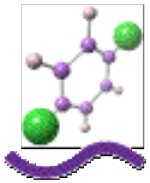
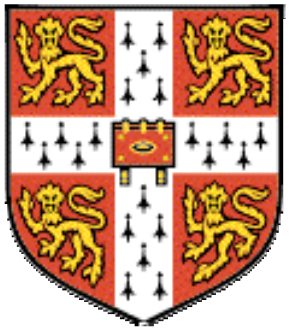


National Institute for
Environmental *e*Science
UNIVERSITY OF CAMBRIDGE AND
NATURAL ENVIRONMENT RESEARCH COUNCIL

Summer school 2002
Linear-scaling ab initio molecular
modelling of environmental processes

FUNDAMENTALS
The quantum-mechanical many-electron problem and Density Functional Theory



Emilio Artacho

Department of Earth Sciences
University of Cambridge

First-principles calculations

- *Fundamental laws of physics*
- *Set of "accepted" approximations to solve the corresponding equations on a computer*
- *No empirical input*

PREDICTIVE POWER

Artillery

$F = m\,a$

Approximations

- *Flat Earth*
- *Constant g*

(air friction: phenomenological)

Fundamental laws for the properties of matter at low energies

Atomic scale (chemical bonds etc.)

Yes BUT

Electrons and nuclei

(simple Coulomb interactions)

=> Quantum Mechanics

$$\hat{H}\Psi(\{\vec{r}_i\}) = E\Psi(\{\vec{r}_i\})$$

Many-particle problem

Schroedinger's equation is exactly solvable for

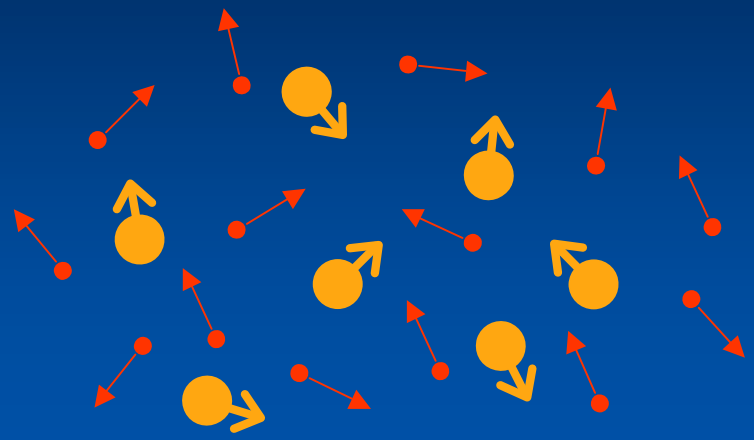
- *Two particles (analytically)*
- *Very few particles (numerically)*

The number of electrons and nuclei in a pebble is $\sim 10^{23}$

$$\hat{H}\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = E\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$$

