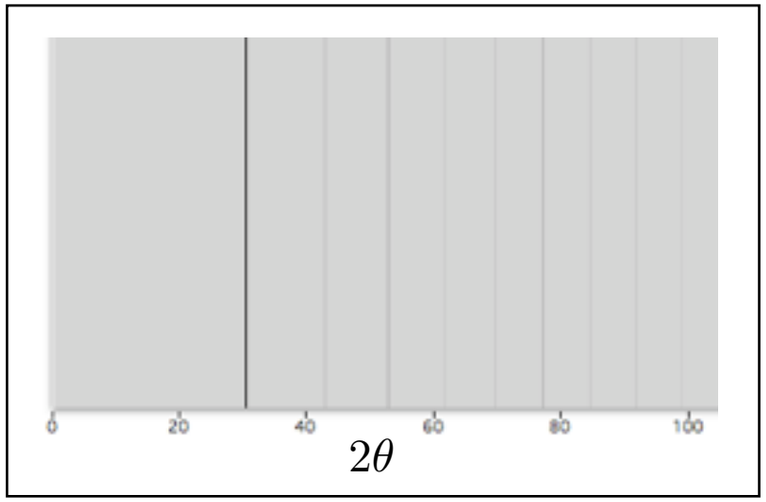
The Power of DFT

Chris J Pickard
Department of Physics & Astronomy
University College London

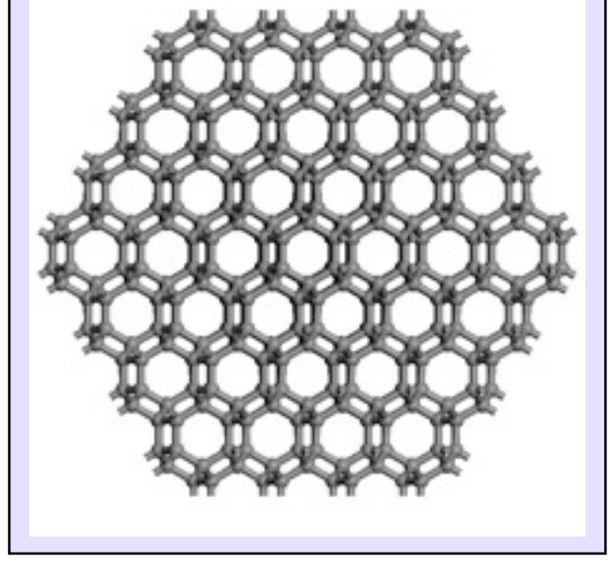
The inverse problem



Experiment

$$n\lambda = 2d\sin\theta$$

Theory



Structure

What kind of theory?

Interpolative

The trained spectroscopist

(Semi-)empirical computational methods

Extrapolative and predictive

First principles or *ab initio*

Quantum mechanics is difficult

$|1\rangle$

$|0\rangle$

$\alpha|0\rangle + \beta|1\rangle$ One particle, two states

Three particles, two states

~~$(\alpha_1|0\rangle + \beta_1|1\rangle)(\alpha_2|0\rangle + \beta_2|1\rangle)(\alpha_3|0\rangle + \beta_3|1\rangle)$~~

$$a|000\rangle + b|001\rangle + c|011\rangle + d|111\rangle +$$
$$e|110\rangle + f|100\rangle + g|101\rangle + h|010\rangle$$

Number of coefficients goes as 2^N

In a material, the number of states and particles is very large

Density functional theory

Hohenberg-Kohn

$$E[\rho] = F[\rho] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}$$

Kohn-Sham

$$F[\rho] = T_s[\rho] + \int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}' + E_{\text{xc}}[\rho]$$

$$T_s[\rho] = -\frac{1}{2}\sum_n \int \psi_n^* \nabla^2 \psi_n d^3\mathbf{r} \quad \rho(\mathbf{r}) = \sum_n \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})$$

Changes the problem to the “easy” independent particle option

Density functional theory

But we still don't know what $E_{\rm xc}[\rho]$ is

The local density approximation

$$E_{\rm xc}[\rho] = \int \epsilon_{\rm xc}(\rho)\rho(\mathbf{r})d^3\mathbf{r}$$

This is "first principles"

