Introduction

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Force-fields (equivalent term: potentials) are commonly used in simulations. These are generally fine, but may sometimes lead to insufficiently precise, or even qualitatively wrong results. Here are popular choices:

$$V_{\mathrm{LJ}}(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{C}{r_{ij}^{6}}$$

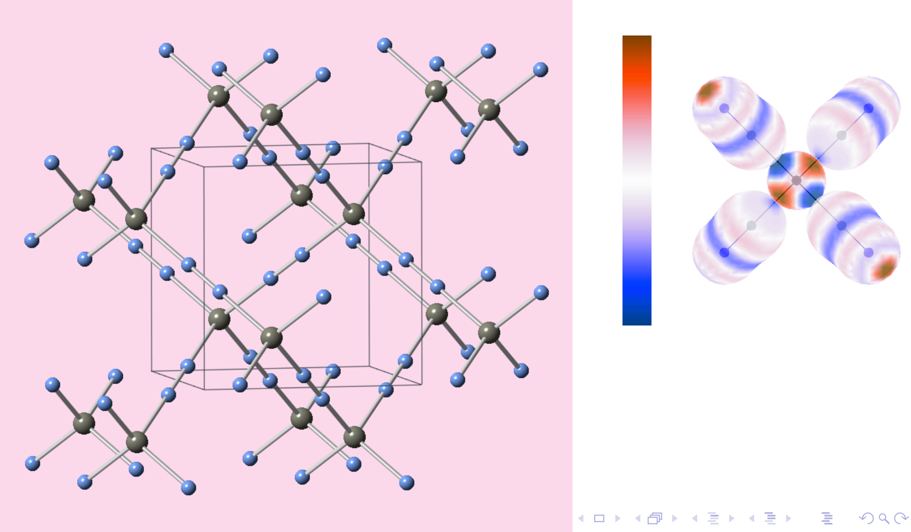
$$V_{\mathrm{exp6}}(r_{ij}) = e^{-\alpha(r_{ij}-\rho_{ij})} - \frac{C_6^{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}$$

- ‘spherical’ atoms
- simple electrostatic models
- ‘static’ potentials

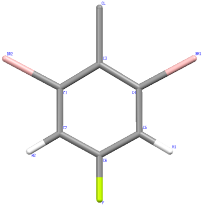
How do we go beyond the limitations of empirical potentials?

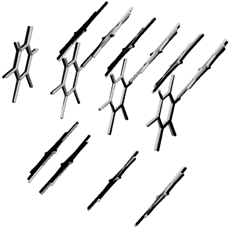
Are point-charges good enough? **Insert fig from Danny Cole (Newcastle)**

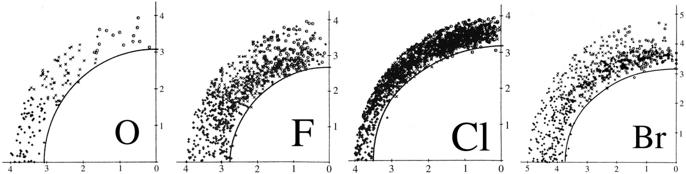
Point charges?: Metal-organic frameworks.



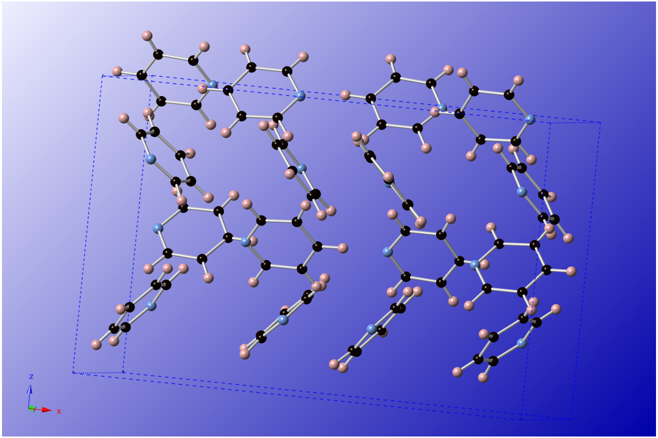
Are atoms spherical?

