf{r}_1,\mathbf{r}_2\right)=\frac{1}{2}N(N-1)\int\Psi^*\left(\mathbf{r}_1',\mathbf{r}_2',\dots,\mathbf{r}_N\right)\Psi\left(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N\right)d\mathbf{r}_3\dots.d\mathbf{r}_N$$

The ***two particle density*** *or* ***pair density function*** *is obtained from the diagonal elements of the two-particle density matrix:*

$$\rho_2\left(\mathbf{r}_1,\mathbf{r}_2\right)=\rho_2\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2\right)=\frac{1}{2}N(N-1)\int\left|\Psi\left(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N\right)\right|^2 d\mathbf{r}_3\dots.d\mathbf{r}_N$$

The single particle density

The ***single particle density matrix*** *is obtained through integration of the* ***two-particle density matrix****:*

$$\rho_1\left(\mathbf{r}_1';\mathbf{r}_1\right)=\frac{2}{N-1}\int\rho_2\left(\mathbf{r}_1',\mathbf{r}_2;\mathbf{r}_1,\mathbf{r}_2\right)=$$

$$N\int\Psi^*\left(\mathbf{r}_1',\mathbf{r}_2,\ldots,\mathbf{r}_N\right)\Psi\left(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\right)d\mathbf{r}_2\ldots d\mathbf{r}_N$$

The ***single particle density*** *is obtained as the diagonal element of the* ***single particle density matrix****:*

$$\rho\left(\mathbf{r}\right)=\rho_1\left(\mathbf{r};\mathbf{r}\right)$$

Clearly $\rho(\mathbf{r})$ *is normalized to* ***N*** *and* $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ *to* ***N(N-1)/2****.*
Knowledge of the two-particle density matrix is sufficient to determine the energy ***E***

$$E[\rho_2] = tr(HP) =$$

$$\int \left[\left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) \right) \rho_1(\mathbf{r}';\mathbf{r}) \right]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r} + \int \frac{\rho_2(\mathbf{r}',\mathbf{r};\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Alternative strategy: ***minimize E[ρ_2]***

Problem is construction of permissible ρ_2*.*
One should be able to construct ρ_2 *from an* ***anti-symmetric*** *many-particle wave function. Not an easy constraint to apply.*

However, even ρ_2 *is not required. For the exact total energy knowledge of the single particle density* $\rho(\mathbf{r})$ *is sufficient*

Density functional theory

The basis for DFT is formed by two theorems, proven in 1963 by ***Hohenberg and Kohn*** *and later extended by* ***Levy*** *to degenerate ground states.*

Theorem 1:

The external potential is uniquely determined by the electron density $\rho(\mathbf{r})$.
Therefore the Hamiltonian is uniquely determined by $\rho(\mathbf{r})$.
Therefore the total energy is a unique functional of the density:

$$E = E[\rho]$$

NB: if $\mathbf{V}_{ext}$ *and* $\mathbf{V}'_{ext}$ *differ only by a constant they are* ***not*** *considered different.*

Proof:

Consider two Hamiltonians with different external potentials. Each Hamiltonian wil have a ***different ground state wave function****. Let us suppose that both ground state wave functions will lead to the same ground state density. Thus schematically:*

$$V_{ext} \Rightarrow H \Rightarrow \Psi \Rightarrow \rho(\mathbf{r}) \Leftarrow \Psi' \Leftarrow H' \Leftarrow V'_{ext}$$

We may use Ψ' *as a* ***trial function*** *for* ***H****. By the variation theorem we have:*

$$E_0 < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | H - H' | \Psi' \rangle$$

Since ***H*** *and* ***H'*** *only differ in* ***external potential*** *this yields:*

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

Interchanging primed and unprimed quantities yields:

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

Adding yields: $E_0 + E'_0 < E'_0 + E_0$

Hence, ground state densities are the same

Density functional theory

Theorem 2:

The density which minimizes the ground state energy is the ***ground state density*** *and the minimum energy is the* ***ground state energy.***

This establishes a variational principle:

For any positive definite trial density ρ_t *such that* $\int \rho_t(\mathbf{r})d\mathbf{r} = N$

$$E[\rho_t] \geq E_0$$

Proof:

ρ_t *determines a unique* $\mathbf{H_t}$*, which determines a unique* Ψ_t*.*

By the variational theorem:

$$E[\rho_t] = \langle \Psi_t | H | \Psi_t \rangle \geq E_0$$

Density functional theory

The fundamental statement of DFT is:

$$\delta\left(E[\rho]-\mu\left\{\int\rho(\mathbf{r})-N\right\}\right)=0$$

The ground state energy and density correspond to the minimum of some functional ***E*[ρ]***, subject to the constraint that the density contains the correct number of electrons* ***N****.*

The Lagrange multiplier μ *is the electronic chemical potential.*

Energy functional

The Hamiltonian has three terms:

$$E = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho]$$

The interaction with external potential ***V_{ext}*** *is straightforward:*

$$V_{ext}[\rho] = \int V_{ext}(\mathbf{r})\,\rho(\mathbf{r})\,d\mathbf{r}$$

$T[\rho]$ *and* $V_{ee}[\rho]$ *are unknown. If good approximations could be developed the ground state energy could be obtained through direct minimization.*

Still a subject of much current research

Kohn-Sham approach

Mapping of a fictitious system of noninteracting Fermions moving in an effective potential onto a real many-body system.
Both systems have the same ***ground state energy***
and the same ***ground state density.***

Real

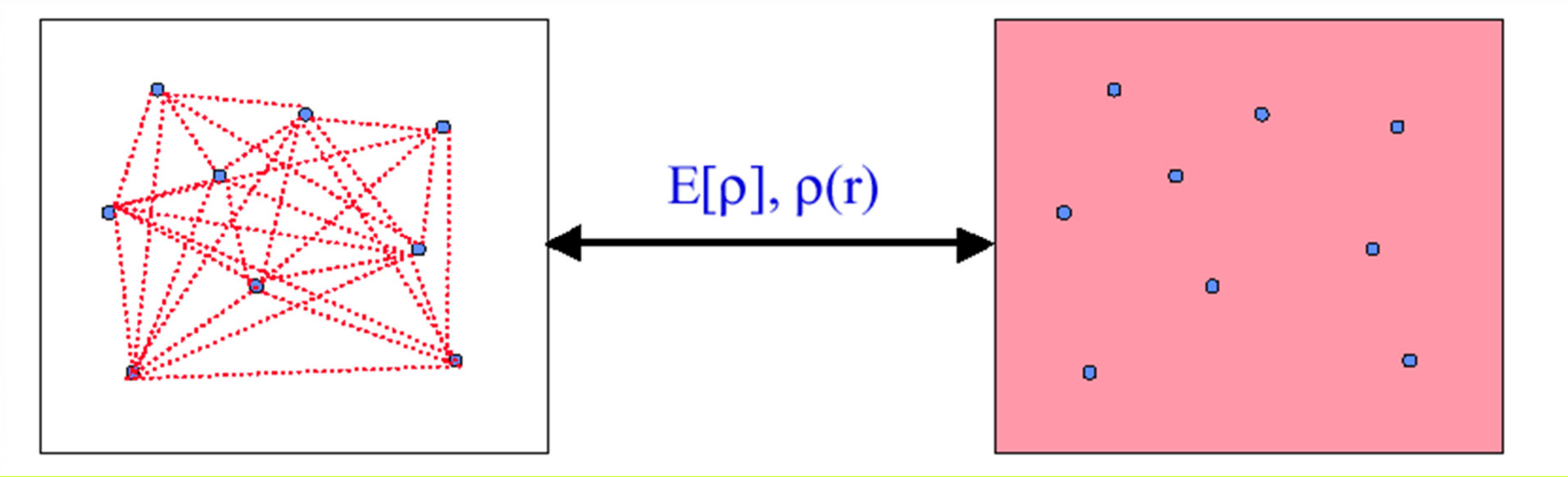
$$\sum_{i>j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)$$