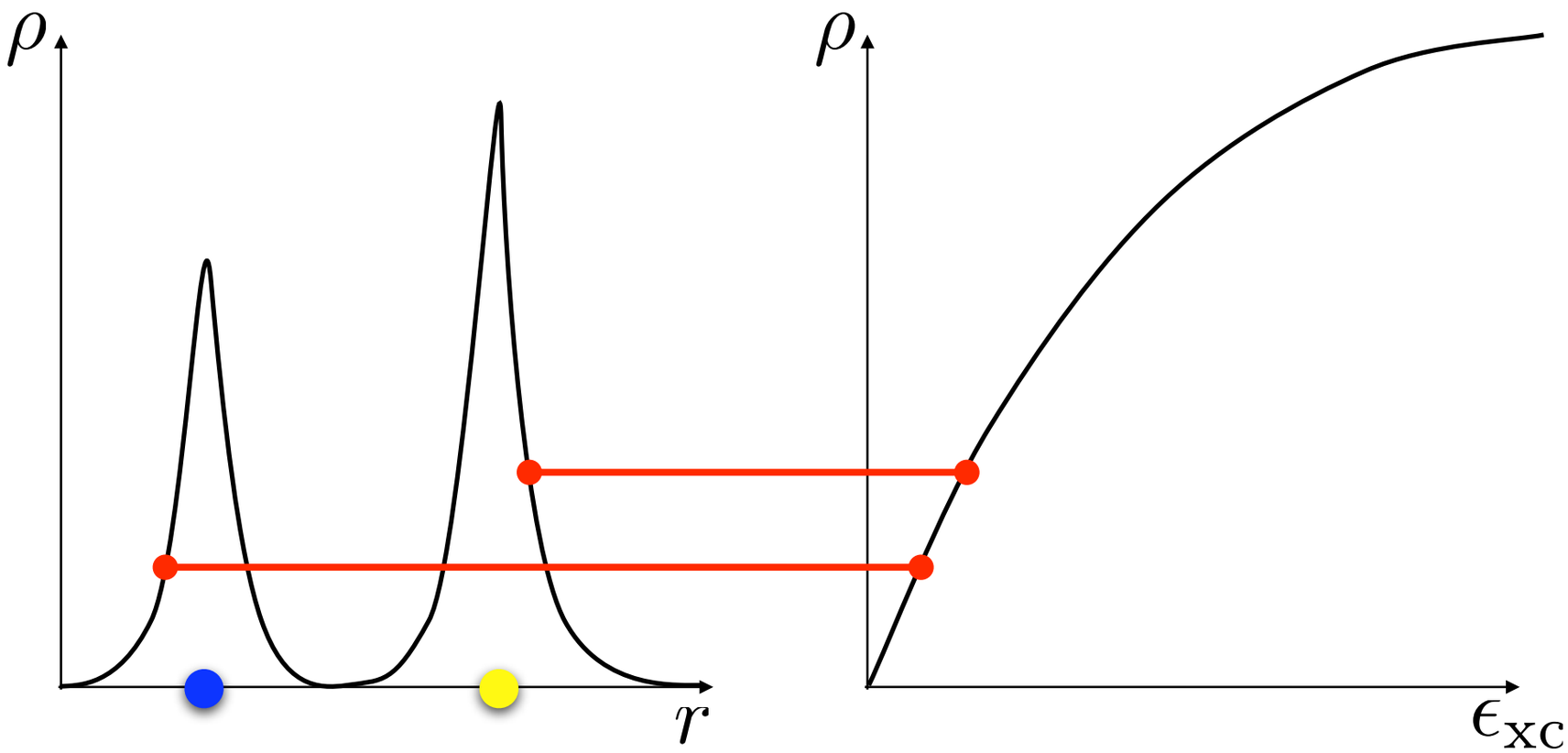
Generalised gradient approximations

$$E_{\rm xc}[\rho] = \int \epsilon_{\rm xc}(\rho, \nabla\rho)\rho(\mathbf{r})d^3\mathbf{r}$$

These may or may not be "first principles"

The LDA

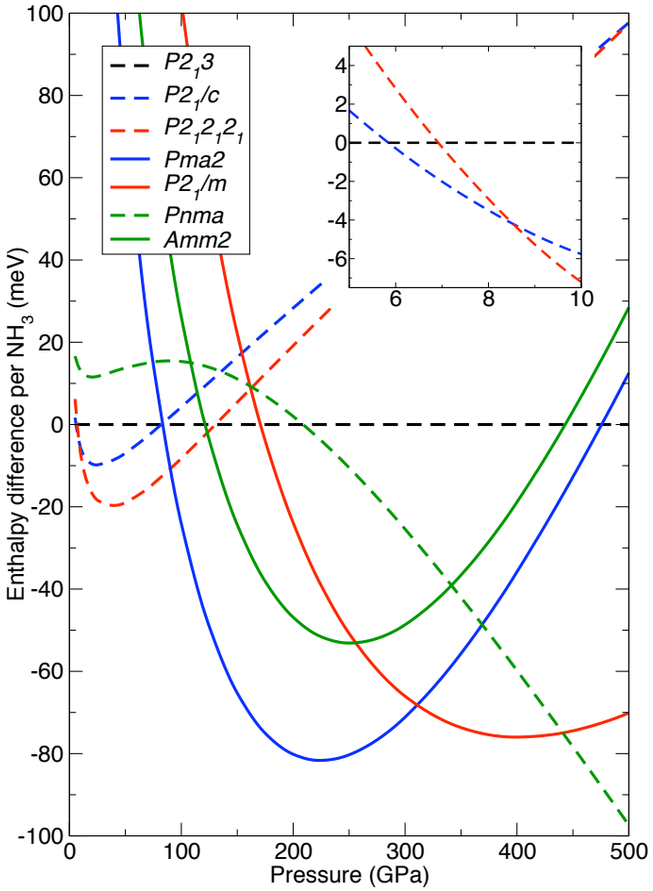
$$E_{\mathrm{xc}}[\rho] = \int \epsilon_{\mathrm{xc}}(\rho)\rho(\mathbf{r})d^3\mathbf{r}$$