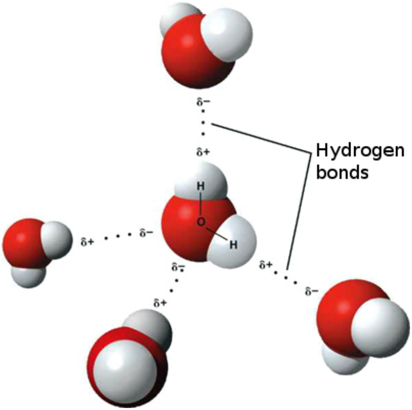


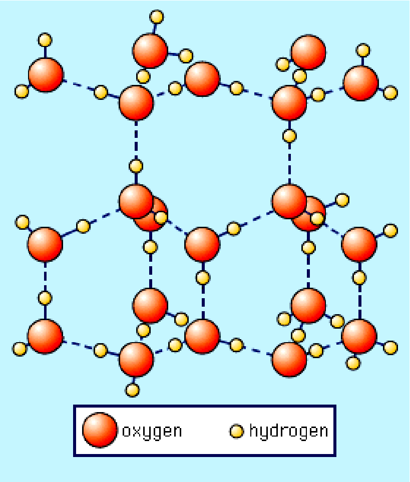




Going beyond static potentials: In systems with strong permanent moments and polarizabilities (water is a good example) the effects of *polarization* and *charge-transfer* can be very important. This introduces a dynamical effect to the potential: it now needs to respond to the *environment*.




δ−
δ+
Hydrogen bonds
H
O
H
δ+
δ−
δ−
δ+
δ+
δ−


oxygen
hydrogen

So we might want to use *many-body* potentials of the form:

$$\begin{aligned} V_{MB}(r_{ij}) = {} & e^{-\alpha(r_{ij}-\rho_{ij}(\Omega))} \\ & - f_6(\beta r_{ij})\frac{C_6^{ij}}{r_{ij}^6} - f_8(\beta r_{ij})\frac{C_8^{ij}}{r_{ij}^8}\cdots \\ & + Q^i_{lm} T^{ij}_{lm,l'm'} Q^j_{l'm'} \\ & + \{\alpha^i_{lm,l'm'}, Q^i_{lm}, \forall i\} \end{aligned}$$

Q: Where do we get the data to develop all these extra terms?
Q: How do we account for bond-breaking and many-body charge transfer?
Q: What about correlation in semi-metallic systems with plasmon modes?

Other reasons for *ab initio* data:

- Comformations used by complex molecules
- Bond-making/breaking
- No experimental data available to parameretize potentials in region of phase-space (simulations of matter under extreme or unusual conditions (see next example).
- Complex electronic excitations coupled with dymanics: charge (electron or proton) transfer. Lots of chaps in UCL doing this sort of thing theoretically and a number here in QM studying such processes experimentally.

AIRSS I

Matter under extreme conditions: Ab initio random structure searching (AIRSS) of Chris Pickard and Richard Needs.

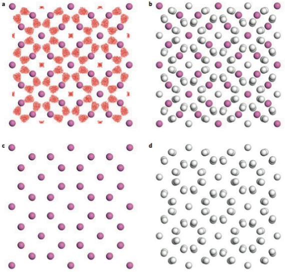


Figure 2 | Host-guest structures. a, The Al16 host-guest structure pictured along the axis of the guest chains, as obtained from density functional theory calculations. The guest atoms are at the centres of the octagonal rings. The red areas show the valence charge density above 65% of its maximum value. **b**, A structure obtained from random structure searching with simple pairwise potentials describing the interactions between 16 'Al' atoms (purple) and 28 'electron' blobs (white). **c**, The positions of the purple 'Al' ions from **b**, which gives a good approximation to the Ba-IV structure. **d**, The white 'electron' blobs from **b**, which give a good approximation to the Rb-IV structure.

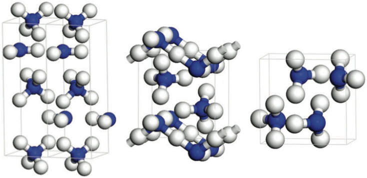
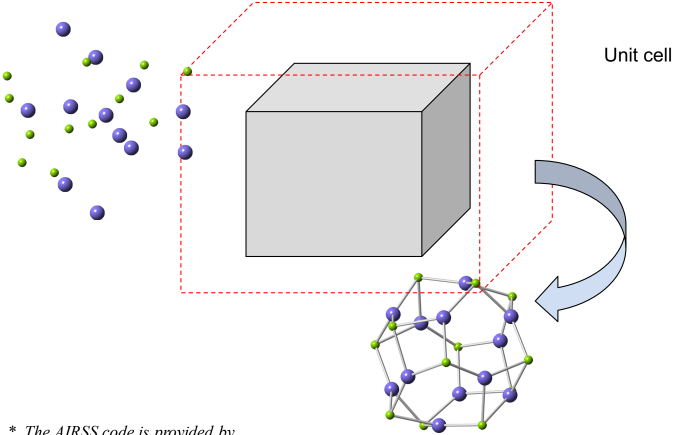


