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# Density Functional Theory for Experimentalists: A Four-Lecture Primer

**F Fernandez-Alonso**

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# Density Functional Theory for Experimentalists: A Four-Lecture Primer

Felix Fernandez-Alonso<sup>1,2,\*</sup>

<sup>1</sup>*ISIS Facility, Rutherford Appleton Laboratory, Chilton,  
Didcot, Oxfordshire OX11 0QX, United Kingdom*

<sup>2</sup>*Department of Physics and Astronomy, University College London,  
Gower Street, London, WC1E 6BT, United Kingdom.*

This report provides a self-contained introduction to density functional theory in the form of four consecutive lectures, originally written for the postgraduate curriculum at University College London. With the experimentalist in mind, they are intended as a first dive into the practice and underlying conceptual framework of modern first-principles materials modelling methodologies. To this end, extensive examples and illustrations are given using the CASTEP code and the Materials Studio software package. All throughout, the emphasis is on the use of these valuable tools in the interpretation of experimental data beyond phenomenological and heuristic models.

The description of the materials world around us using first-principles (or *ab initio*) electronic-structure methods has experienced an explosive growth over the past couple of decades. Much of this progress is owed to conceptual and methodological developments within the framework of what has become to be known as *Density Functional Theory* (DFT), originally formulated in its most general form by Hohenberg, Kohn, and Sham in the 1960s. Conceptually speaking, this pioneering work led to the realisation that the calculation of ground-state properties does not require explicit knowledge of the underlying wavefunction (as formally implied by the many-body Schrödinger equation), but rather of the more manageable electronic density.

A great deal of progress has taken place since then. On the one hand, the computational power available today (even on a relatively modest desktop computer) was simply unthinkable a few years ago. In parallel, a plethora of user-friendly and well-documented computer codes are now easily within the reach of anyone willing to try them out (see, e.g., Ref. [1]). The number of people using these tools can now be counted by the thousands around the globe, and such a trend continues to be on the rise. Likewise, research programmes increasingly rely on the use of computational tools to interpret and understand complex experimental data. The recent international review of the TOSCA neutron spectrometer at ISIS is a good example of the above, with over half of its publications in the past five years involving some form of modelling.<sup>2</sup> Much of this success stems from the relative ease whereby neutron observables can be calculated from first principles,<sup>3,4</sup> as well as by ongoing efforts to develop the requisite software tools.<sup>5,6</sup> Moreover, the use of online resources for the dissemination of inelastic-neutron-scattering data<sup>7</sup> has also created additional scientific opportunities to revisit and re-interpret neutron data in the light of new methodological developments, e.g., new DFT functionals. The increasingly important synergy between experiment and computation has also been recognised as an important training need for next-generation users of

neutron and muon facilities (see, for example, the syllabi in Refs. [8–10]).

The four lectures that follow have been prepared with the experimentalist in mind, as it is increasingly recognised that many of the traditional barriers to the practice of first-principles calculations are no longer applicable, and a sharp distinction between those who ‘do experiments’ and those who ‘do computational experiments’ may no longer be of relevance in a range of research areas including solid-state physics, chemistry, or biology. Emphasis has been placed on ‘learning by doing’ and, as such, these course materials rely heavily on the presentation of specific examples to be attempted by the student in the classroom – there is no substitute for making a few mistakes along the way! To avoid unnecessary complexity at an early stage of the learning process, all worked examples rely on the use of an intentionally limited toolkit, namely, the CASTEP code<sup>11</sup> and the Materials Studio software package.<sup>12</sup> Once the foundations have been laid down, the application and implementation of the principles learnt throughout the course to other codes such as VASP<sup>13</sup> should be relatively straightforward. Each lecture has been designed to last around two hours, and the entire course could be delivered quite comfortably over a period of four to six weeks. Participants in this course are expected to have a working knowledge of quantum mechanics, at a level typically covered during a first degree in the physical sciences.

*Lecture 1 (Fundamentals: Materials Modelling, Electronic Structure & DFT)* provides the necessary conceptual and theoretical background. As such, it is perhaps the least interactive of all four lectures and, therefore, the one which the highest risk of detracting non-theorists from further engagement. To circumvent this potential risk, a few examples are given to illustrate the benefits (or, sometimes, the sheer need!) associated with the use of DFT-based first-principles calculations along with experimental research programmes. The examples presented have been drawn from recent research work primarily carried out using the ISIS Molecular Spec-

troscopy instrument suite<sup>14</sup> in close partnership with the STFC Scientific Computing Department.<sup>15</sup> These include the study of the uptake of molecular hydrogen by carbon-based nanostructures,<sup>16–20</sup> the accurate description of soft layered materials,<sup>21</sup> mass-resolved neutron-spectroscopic studies of light nuclides including hydrogen and lithium,<sup>22,23</sup> and ferroelectricity in novel organic materials.<sup>24,25</sup> This first lecture concludes with an appraisal of the current merits and limitations of DFT, the most clear example of the latter being its application to the study of strongly correlated electron systems. In the atomic and molecular world, current challenges include reliable predictions beyond the harmonic approximation for quantum systems,<sup>26</sup> or the implicit inclusion of disorder over mesoscopic length scales, presently limiting the analysis of experimental data to (approximate) spectral assignments based on prior knowledge for similar systems.<sup>27</sup> Beyond the study of well-defined normal modes of vibration, much remains to be explored to attain a similar degree of utilisation of *ab initio* methods to predict the dynamical response of low-energy and stochastic motions in condensed matter, an area where inelastic and quasielastic neutron scattering techniques will continue to offer unrivalled capabilities relative to other experimental probes. Whereas the study of phonon structure in materials has reached a level of near-to-complete maturity, first-principles molecular dynamics simulations are still a challenge beyond the first few picoseconds. Nonetheless, we anticipate that the added value associated with the parallel use of state-of-the-art instrumentation and computation will bring much-needed insights into research areas of a clear technological relevance, including gas storage and sequestration in nanoporous media, or ion transport mechanisms in battery and fuel-cell materials. The aforementioned, as well as (many) other illustrations of the use of computational modelling in the current ISIS science programme can be found throughout the STFC ePUBS repository<sup>28</sup> and, in particular, in the Annual Reports of the SCARF cluster.<sup>29–32</sup>