Calculated using QMC by Ceperley & Alder,
PRL 45, 566, 1980

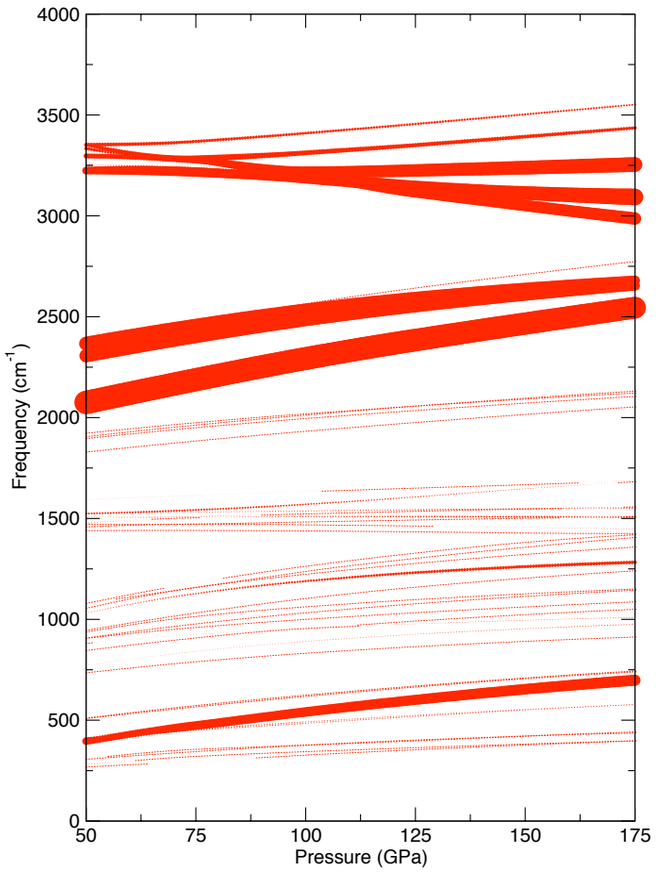
GGAs and beyond: PW91, PBE, BLYP [B3LYP, PBE0]

Total Energy



Relative stability

Derivatives



Temperature

Forces/stresses

Spectroscopy

The plane wave pseudopotential method

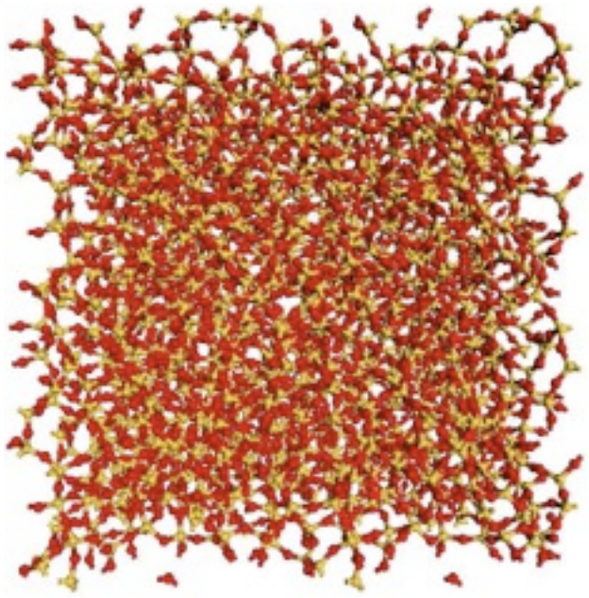
The dominant electronic structure method in:
materials science, condensed matter physics, (chemistry!)