Fictitious

$$V_H(\mathbf{r})+V_{xc}(\mathbf{r})$$

$$\phi_i(\mathbf{r})$$



Kohn-Sham approach

Fictitious system of N non-interacting electrons, described by a single determinant formed from N "orbitals" ϕ_i:

$$\Psi_{KS} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_1(\mathbf{r}_N) \\ \vdots & & \vdots \\ \phi_N(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

Kinetic energy:

$$T_s[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\int \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})\,d\mathbf{r}$$

T_s *is not the true kinetic energy!*

Density is:

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

ρ constructed from anti-symmetric wave-function: permissible

Kohn-Sham approach

Electron-electron interaction consists of the ***Coulomb*** *interaction (Hartree) and the* ***exchange*** *interaction. The* ***Coulomb*** *term is:*

$$V_H[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

All known terms have been extracted.
Lump remainder in ***exchange-correlation functional.***

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho]$$

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - V_H[\rho])$$

E_{ex} *simply corrects for errors made in using a* ***non-interacting*** *kinetic energy and a* ***classical*** *electron-electron interaction.*

Kohn-Sham approach

Minimize functional:

$$\left[-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})+\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+V_{xc}(\mathbf{r})\right]\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r})$$

$$V_{xc}(\mathbf{r})=\frac{\partial E_{xc}(\rho)}{\partial\rho}$$

*These are the **Kohn-Sham** equations*

- *No approximations*
- *If **E_{ex}[ρ]** were known we could determine ground state and density exactly.*
- *Computational cost: **N3***
- *Can be reduced to: **N***

Homogeneous electron gas

For the ***non-interacting*** *electron gas the kinetic and exchange energy per particle can be computed exactly.*

$$T[\rho] = 2.87\int \rho^{5/3}(\mathbf{r})\,d\mathbf{r}$$

$$E_x[\rho] = 0.74\int \rho^{4/3}(\mathbf{r})\,d\mathbf{r}$$

This suggests the following form:

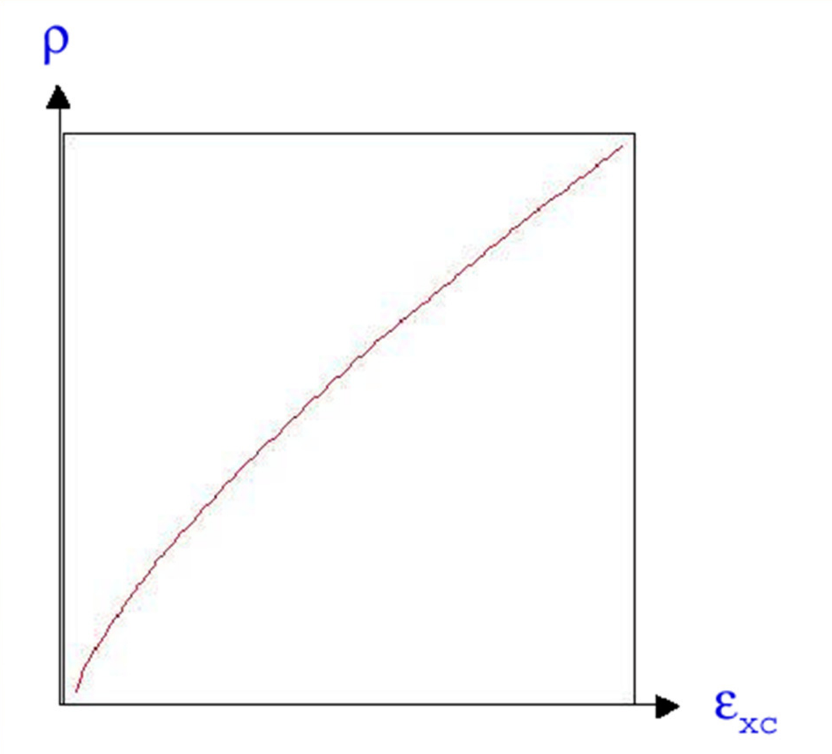
$$E_{ex}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))\,d\mathbf{r}$$

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

$$\varepsilon_x(\rho) = -\rho^{1/3}$$

Homogeneous electron gas

The homogeneous electron gas consists of ***N interacting electrons*** *in a* ***volume V*** *with a uniform background charge density (****jellium****). For the jellium the exact dependence of* $e_{xc}(r)$ *has been computed through* ***quantum Monte Carlo*** *simulations (Ceperley and Alder, 1980).*

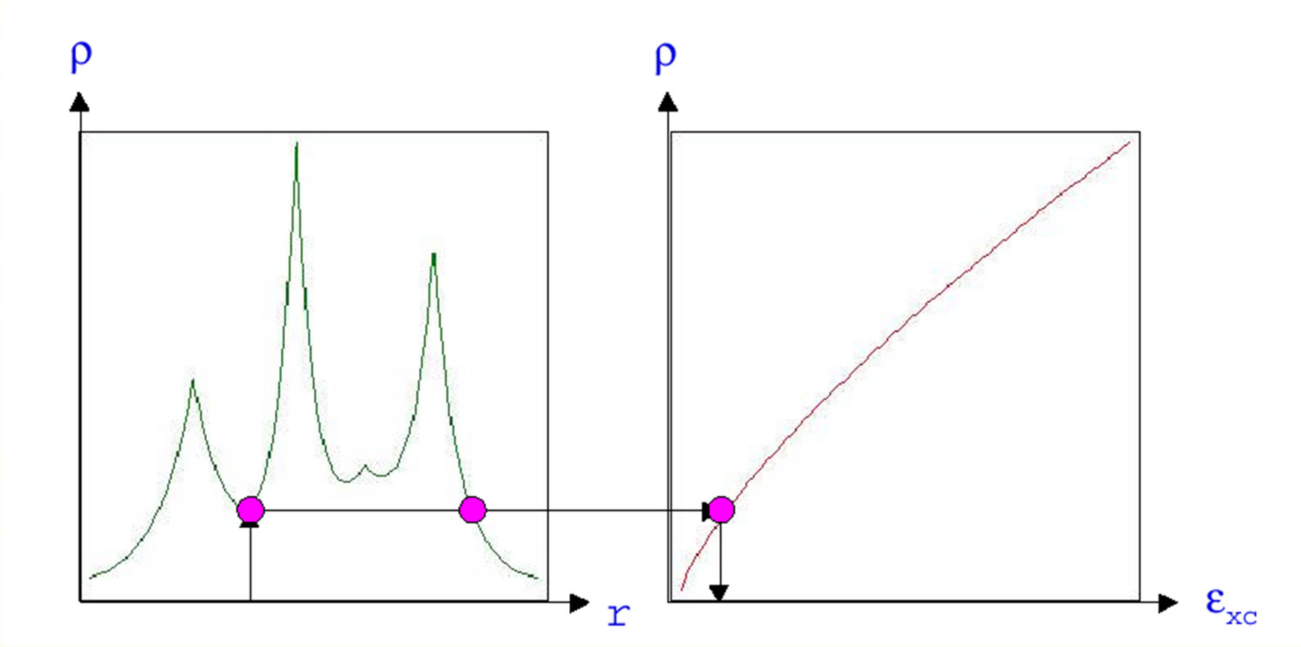


Fit to functional form: ***Local density approximation (LDA)***

Local Density Approximation

Assume the exchange energy at point **r** *is determined by the local density* $\rho(\mathbf{r})$ and is the same as for the homogeneous electron gas.