=> APPROXIMATIONS

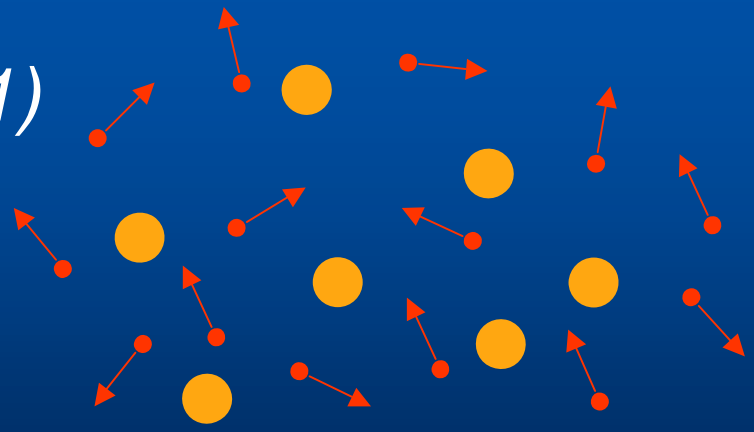
Born-Oppenheimer



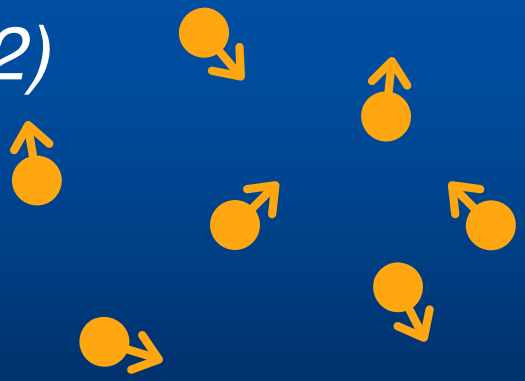
$$\frac{m_n}{m_e} >> 1$$

- *Nuclei are much slower than electrons*

(1)



(2)



electronic/nuclear decoupling

$$\hat{H} = -\sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 - \sum_{i} \frac{1}{2} \nabla_i^2 + \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_{i,\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{\alpha,\beta>\alpha} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}}$$

electrons

$$\hat{H}^{el}_{\{\vec{R}_{\alpha}\}} = -\sum_{i} \frac{1}{2} \nabla_i^2 + \sum_{i,j>i} \frac{1}{r_{ij}} + V^{ext}_{\{\vec{R}_{\alpha}\}}(\{\vec{r}_i\})$$

$$\hat{H}^{el}_{\{\vec{R}_{\alpha}\}} \Psi^{el}_{n,\{\vec{R}_{\alpha}\}}(\{\vec{r}_i\}) = E^{el}_n(\{\vec{R}_{\alpha}\}) \Psi^{el}_{n,\{\vec{R}_{\alpha}\}}(\{\vec{r}_i\})$$

nuclei

$$\hat{H} = -\sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 + E^{el}_n(\{\vec{R}_{\alpha}\})$$

Classical =>

$$\vec{F}_{\alpha} = \frac{\partial}{\partial \vec{R}_{\alpha}} E^{el}_0(\{\vec{R}_{\alpha}\})$$

Many-electron problem

Old and extremely hard problem!

Different approaches

- *Quantum Chemistry (Hartree-Fock, CI…)*
- *Quantum Monte Carlo*
- *Perturbation theory (propagators)*
- *Density Functional Theory (DFT)*

Very efficient and general

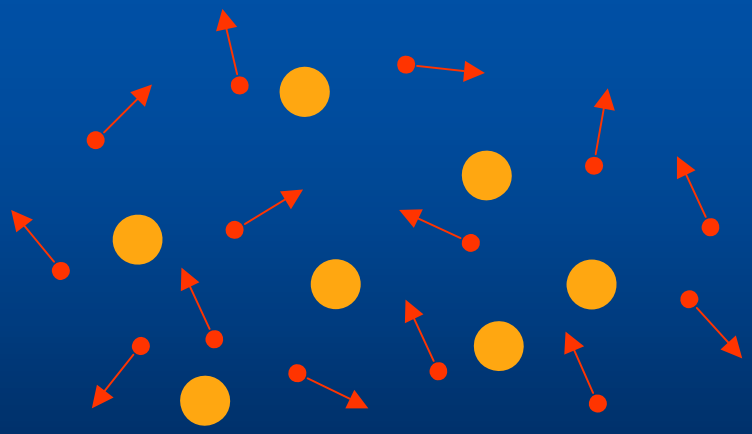
BUT implementations are approximate and hard to improve (no systematic improvement)

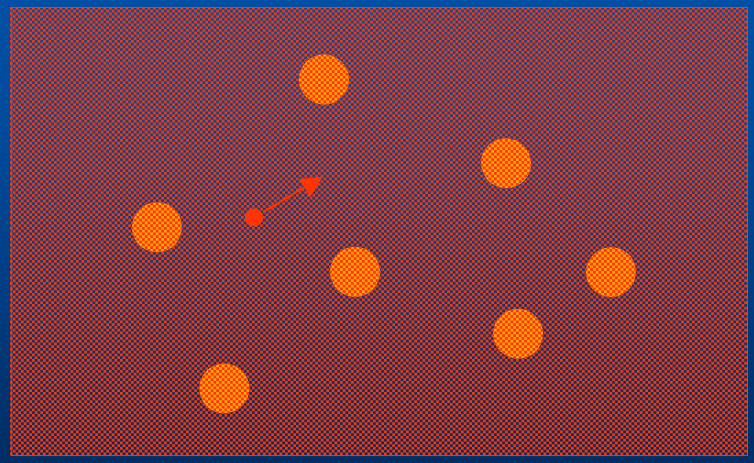
(… actually running out of ideas …)