It offers an excellent balance of accuracy and computational efficiency

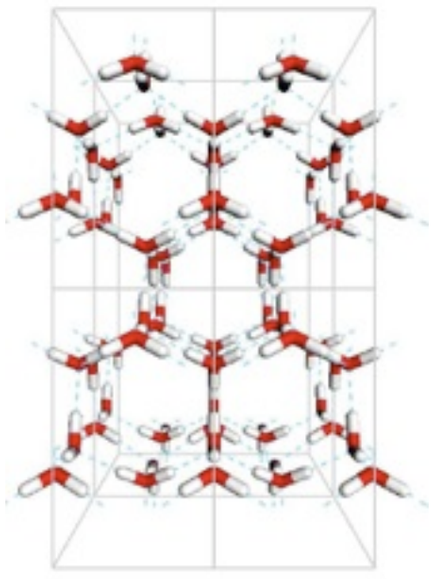
There are many mature codes available:
e.g. **CASTEP**

The trend is towards property calculation ...
NMR, vibrational, optical

Applies widely

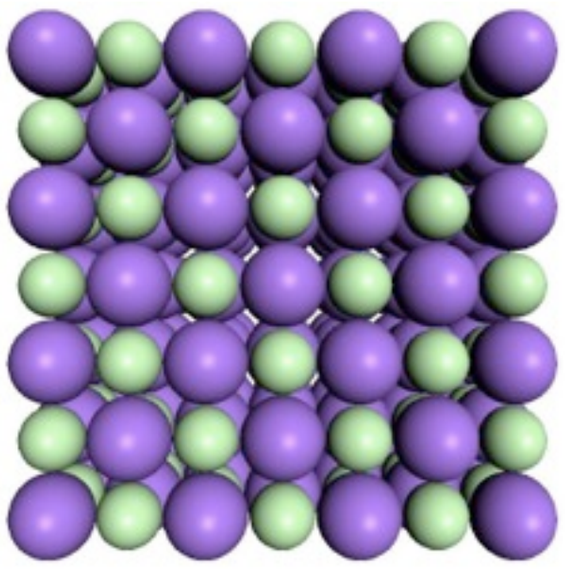


Glass

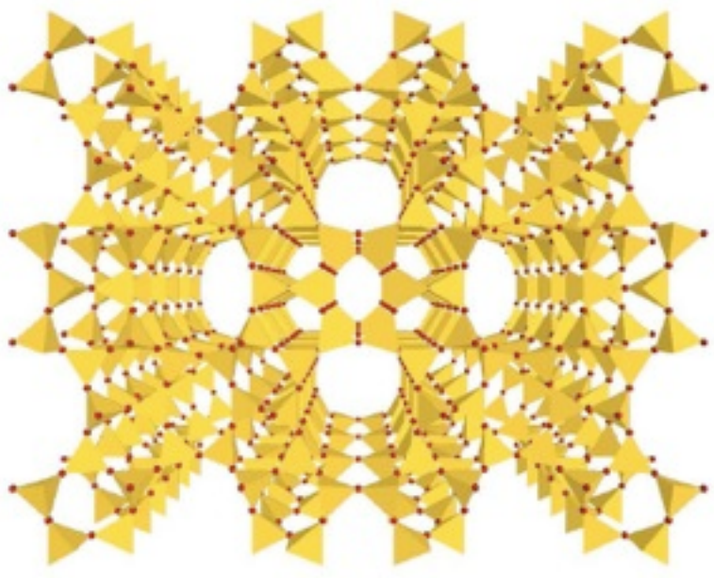


Ice

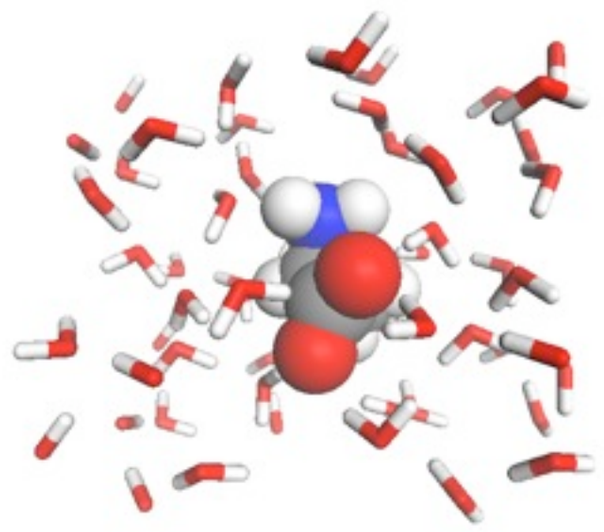