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



SO,

- *For the ground state energy and density there is an exact mapping between the many-body system and a fictitious non-interacting system.*

- *DFT-people study the fictitious system*

- *The fictitious system is subject to an unknown potential derived from the exchange-correlation functional.*

- *The energy functional may be approximated as a function of the local density only*

Why does DFT work?

The pair density determines the total energy – does the LDA reproduce the pair density ?

The ***exchange correlation hole*** *is the* ***conditional*** *probability of finding an electron at* $\mathbf{r}_2$ *given that these is an electron at* $\mathbf{r}_1$

$$\rho_{xc}\left(\mathbf{r}_1,\mathbf{r}_2\right)=\frac{\rho_2\left(\mathbf{r}_1,\mathbf{r}_2\right)}{\rho\left(\mathbf{r}_1\right)}-\rho\left(\mathbf{r}_1\right)$$

It is the hole the electron at $\mathbf{r}_1$ *digs for itself in the surrounding density.*

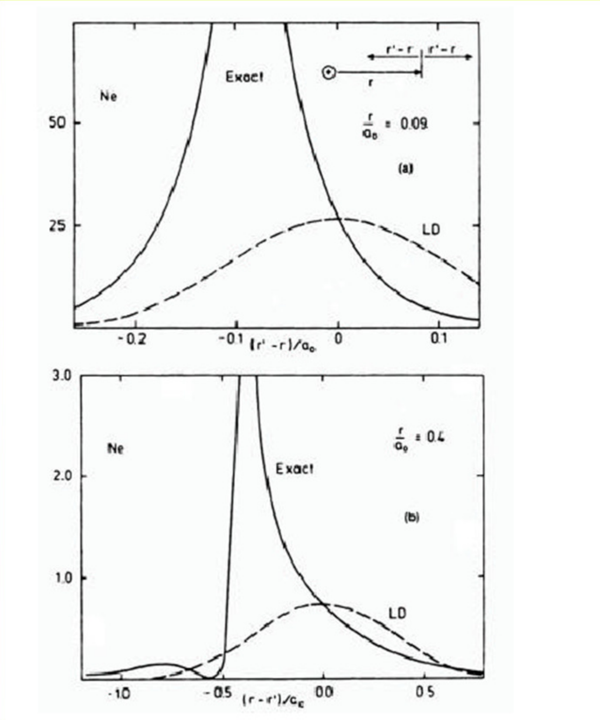
Why does DFT work?

There are a number of properties which will be satisfied by the exact exchange correlation hole.

For instance it should normalise to exactly one electron:

$$\int \rho_{xc}\left(\mathbf{r}_1,\mathbf{r}_2\right)d\mathbf{r}_2=-1$$

Both the LDA and Hartree-Fock theory satisfy this sum-rule.



How well does LDA reproduce the correlation hole?

Clearly not very well

Why does DFT work?

How can ***V_H*** *be reasonable if ρ_{xc} is wrong?*

$$V_H = \frac{1}{2}\int\int \frac{\rho_2(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2$$

The Coulomb energy depends only on $\mathbf{u}=\mathbf{r}_1-\mathbf{r}_2$

$$V_H = \frac{1}{2}\int 4\pi u^2\left[\int \frac{\rho_2(\mathbf{r}_1,\mathbf{r}_1+\mathbf{u})}{u}\frac{d\Omega_u}{4\pi}\right]du$$

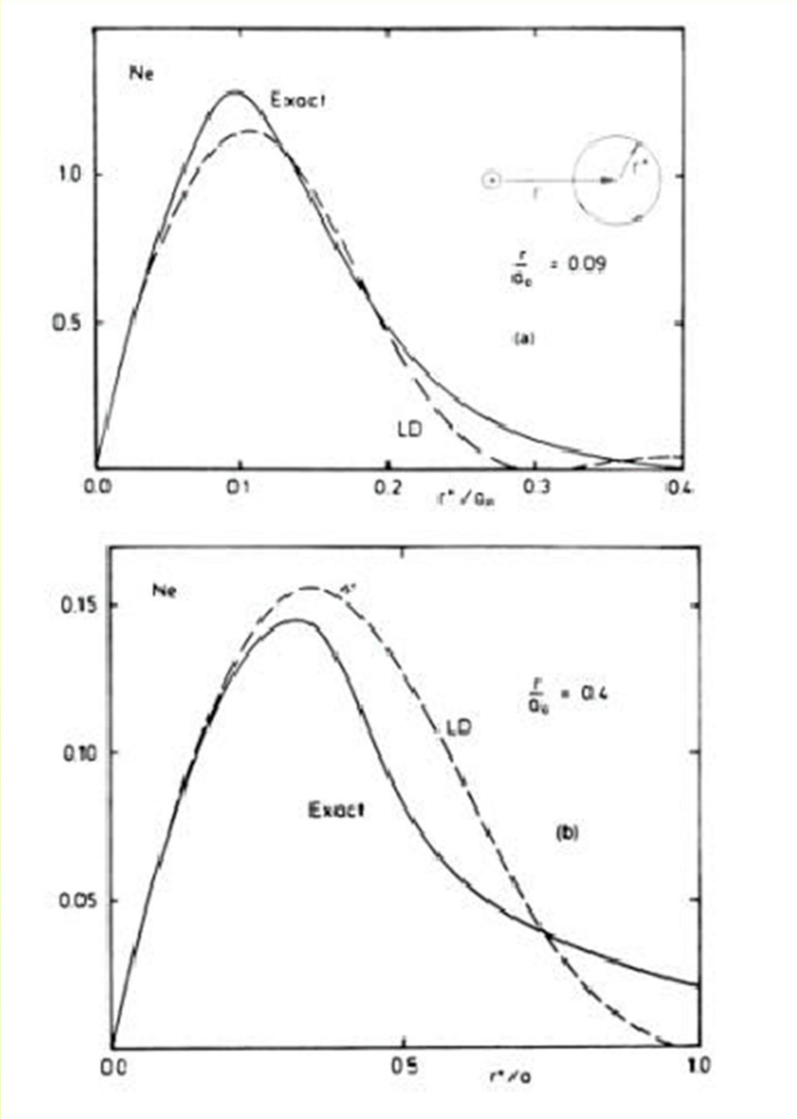
Thus ***V_H*** *depends only on the* ***spherical average $\rho(u)$*** *of the pair density*

$$\rho(u) = \int \rho_2(\mathbf{r}_1,\mathbf{r}_1+\mathbf{u})\frac{d\Omega_u}{4\pi}$$

Why does DFT work?