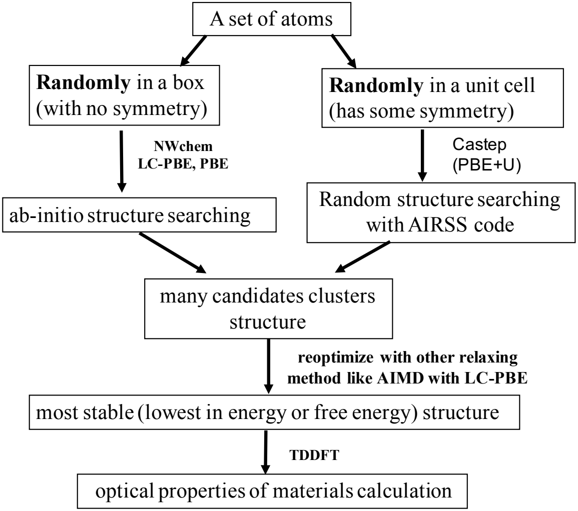
Figure 3 The *Pma*2, *P*2$_1$ / *m* and *Pnma* structures. The white spheres indicate hydrogen atoms and the blue spheres nitrogen atoms. The *Pma*2 structure (shown at 100 GPa) was calculated to be stable in the pressure range 90–331 GPa. It consists of alternate layers of approximately tetrahedral NH_4^+ ions and approximately right-angled NH_2^- ions. The NH_2^- ions are efficiently packed in a square-planar array, with the H atoms pointing towards the N atoms of neighbouring NH_2^- ions. The NH_4^+ ions are arranged in a square-planar array that is commensurate with the NH_2^- layers. The *P*2$_1$ / *m* structure (shown at 300 GPa) is stable in the range 331–440 GPa and consists of buckled NH_4^+ and NH_2^- layers with some symmetric hydrogen bonding between NH_2^- ions. The *Pnma* structure (shown at 450 GPa), calculated to be stable above 440 GPa, is a dense molecular phase. As shown in Fig. 1, this phase is quite competitive with the other molecular phases at low pressures.

AIRSS



* *The AIRSS code is provided by*
C. J. Pickard and R. J. Needs, Physical Review Letters 97, 1 (2006),
C. J. Pickard and R. J. Needs, Nature Materials 9, 624 (2010).

Schematic



A set of atoms

Randomly in a box (with no symmetry)

Randomly in a unit cell (has some symmetry)

NWchem LC-PBE, PBE

Castep (PBE+U)

ab-initio structure searching

Random structure searching with AIRSS code

many candidates clusters structure

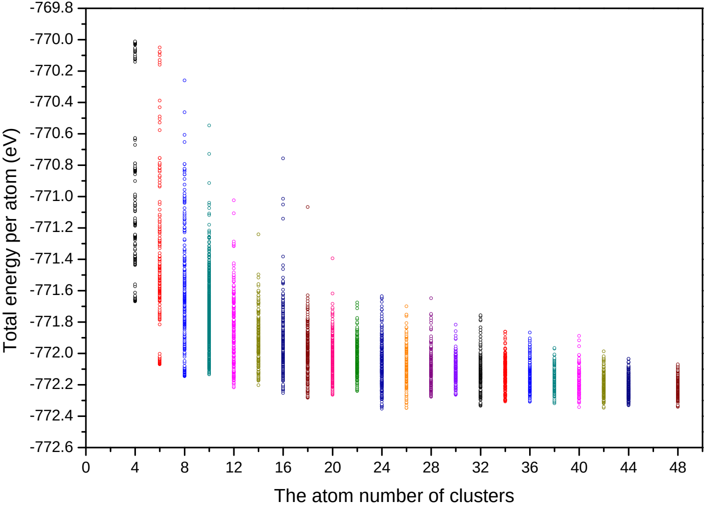
reoptimize with other relaxing method like AIMD with LC-PBE