Polymer



Simple crystal



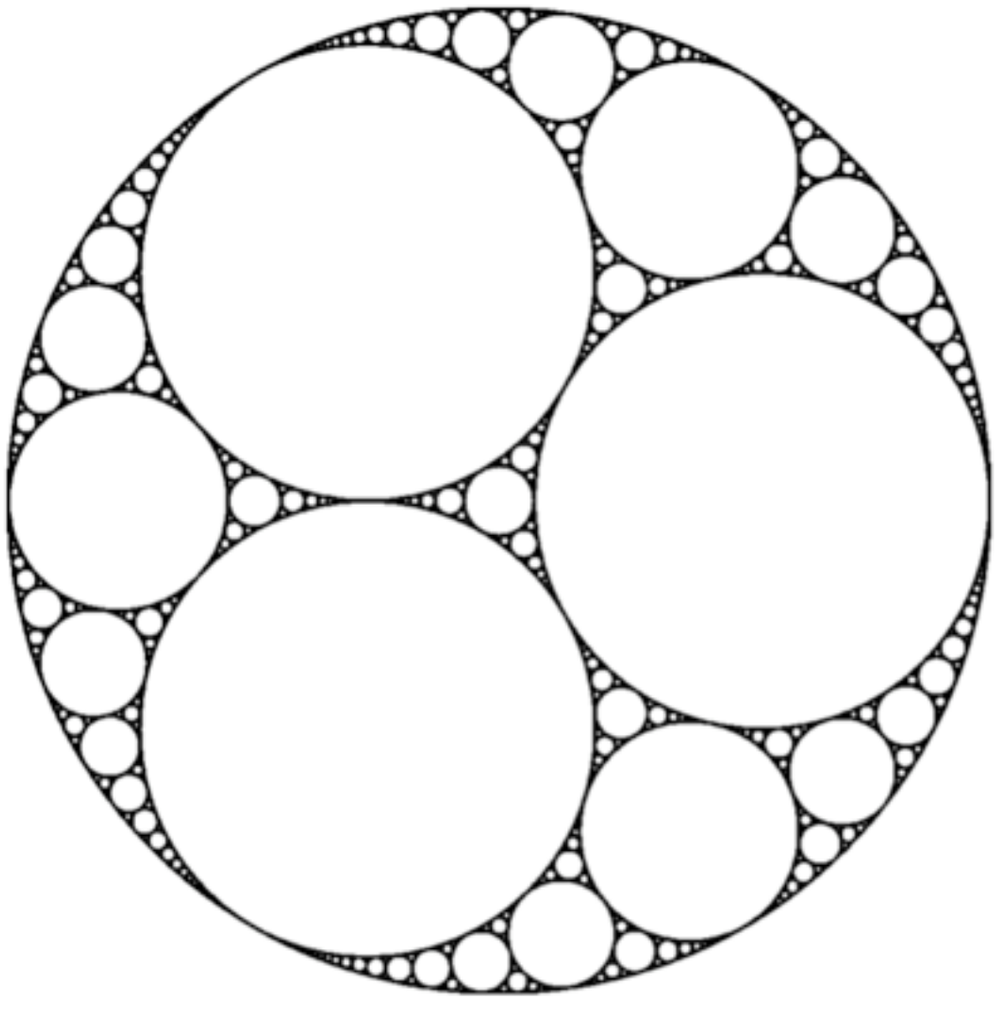
Zeolite

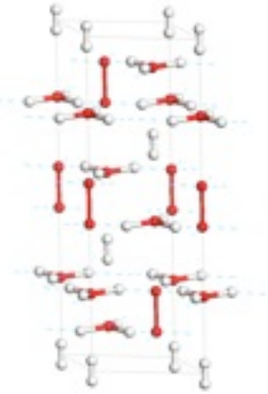


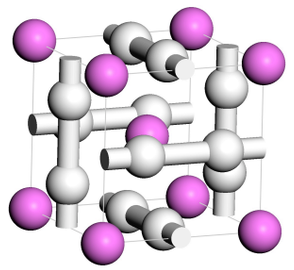
Solution

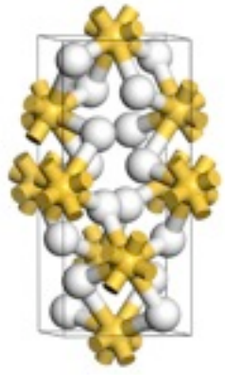
Shaking it

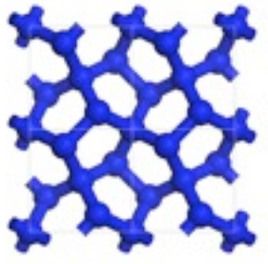
structures from nothing

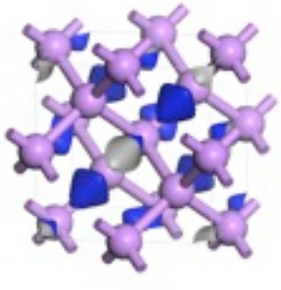


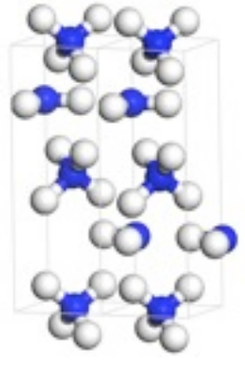