Spherical average of $\rho_{xc}(\mathbf{r}_1,\mathbf{r}_2)$

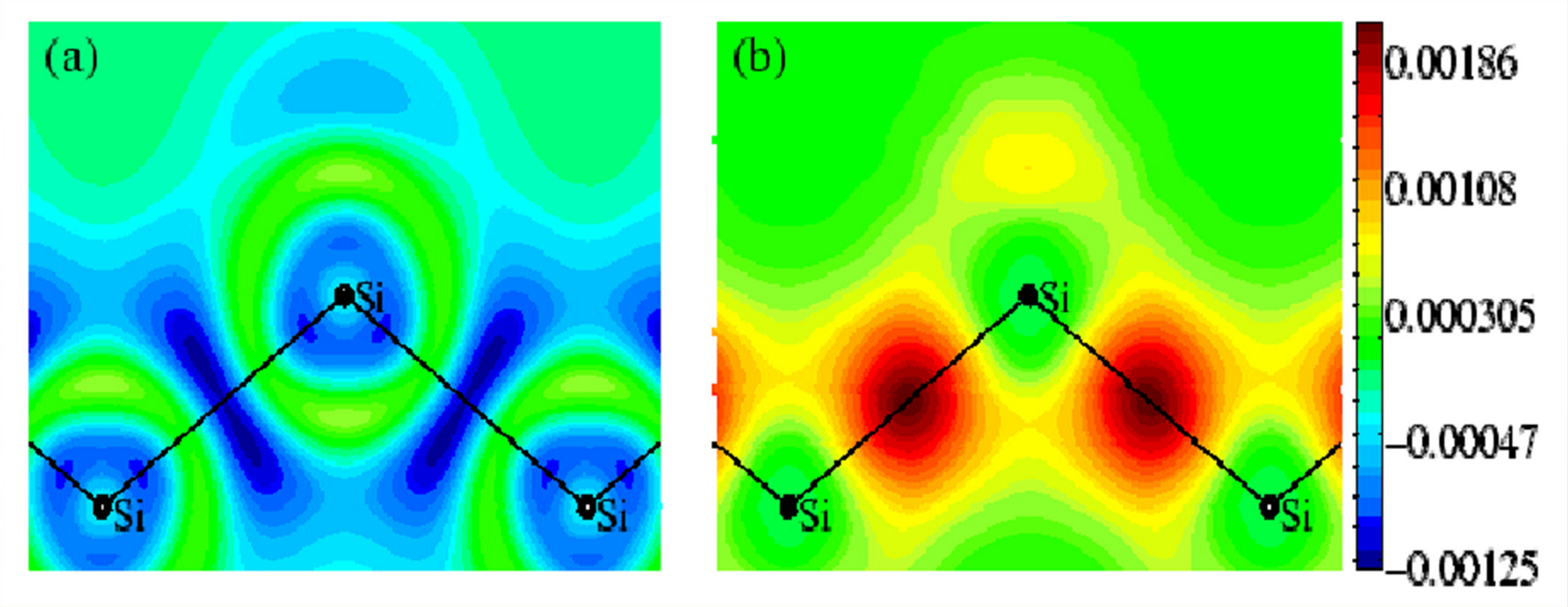
The LDA works in part because it generates a ***reasonable estimate*** *of the spherical average – despite being a* ***poor approximation*** *to the pair density!*



Why does DFT work?

*The difference between the **exact** (V-QMC) and **LDA** energy density in bulk silicon (au).*

Exchange *Correlation*



Exchange: Overestimate

Correlation: Underestimate

***Cancellation** of errors in the exchange and correlation energy densities*

Why does DFT work?

- *Exact properties of the xc-hole maintained*
- *The electron-electron interaction depends only on the spherical average of the xc-hole – this is reasonably well reproduced*
- *The errors in the exchange and correlation energy densities tend to cancel*

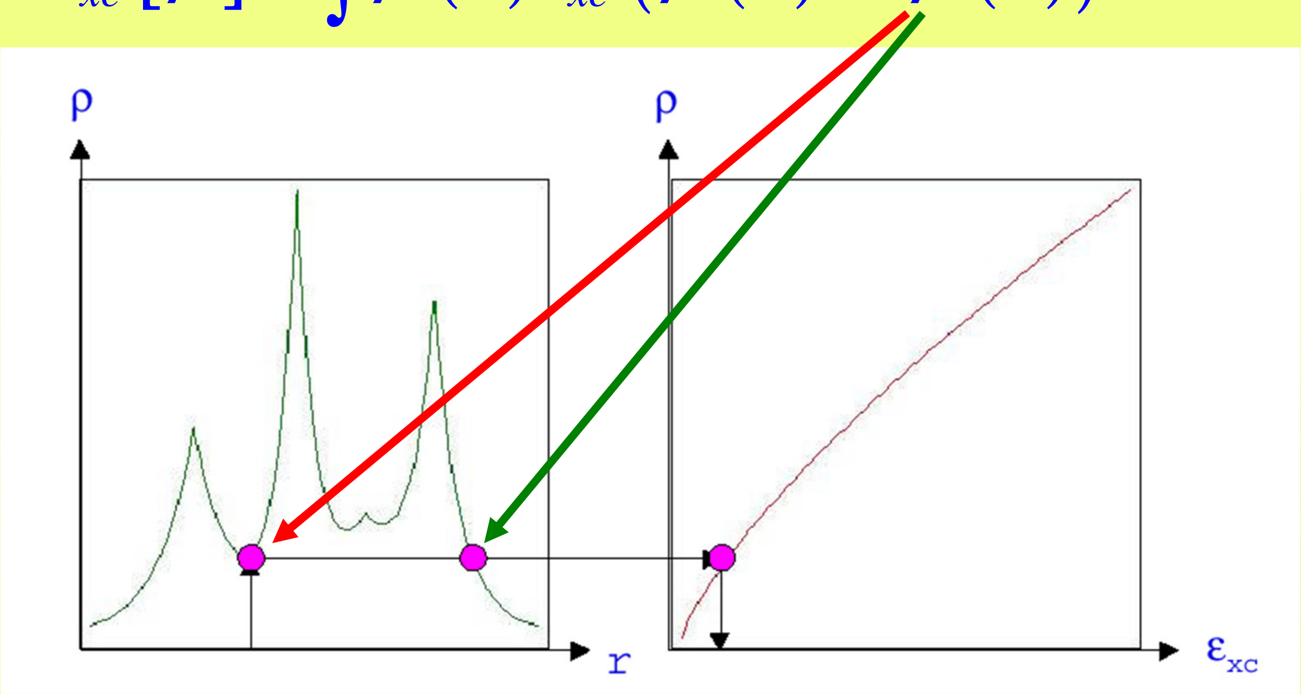
Improving on the LDA is non-trivial.

Beyond LDA

Role of Generalized Gradient Approximation (GGA)

Exchange correlation energy depends also on the gradient of the density at point **r**

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right)d\mathbf{r}$$



Two points with the same density now make different contributions to ***E_{xc}***

Beyond LDA

Families of approximations to $E_{ex}[\rho]$

LDA

$$\varepsilon_{ex}^{LDA}[\rho] = \varepsilon_{xc}\left(\rho(\mathbf{r})\right)$$

GGA

$$\varepsilon_{ex}^{GGA}[\rho] = \varepsilon_{xc}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right)$$

Meta-GGA

$$\varepsilon_{ex}^{meta}[\rho] = \varepsilon_{xc}\left(\rho(\mathbf{r}), \left|\rho(\mathbf{r})\right|, \nabla^2\rho(\mathbf{r}), \sum_i \left|\nabla\phi_i\right|^2\right)$$

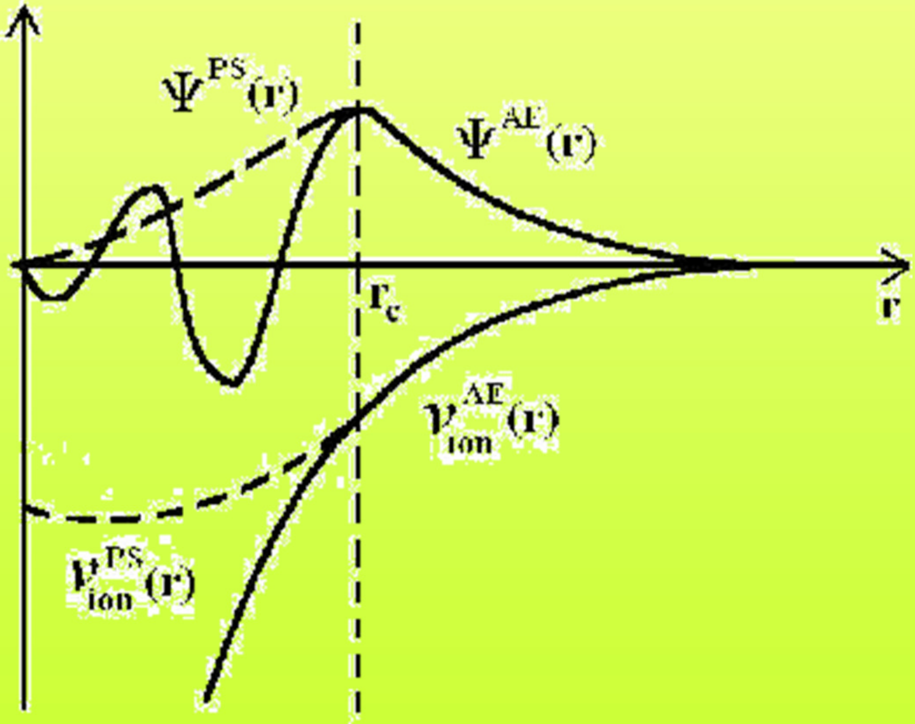
There is a host of other approximations with greater or less sophistication