Density-Functional Theory

1. $\Psi(\{\vec{r}_i\}) \Leftrightarrow \rho(\vec{r})$ *particle density*

2. *As if non-interacting electrons in an effective (self-consistent) potential*





Hohenberg - Kohn

$$\Psi(\{\vec{r}_i\}) \Rightarrow \rho(\vec{r})$$

For our many-electron problem $\hat{H} = T + V_{ee} + \sum_{i=1}^{N} V_{ext}(\vec{r}_i)$

1. $E[\rho(\vec{r})] \equiv \int d^3\vec{r}\, V_{ext}(\vec{r})\,\rho(\vec{r}) + F[\rho(\vec{r})] \geq E_{GS}$

(depends on nuclear positions)

(universal functional)

2. $E[\rho_{GS}(\vec{r})] = E_{GS}$

PROBLEM:
Functional unknown!

Kohn - Sham

Independent particles in an effective potential

They rewrote the functional as:

$$E[\rho] = T_0[\rho] + \int d^3\vec{r}\,\rho(\vec{r})\left[V_{ext}(\vec{r}) + \tfrac{1}{2}\Phi(\vec{r})\right] + E_{xc}[\rho]$$

Kinetic energy for system with no e-e interactions

Hartree potential

The rest: exchange correlation

Equivalent to independent particles under the potential

$$V(\vec{r}) = V_{ext}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}$$

E_{xc} & V_{xc}

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

Local Density Approximation (LDA)

$$V_{xc}[\rho] \approx V_{xc}(\rho(\vec{r}))$$

(function parameterised for the homogeneous electron liquid as obtained from QMC)

Generalised Gradient Approximation (GGA)

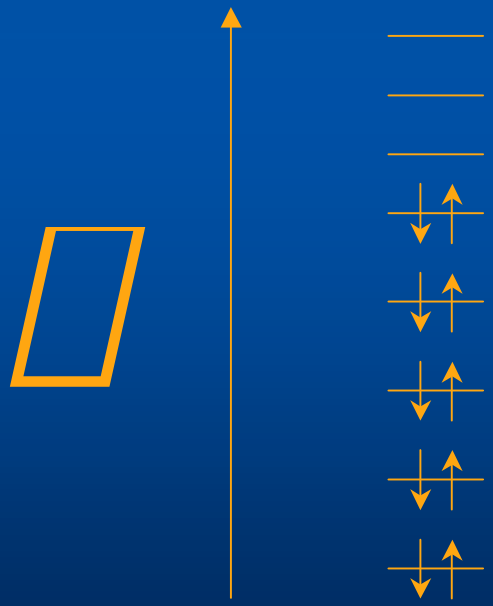
$$V_{xc}[\rho] \approx V_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

(new terms parameterised for heterogeneous electron systems (atoms) as obtained from QC)