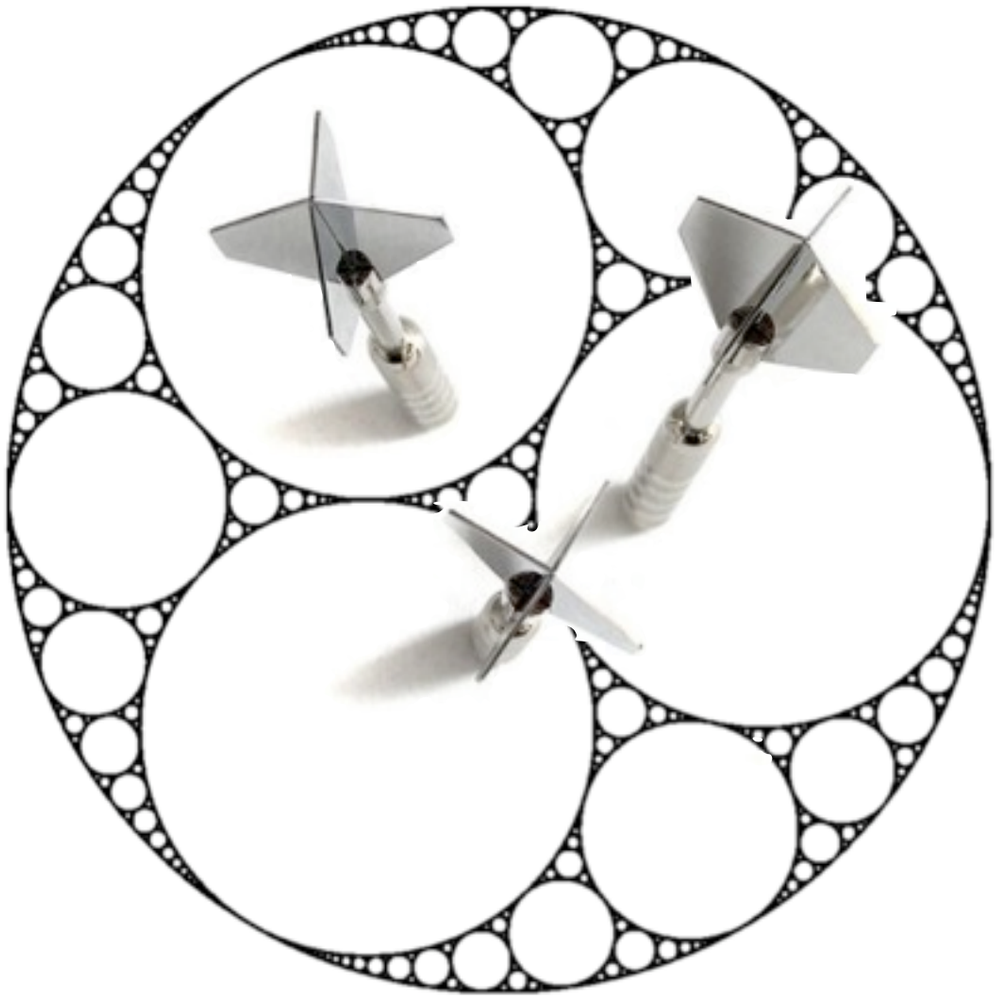


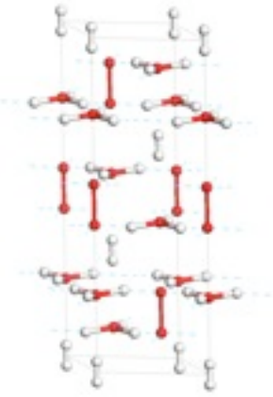
AIRSS

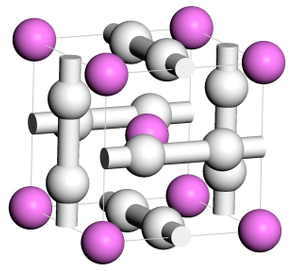
Ab Initio Random Structure Searching

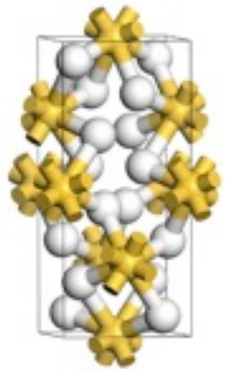
Shaking it

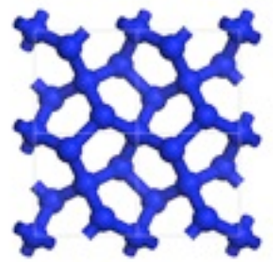
structures from nothing

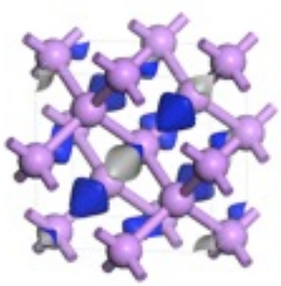


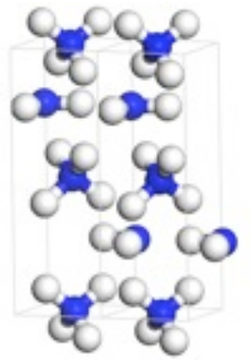