Pseudopotentials

- *Plane wave basis set:* ***large number of plane waves*** *because of rapidly oscillating wavefunctions in core region (due to orthogonality requirement)*

- *Physical properties depend on* ***valence*** *electrons much more than on* ***tightly bound core*** *electrons*

Pseudopotential approximation *remove core electrons in favour of a* ***weak pseudopotential****, which acts on a set of pseudo wavefunctions rather than on the* ***true valence*** *wave functions.*



Pseudopotentials

- *Pseudopotential constructed such that there are no radial nodes inside core region.*
- *Pp and pseudo wavefunction are idential to true potential and all electron wave function outside core region*
- *Scattering properties of pseudo wavefunctions are identical to those of ion+ true wavefunction*

Norm conservation:

$$\int_0^{r_c} \left|\Psi_{AE}(r)\right|^2 d\mathbf{r} = \int_0^{r_c} \left|\Psi_{ps}(r)\right|^2 d\mathbf{r}$$

Ultrasoft Pseudopotentials

- *Norm conservation condition still leads to large number of plane waves for 2p (C,O,N) and 3d (Fe,Ni,Co,Ti) elements because of insufficient screening by core electrons.*

- *relax norm conservation and correct for it!*

  Partition total valence electron density into hard and soft contributions (Vanderbilt (1990):

$$n(\mathbf{r}) = \sum_n \left\{ |\phi_n(\mathbf{r})|^2 + \sum_{ij} Q_{ij}(\mathbf{r}) \langle \phi_n | \beta_i \rangle \langle \beta_j | \phi_n \rangle \right\}$$

β_i	***projector functions***
$Q_{ij}(r)$:	***augmentation functions***

Typically energy cut/off E_c *for ultrasoft pp´s* ***half*** *of conventional pp´s.*

Some conclusions and empirical facts

- Approximations to DFT are state of the art in materials simulation but do not provide a systematic approach to the exact result.

- With a judicious choice of functional
  - atomisation energies are typically accurate to 3-5 kcal/mole,
  - structures to 0.01 Å,
  - frequencies to 40-60 cm^{-1}.

- LDA underestimates the band gap, GGA overestimates (typically by 0.5-1 eV).

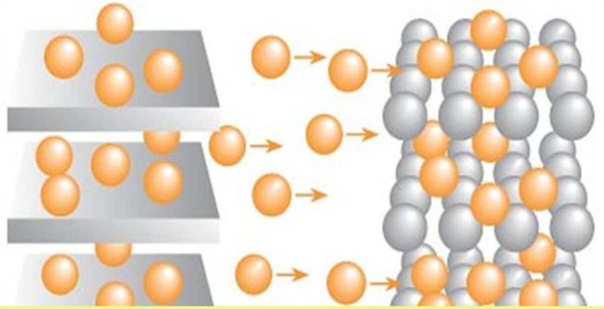
- Much larger errors are possible in “difficult” systems.

- Heavily parametrized functionals gain a little for the training set but are generally less transferrable.

Applications in sustainable energy research

- *Materials for hydrogen storage*
- *Electrode materials in Li-batteries*
- *Photovoltaics*
- *Fuel cells*
- *Electrolytes*

Intercalation compounds



Common processes:

- *Accommodation of guest-ions*
- *Accommodation of donated electron density*
- *Diffusion of guest ions*