Independent particles

$$\hat{h} = -\frac{1}{2}\nabla^2 + V(\vec{r})$$

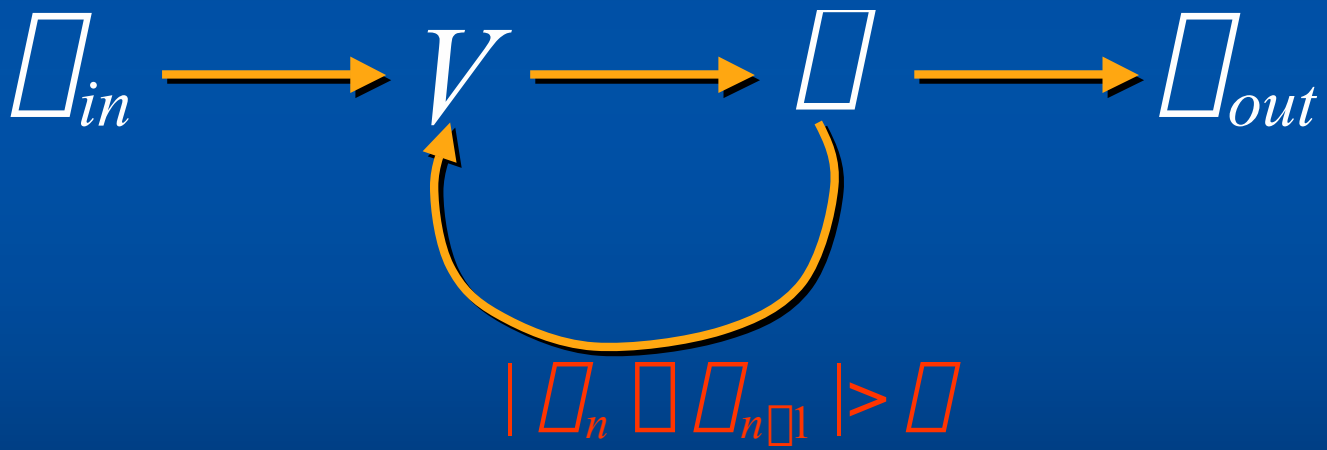
$$\hat{h}\phi_n(\vec{r}) = \varepsilon_n \phi_n(\vec{r})$$



$$\rho(\vec{r}) = \sum_{n}^{occ} |\phi_n(\vec{r})|^2$$

Self-consistency

PROBLEM: The potential (input) depends on the density (output)



Solving: 1. Basis set

$$\psi_n(\vec{r}) = \sum_\alpha c_{\alpha n}\phi_\alpha(\vec{r})$$

unknown

Expand in terms of a finite set of known wave-functions $\phi_\alpha(\vec{r})$

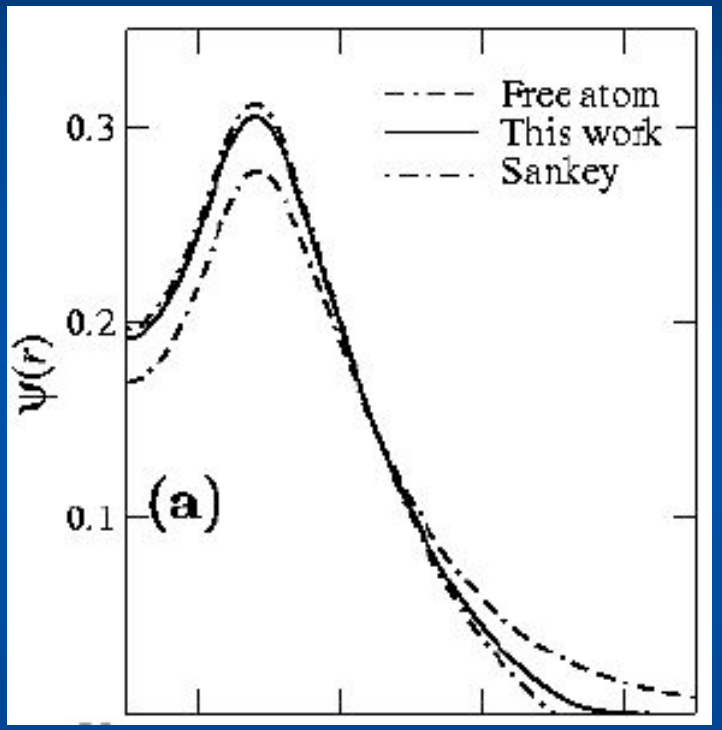
$$\hat{h}\psi_n(\vec{r}) = \varepsilon_n\psi_n(\vec{r}) \longrightarrow \sum_\alpha c_{\alpha n}\hat{h}\phi_\alpha(\vec{r}) = \varepsilon_n\sum_\alpha c_{\alpha n}\phi_\alpha(\vec{r})$$