most stable (lowest in energy or free energy) structure

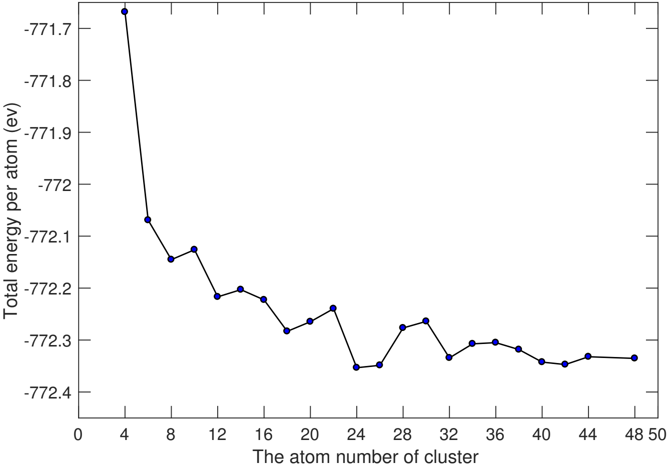
TDDFT

optical properties of materials calculation

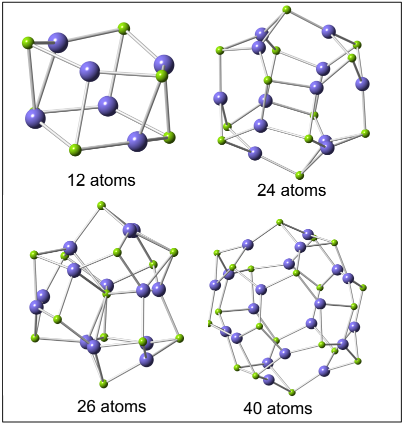
CdSe clusters I



CdSe clusters II



CdSe clusters III



12 atoms

24 atoms

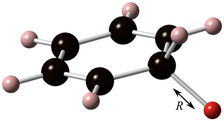
26 atoms

40 atoms

Other examples I

Muon spectroscopy

: Probing local magnetic fields using muons.



- Muons are about 10 times lighter than a proton.
- They capture an electron forming a hydrogen-like atom called muonium.
- Bind to a site.
- The muon precesses in the local magnetic field.
- The precession influences the decay process and hence can be used to measure the local field.

Electronic structure methods I

- Single-determinant methods: Hartree–Fock (HF), Density functional theory (DFT), Moller-Plesset perturbation theory at various orders (MP2, MP3, MP4,...), Configuration interaction (CI), Coupled-cluster methods (CCSD, CCSD(T), CCSDT,...), Full-configuration interaction (FCI)
- Multi-configutation methods: MCSCF, MRCI, ...
- Basis sets: STO-3G, 6-31G, 6-31G*, aug-cc-pVDZ, aug-cc-pVTZ, ...
- Programs: Castep, DALTON, **NWChem, Psi4**, ADF, Molpro, Gaussian, Onetep, CamCASP, SAPT2008,...

Q: What do all of these mean?

Q: How do we choose the appropriate method/basis/program?

Electronic structure methods II

- Properties of the exact wavefunctions
- The Variational Method
    - Hückel Theory (Tight-Binding)
- Second-Quantization
- Survey of wavefunction methods with simple examples.
- Hartree–Fock (HF) Theory
- Post-HF methods: CI, CC, MBPT
- Density-Functional Theory (DFT)
    - Failures of DFT: van der Waals
    - Failures of DFT: Charge-Transfer
- Intermolecular perturbation theory
- Fixes for DFT

Electronic structure methods III

- We will study all of these topics while exploring them numerically using the NWCHEM and (maybe) CAMCASP programs.
- Our aim will be to apply these techniques to a variety of systems, and to develop a deep understanding of these methods in the context of a recent research.
- We will attempt to match what we learn theoretically with numerical experiments.

Electronic structure methods IV

Marking:

- Homework: 20%. Will be given weekly and collected the following week. Important problems will be discussed in the class.
- Lab work: 20% of your mark will be based on your laboratory work performed during the course of the semester. You will maintain a laboratory book for this purpose. At the end of each lab session, a few (one to three) items of work will be expected from you. Your mark will be based on this work and on the overall quality of your lab book.
- Exam: 60% of your mark will be a written exam.

Electronic structure methods V

References:

- *Molecular Electronic Structure Theory*, Helgaker, Olsen, Jorgensen.
- *Modern Quantum Chemistry*, Szabo & Ostlund.
- *Density functional theory of atoms and molecules*, Parr and Yang
- *Time-dependent density functional theory*, Carsten Ulrich
- *Many-Body Methods in Chemistry and Physics*, Shavitt and Bartlett.
- *Introduction to computational chemistry*, Jensen.

Electronic structure methods VI

Class preparation:

- *Homework*: You will be expected to come up and solve problems! Homework will be collected at the *start* of the class.
- *Reading assignments*: These will be mainly from the book by Szabo & Ostlund, but will also include research papers and other reference books. You are expected to come prepared.
- *YouTube tutorials*: I will assign YouTube lectures prepared by colleagues. You will be expected to watch these. Some of the class discussions and homework will be based on these tutorials.
- *Lab work*: Not all lab work needs to be done in the laboratory. At times you will be asked to complete some numerical calculations before the lecture.

Electronic structure methods VII

Office and office hours:

- Office: 216 GOJ
- Hours: Monday 1pm to 2pm and Wednesdays 2pm to 3pm.

Use the office hours to get suggestions for your homework and assignments!

Electronic structure methods VIII

Computing:

- We will be using the computers in the second-floor teaching lab to connect to our computational workstations.
- The working environment is Linux. So you will be expected to learn how to use the Linux environment. Your first assignments will address exactly this.
- If you have a laptop, bring it along. On a Mac you will probably already have everything you need installed. On a Windows machine you will need to install something to allow X-sessions. Possibilities include MOBAXTERM, but there more, and better options. You might want to consider CYGWIN and PUTTY. If you have a Windows 10 machine, install the Subsystem for Linux.