Hydrogen storage

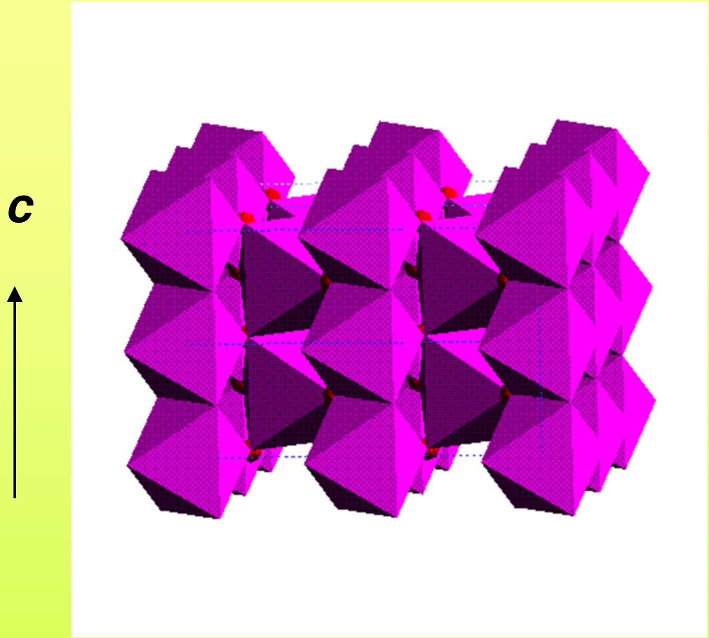
Li-rechargeable batteries

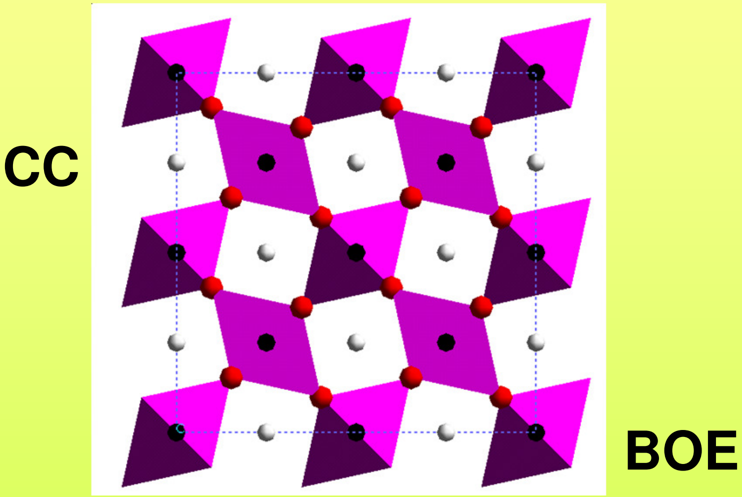
Fuel cells

Hybrid devices

Generic description of intercalation compounds

Hydrogen in rutile





Inconsistency between the geometry of either sites and OH frequency

Correlation between $\nu_{O\text{-}H}$ and r O..O

CC: 3.33 Å 3600 cm^{-1} BOE: 2.52 Å 2300 cm^{-1}

Observed: 3288 cm^{-1} ~ 2.8 Å

Experiment

IR adsorption: CC, BOE

Raman scattering: TiO_2 CC
$Al\text{-}TiO_2$ BOE

EPR: $Fe\text{-}TiO_2$ CC

Neutron diffraction:
Natural mantle TiO_2 BOE

Calculations: H in TiO_2 rutile

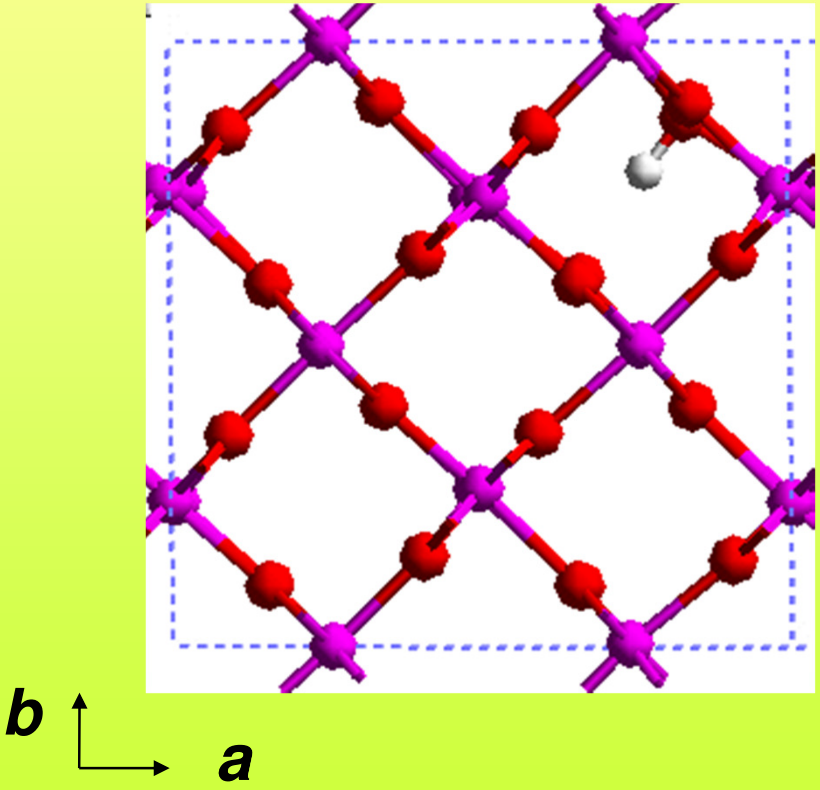
- Random H- occupation of CC-sites
- OH…O in [110]
  or [1-10]
- Modification of geometry
  of occupied sites

r O..O 2.9 Å

OH-frequency :

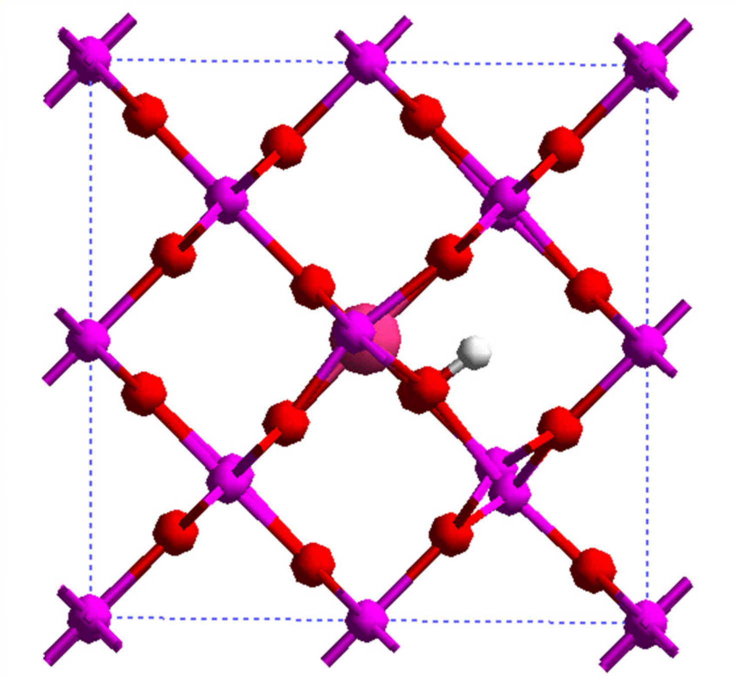
Calc: $3280\ cm^{-1}$

Exp: $3288\ cm^{-1}$



Calculations: H in doped rutile

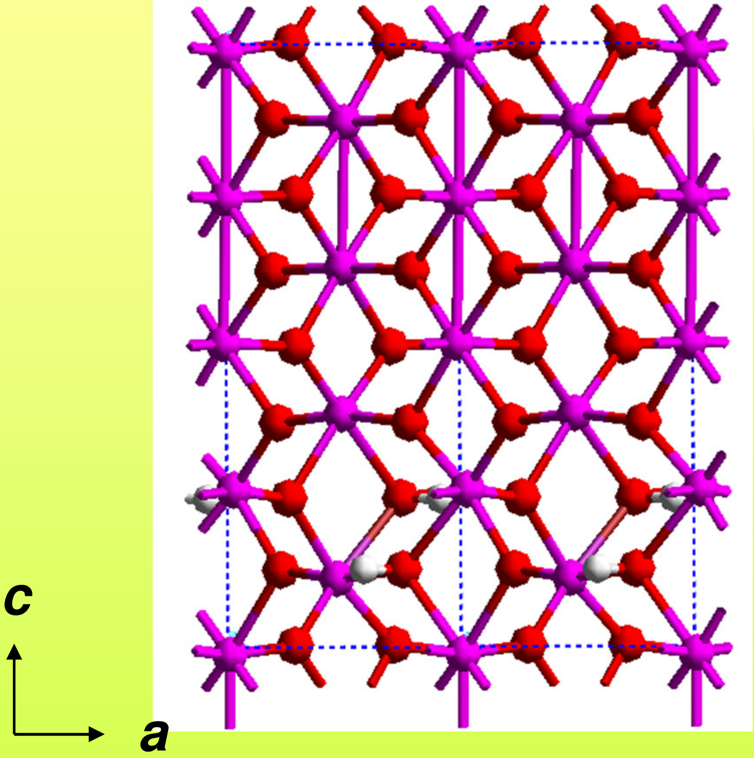
- **Preferred H- occupation of CC-sites leading to the additional symmetry element**

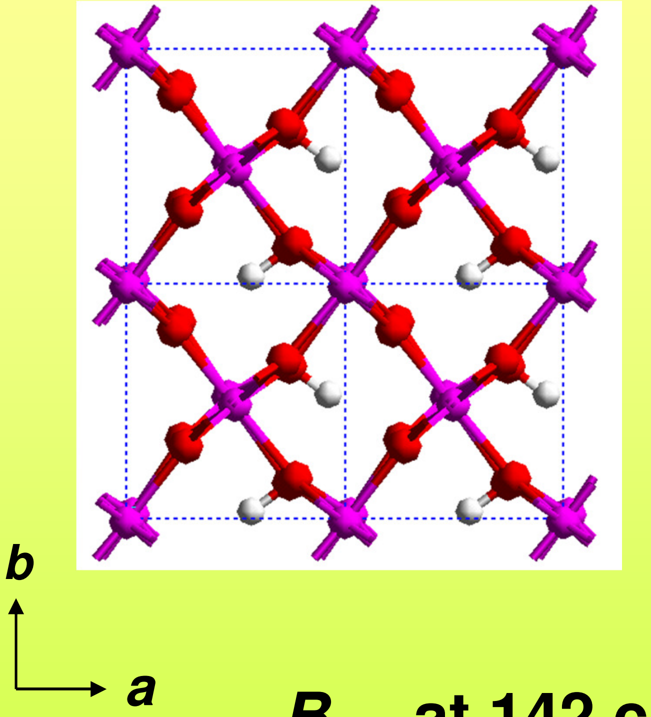


Site preference
OH…O in [110]
Al: 0.22 eV
Fe: 0.4 eV

H in Fe-rutile:
Calc: (0.54a, 0.1b, 0)
Exp: (0.56a, 0.11b, 0)