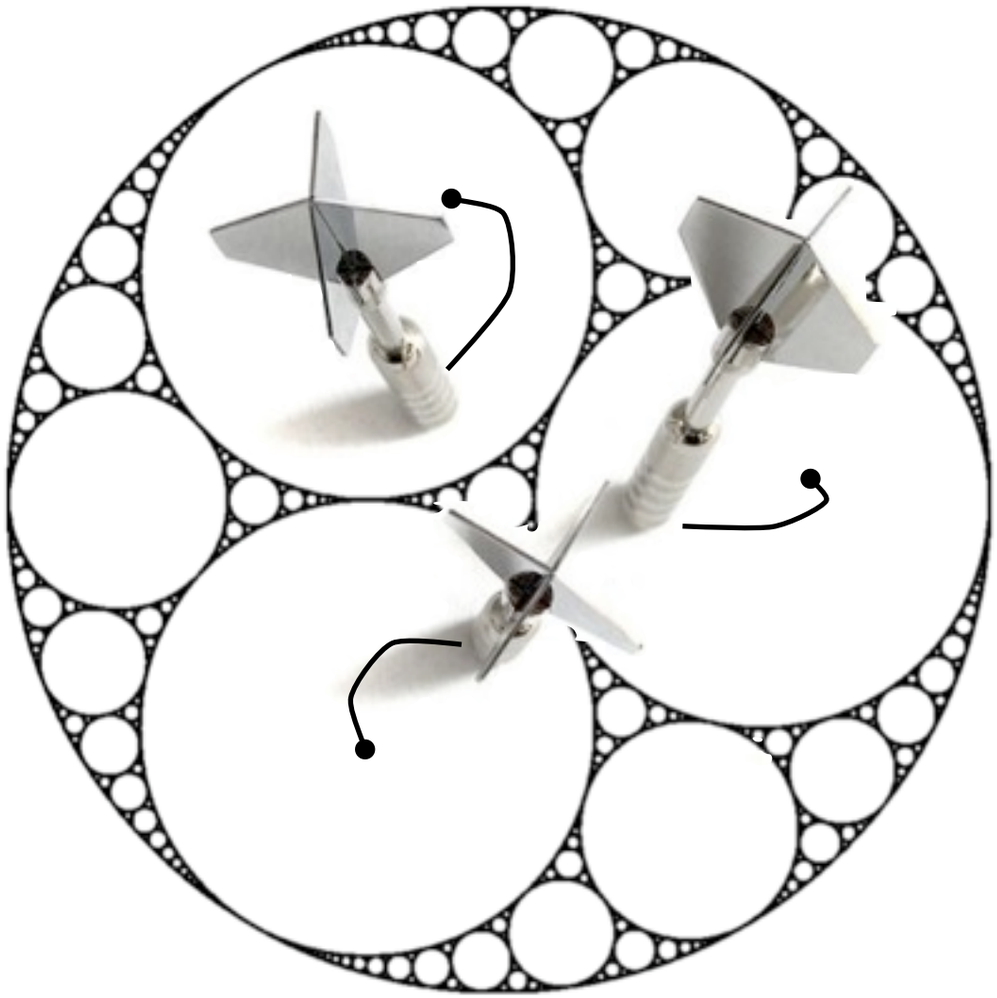


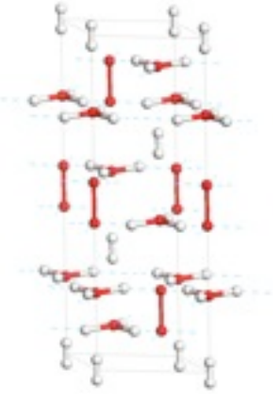
AIRSS

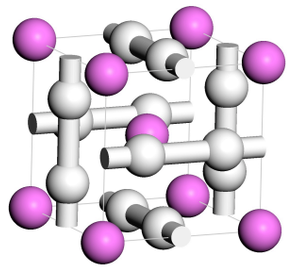
Ab Initio Random Structure Searching

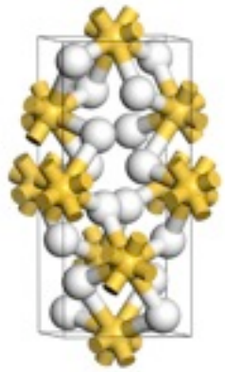
Shaking it

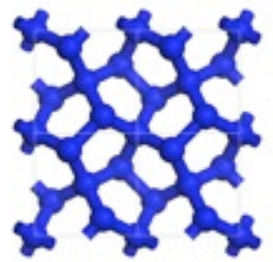
structures from nothing

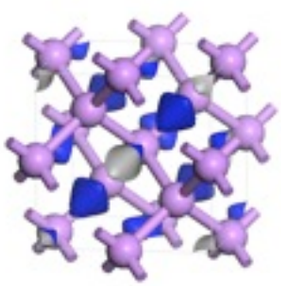


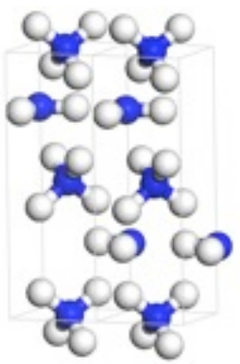