Def $h_{\alpha\beta} \equiv \int \phi_\alpha^*(\vec{r})\hat{h}\phi_\beta(\vec{r})d^3\vec{r}$ and $S_{\alpha\beta} \equiv \int \phi_\alpha^*(\vec{r})\phi_\beta(\vec{r})d^3\vec{r}$

$$\sum_\beta h_{\alpha\beta}c_{\beta n} = \varepsilon_n\sum_\beta S_{\alpha\beta}c_{\beta n}$$

$$\underset{\sim}{H}\mathbf{C}_n = \varepsilon_n\underset{\sim}{S}\mathbf{C}_n$$

Basis set: Atomic orbitals



Strictly localised

(zero beyond cut-off radius)

Solving: 2. Boundary conditions

- *Isolated object (atom, molecule, cluster):*
  open boundary conditions
  (defined at infinity)

- *3D Periodic object (crystal):*
  Periodic Boundary Conditions

- *Mixed: 1D periodic (chains)*
  2D periodic (slabs)

k-point sampling

Electronic quantum states in a periodic solid labelled by:

- *Band index*
- *k-vector: vector in reciprocal space within the first Brillouin zone (Wigner-Seitz cell in reciprocal space)*
- *Other symmetries (spin, point-group representation…)*

$$\rho(\vec{r}) = \sum_{n}^{occ} |\psi_n(\vec{r})|^2 \int_{\vec{k}\in B.Z} d^3\vec{k}$$

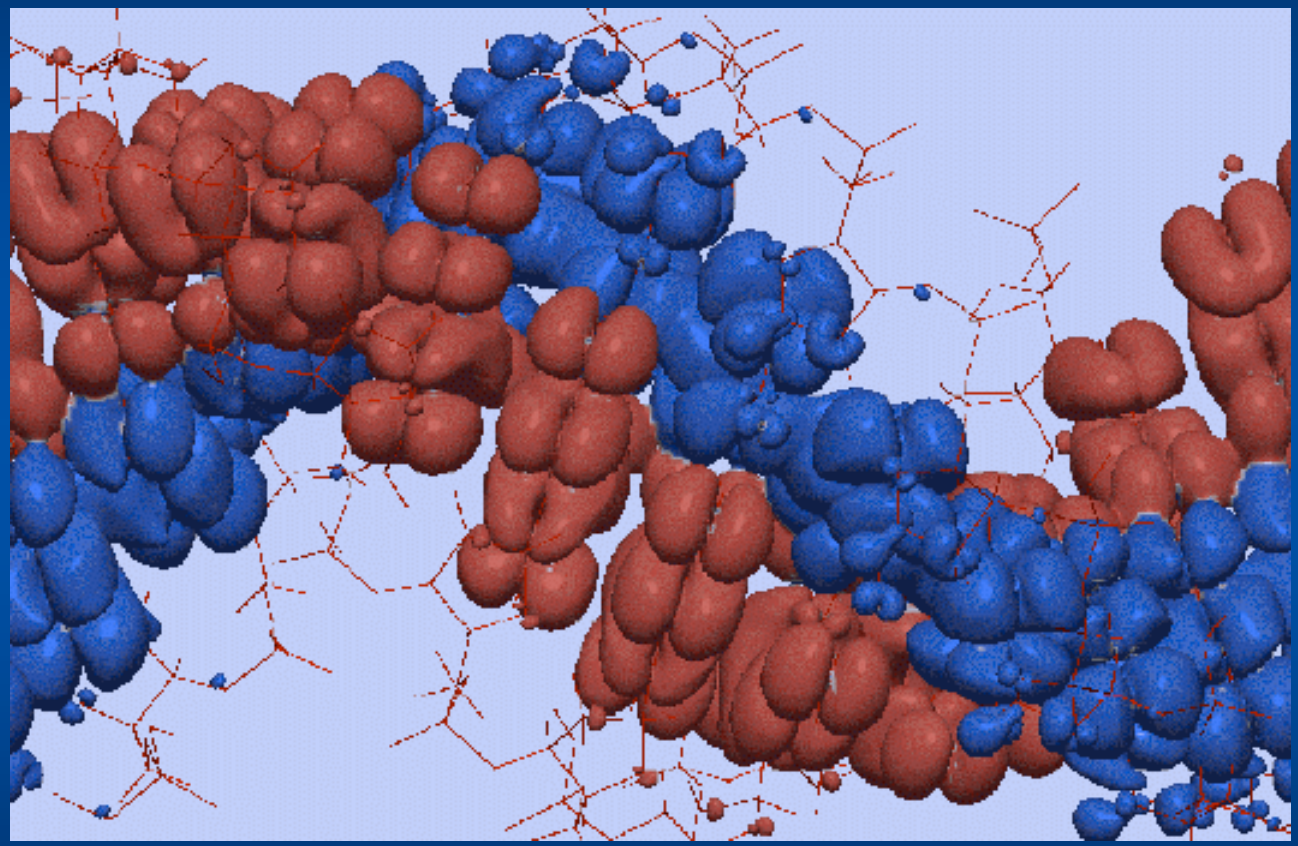
Approximated by sums over selected k points