Ordering



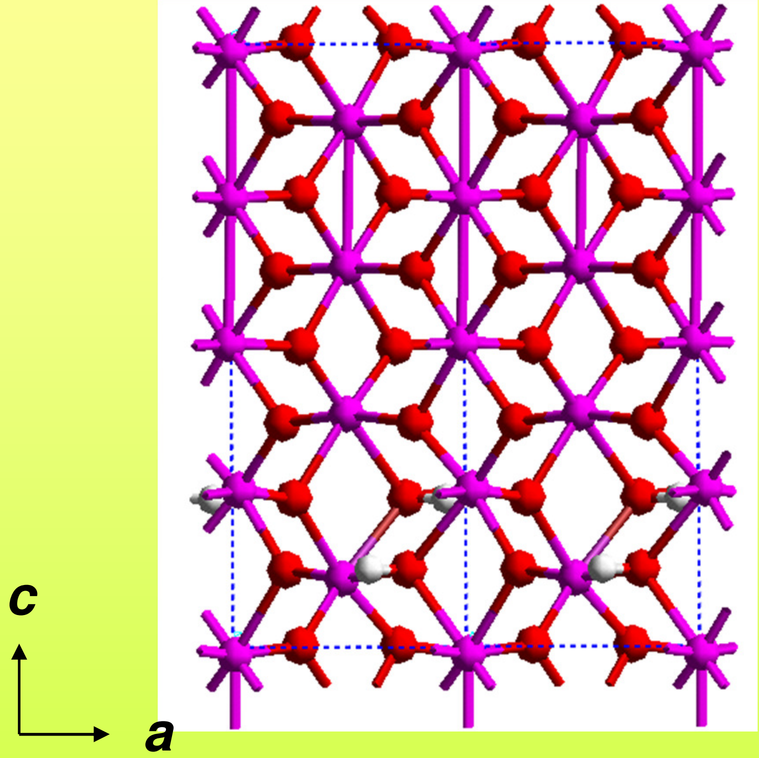


Insertion up to H/Ti=1/8
Ordering in rumpled ab-planes
separated in the *c*-direction

B_{1g} at 142 cm^{-1}

H-site:
closed in [110]
opened in [1 -10]

Ordering



Trapping mechanism:

D_c : 0.8 eV at H/Ti=1/16
1.6 eV at H/Ti=1/8

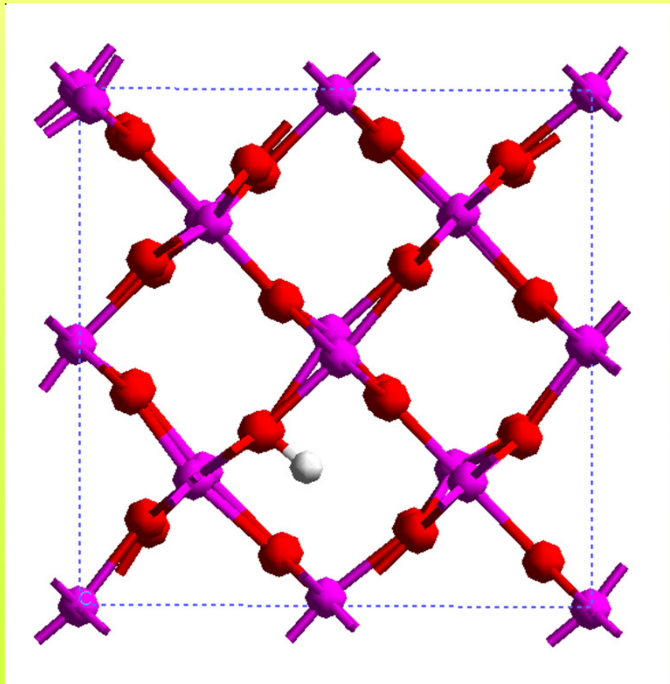
Embrittlement:

Strong elongation of the Ti-O bonds (to 2.15 Å) due to localisation of donated charge

Hydrogen in defected rutile

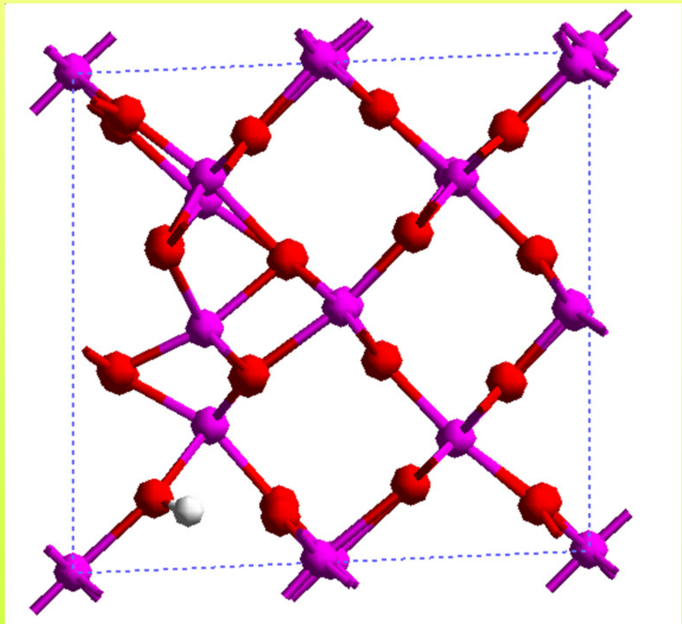
Charged vacancy

H in CC-sites



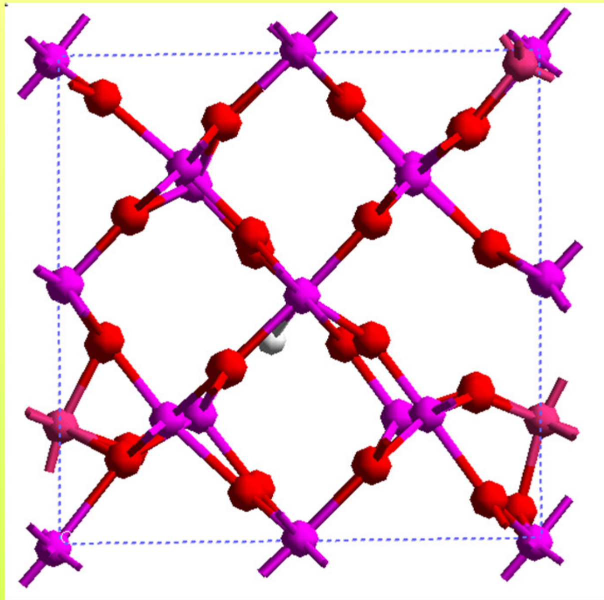
Reconstructed vacancy

H near the two-fold coordinated O



Hydrogen in defected rutile

Al-TiO_2



H near the BOE

Complex defects:

2 Al-ions sharing a face and O-vacancy as a 2nd neighbour

U.Gesenhues and T.Rentschler
J.of Solid State Chemistry
143, 210 (1999)

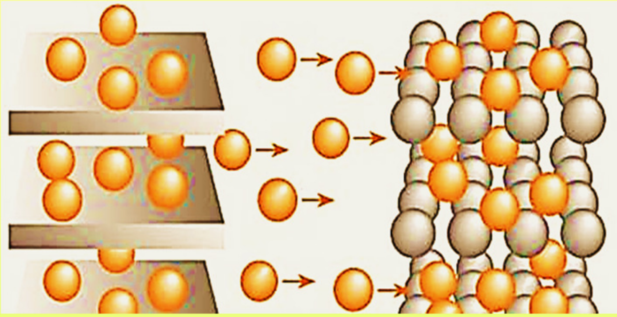
Conclusions

Ab initio simulations on hydrogen in rutile enables us

- to resolve a long standing controversy regarding the H-insertion sites in rutile and doped rutile
- to predict positions of hydrogen in doped rutile
- to show that experiments on natural samples may have no relevance to experiments on the clean laboratory samples
- To explain the mechanisms leading trapping on hydrogen in rutile and embrittlement of H-rutile
- To determine the maximum H-concentration