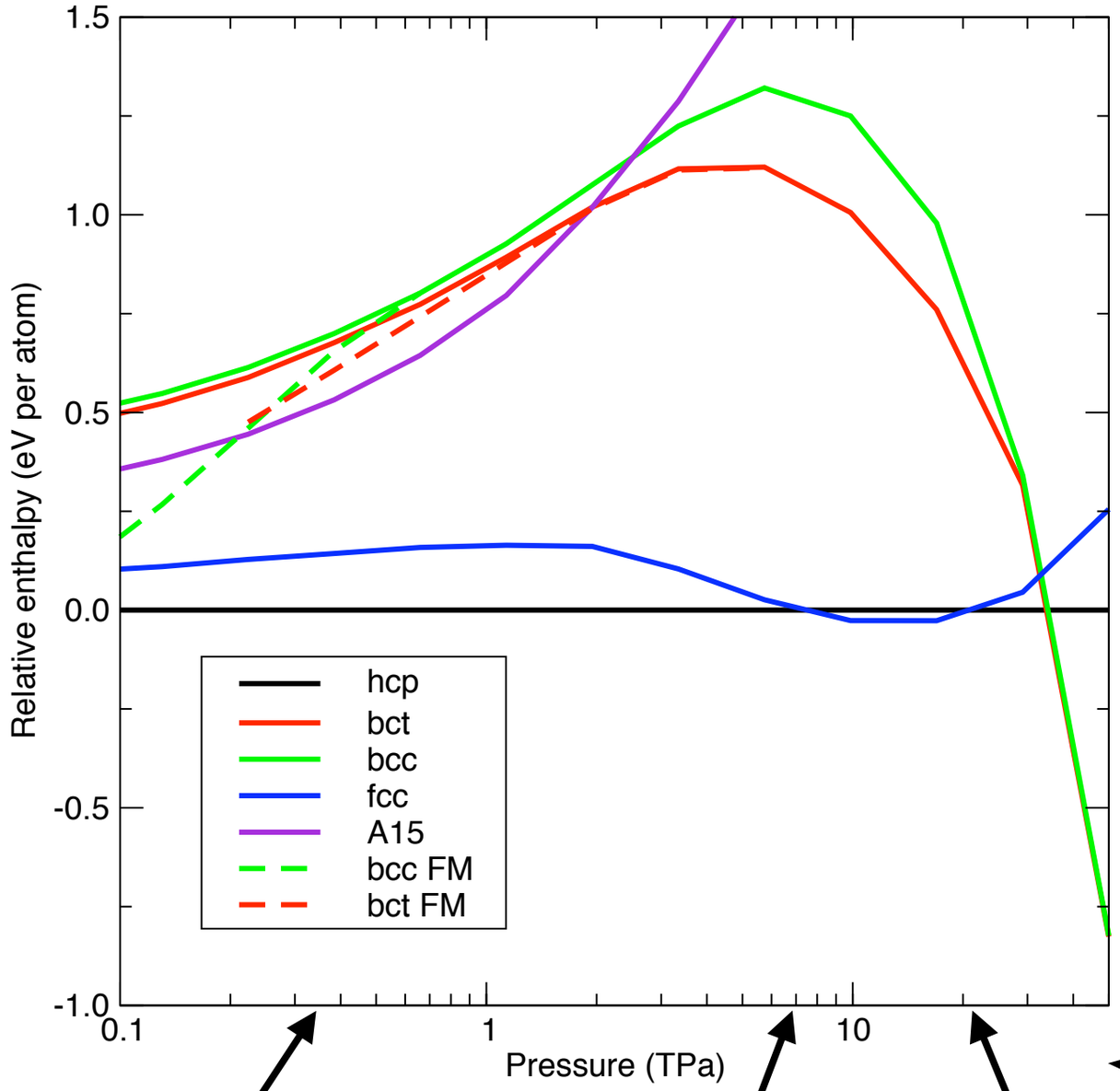


AIRSS

Ab Initio Random Structure Searching

Pushing it

Iron to TPa



You need good PSPs
but DFT should be fine ...

Packing fractions:
fcc/hcp 74.05%
bcc 68.01%

Earth Jupiter Exoplanets Neutron stars

The Power of DFT

Wide applicability

Balance of computational effort and accuracy

An inverse lottery - you normally win!