Some materials' properties

		Exp.	LAPW	Other PW	PW	DZP
	a (Å)	3.57	3.54	3.54	3.53	3.54
C	B (GPa)	442	470	436	459	453
	E_c (eV)	7.37	10.13	8.96	8.89	8.81
	a (Å)	5.43	5.41	5.38	5.38	5.40
Si	B (GPa)	99	96	94	96	97
	E_c (eV)	4.63	5.28	5.34	5.40	5.31
	a (Å)	4.23	4.05	3.98	3.95	3.98
Na	B (GPa)	6.9	9.2	8.7	8.7	9.2
	E_c (eV)	1.11	1.44	1.28	1.22	1.22
	a (Å)	3.60	3.52	3.56	-	3.57
Cu	B (GPa)	138	192	172	-	165
	E_c (eV)	3.50	4.29	4.24	-	4.37
	a (Å)	4.08	4.05	4.07	4.05	4.07
Au	B (GPa)	173	198	190	195	188
	E_c (eV)	3.81	-	-	4.36	4.13

Absence of DC conductivity in -DNA

P. J. de Pablo *et al. Phys. Rev. Lett.* 85, 4992 (2000)

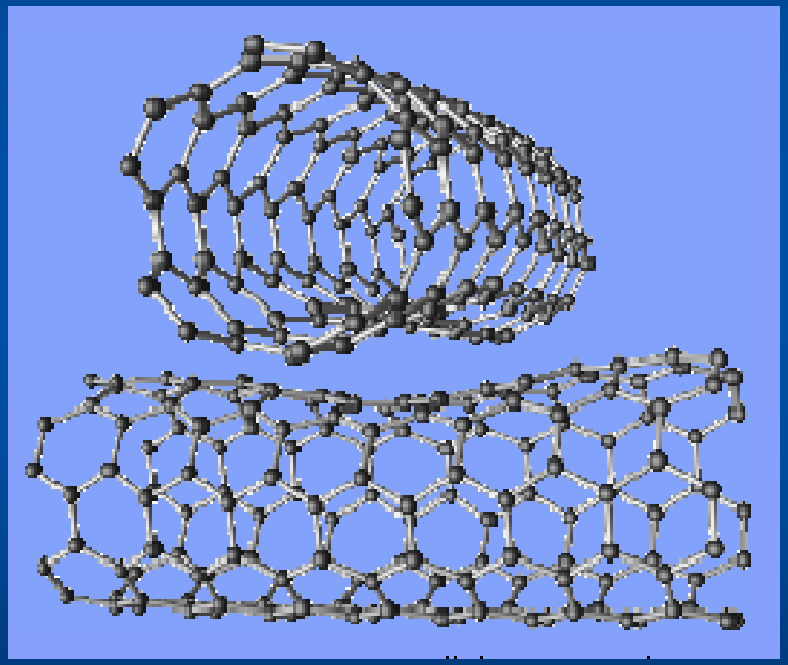


Effect of sequence disorder and vibrations on the electronic structure

=> Band-like conduction is extremely unlikely: ***DNA is not a wire***

Pressing nanotubes for a switch