Mechanisms underlying intercalation of small cations in transition metal oxides

Intercalation compounds

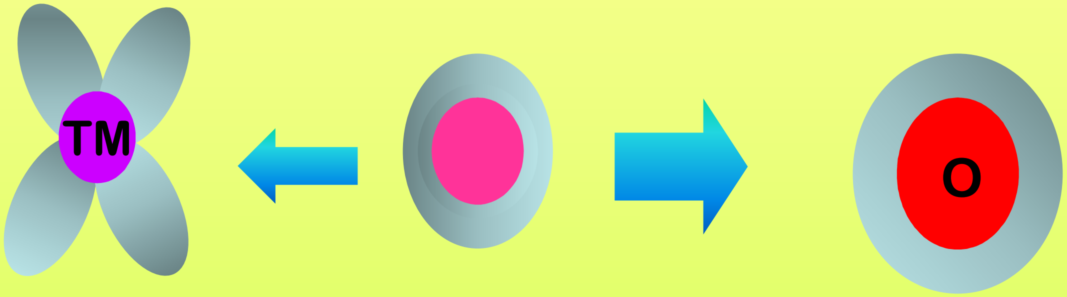


Common processes:

- *Accommodation of guest-ions*
- *Accommodation of donated electron density*
- *Diffusion of guest ions*

Generic model enabling prediction of intercalation properties from the structural motif

Key concept: Charge Transfer

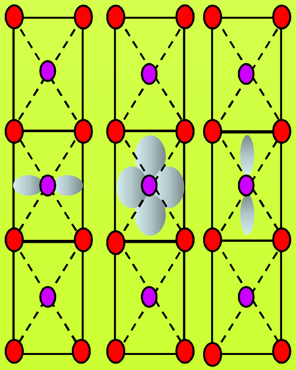


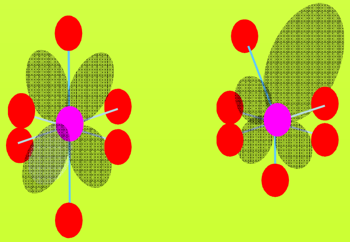
Accommodation in particular *d*-orbitals to minimise electrostatic repulsion with valence charge

Volume expansion
Mitigate size effect of Li-ions

⇩

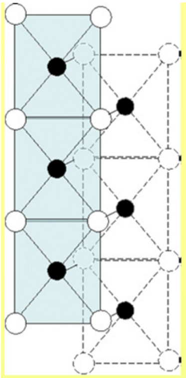
Anisotropic deformations



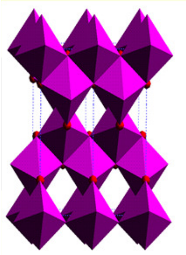


⇩

Phase transformations



Model of intercalation behaviour of TM-oxides



Edge sharing motif

d-orbitals to be occupied by donated charge

Local distortions

Anatase

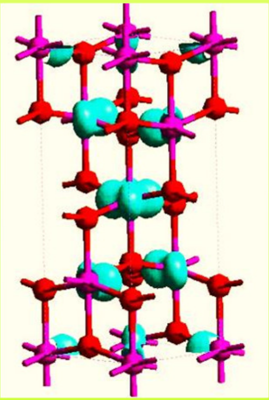
Degenerate

Cooperative distortion

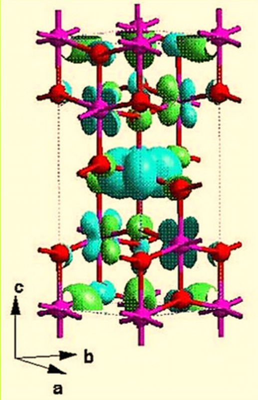
New Li-sites

Stable Li-rich phase

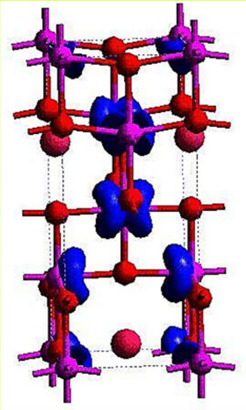
Two phase intercalation at flat potential



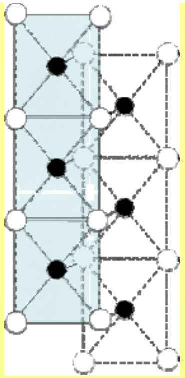
[Li]/[Ti]=0.625



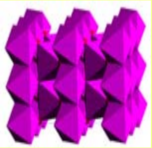
mixed state



[Li]/[Ti]=0.5



Model of intercalation behaviour of TM-oxides



Edge sharing motif

d-orbitals to be occupied by donated charge

Local distortions

Single

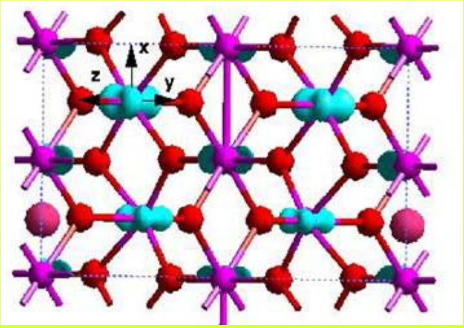
Homogeneous Intercalation at declining potential

Possible limitations by diffusion

To

Particle size

Rutile

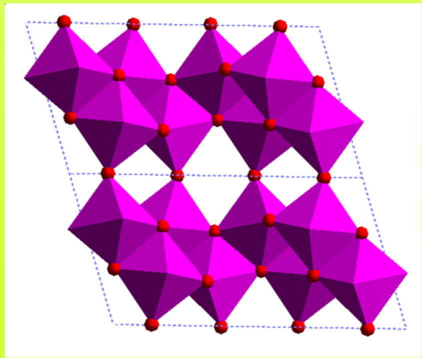


Single phase insertion: effect of nanosize

- *Enhanced diffusion: enhanced Li-uptake*
- *Structural expansion less constrained*
- *Larger single phase insertion domains*
- *Very small nanoparticles: single phase insertion (except electron rich systems)*
- *Different phase behaviour for specially tailored nanoparticles*

Applications of the model

- *Rationalise observed behaviour*
- *Suggest when going "nano" is beneficial*
- *Pre-screening of potential electrode materials and hypothetical structures*
- *Prediction of new phases and reactions*
- *Tuning intercalation properties*



TiO2(B)

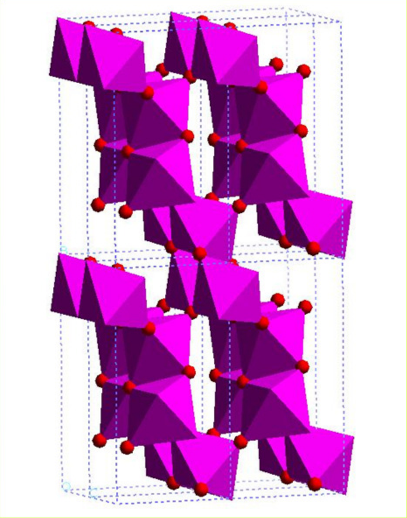
Highest Li uptake 1.25 Li-Ti

Ramsdellite

$Li_{0.5}TiO_2 \longleftrightarrow LiTiO_2$

1.25 eV

Experiment: 1.3 eV



Conclusions

- *Ab initio simulations helps to understand intercalation behaviour of transition metal oxides in their polycrystalline and nano-form, an to predict some new morphiologies with superior properties*
- *Tomorrow we will consider applications of ab initio modelling combined with statistical treatment of the system to some other classes of materials*