Pushed them together, relaxed &
calculated conduction at the contact: SWITCH



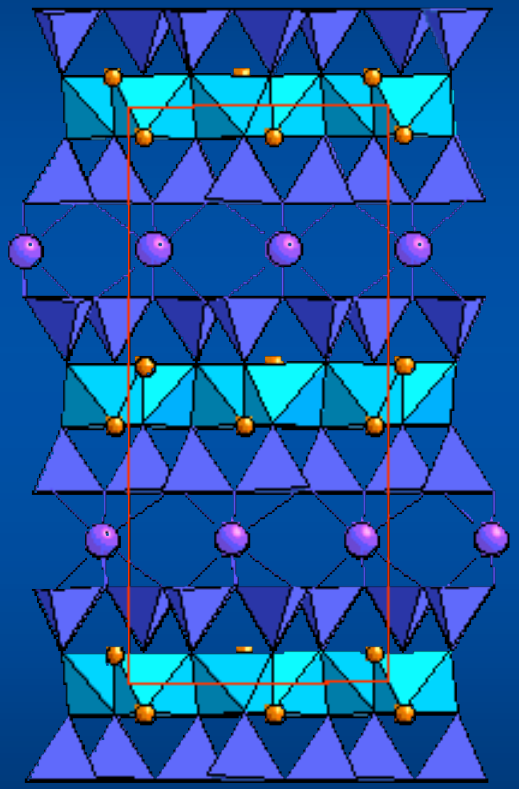
M. Fuhrer *et al.* *Science* *288, 494 (2000)*

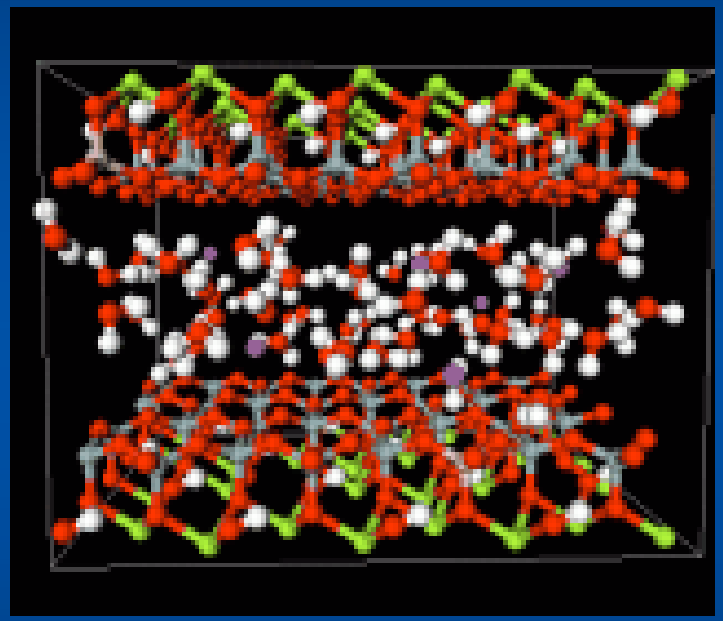
Y.-G. Yoon *et al. Phys. Rev. Lett. 86, 688 (2001)*

Pyrophyllite, illite & smectite

Structural effects of octahedral cation substitutions

C. I. Sainz-Diaz *et al.* (American Mineralogist, 2002)





WET SURFACES

Organic molecules intercalated between layers

M. Craig *et al.* (Phys. Chem. Miner. 2002)

Recap

- *Born-Oppenheimer: electron-nuclear decoupling*
- *Many-electron -> DFT (LDA, GGA)*
- *One-particle problem in effective self-consistent potential (iterate)*
- *Basis set => Solving in two steps:*
    1. *Calculation of matrix elements of H and S*
    2. *Diagonalisation*
- *Extended crystals: PBC + k sampling*