Starting with *Lecture 2 (The Practice of DFT Calculations using the CASTEP Code & Materials Studio)*, the use of a computer (a laptop would do) becomes a primary prerequisite to get the most out of the course. This lecture presents the main ingredients of periodic DFT methods, including basis sets, pseudopotentials (norm-conserving and soft), and the definition of energy cut-offs and  $k$ -point grids. Hands-on practical exercises start with the simplest possible case (a hydrogen atom in a box!) to explore the generic input and output associated with any CASTEP calculation. Using Materials Studio, we also calculate a few basic properties. This first (and rather trivial) example is complemented with calculations of the hydrogen molecule and crystalline silicon. In this last case, the merits and strengths of periodic DFT methods should become immediately apparent to the novice.

From a practical viewpoint, *Lecture 3 (A Closer Look under the Hood: from Structure to Properties)* extends

the previous discussion to give a more detailed account of the inner-workings of CASTEP and its execution in command-line mode. Input and output files are examined in depth using our previous example of the silicon crystal. In this way, the student can become familiar with the use of CASTEP as a stand-alone tool, including the use of symmetry constraints to simplify and improve computational efficiency. At this stage, we also revisit and stress the importance of convergence tests with basic tasks including energy and geometry optimisation. Armed with these new concepts and tools applied to a series of several solid-state systems, this lecture concludes with an overview of properties amenable to computation as well as the connection to experimental studies, e.g., electronic band structure, optical response, phonons, IR and NMR spectra, thermodynamic functions, etc. Students are also encouraged to think of a particular problem they would like to tackle and to bring it with them to the next (and last) lecture.

*Lecture 4 (More Properties & a Few Advanced Features)* builds upon *Lecture 3* and starts with a discussion of atomic and molecular vibrations. The student is encouraged to set up and run his/her own calculation and to find ways of visualising the output. Common methods to perform phonon calculations are also discussed in some detail, including finite displacements and density functional perturbation theory. To conclude this discussion, the connection between phonon-dispersion relations and thermodynamic properties is explored for the case of periodic solids. The last few slides of this lecture go back to the basics of pseudopotentials, how they are constructed, as well as their general properties. Understanding how CASTEP deals with pseudopotentials provides a significant amount of hitherto untapped power and flexibility. We first explore these features by looking at carbon, where the student is asked to define a series of electronic configurations including all core electrons. The discussion is extended to the treatment of lithium and beryllium. These ideas are finally tested on diamond and should give the student sufficient confidence to consider (without fear!) the full flexibility offered by the CASTEP package in the description of electronic structure. The course concludes with a few general tips on scripting (recommended for complicated jobs) as well as a recap on what has been learnt and how one could take things a few steps further.

In closing this preamble, I wish to thank Dr Mark Ellerby and Prof Neal T Skipper for encouraging me to prepare and give these lectures at University College London. Dr Keith Refson from the STFC Scientific Computing Department at the Rutherford Appleton Laboratory is gratefully acknowledged for introducing me to the fascinating world of DFT and CASTEP during my early days at ISIS, as well as for his continuing and growing interest and support in integrating these tools into our experimental research programme. Closer to home, I am particularly indebted to Drs Matthias J. Gutmann, Maciej Krzysztyniak, Sanghamitra Mukhopadhyay, and

Stewart F Parker for a very enjoyable journey together in a number of research projects, where computational modelling has been at the heart of our efforts, joys, and preoccupations. The bulk of the computing resources

leading to the examples presented in this work have been provided by the e-Science Facility run by the STFC Scientific Computing Research Infrastructures Group.<sup>33</sup>

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- \* E-mail: [felix.fernandez-alonso@stfc.ac.uk](mailto:felix.fernandez-alonso@stfc.ac.uk)
- <sup>1</sup> <http://www.psi-k.org/codes.shtml>
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- <sup>5</sup> <http://www.isis.stfc.ac.uk/instruments/tosca/software/>
- <sup>6</sup> <http://www.mantidproject.org/>
- <sup>7</sup> Inelastic neutron-scattering database: <http://www.isis.stfc.ac.uk/instruments/tosca/ins-database/>
- <sup>8</sup> ISIS Neutron Training Course: <http://www.isis.stfc.ac.uk/learning/neutron-training-course/>
- <sup>9</sup> ISIS Muon Spectroscopy Training School: <http://www.isis.stfc.ac.uk/groups/muons/muon-training-school/>
- <sup>10</sup> Oxford Neutron School: <http://www.oxfordneutronschool.org/>
- <sup>11</sup> CASTEP homepage: <http://www.castep.org/>
- <sup>12</sup> Materials Studio: [http://en.wikipedia.org/wiki/Materials\\_Studio](http://en.wikipedia.org/wiki/Materials_Studio)
- <sup>13</sup> VASP homepage: <http://www.vasp.at/>
- <sup>14</sup> ISIS Molecular Spectroscopy Group: <http://www.isis.stfc.ac.uk/groups/molecular-spectroscopy/>
- <sup>15</sup> STFC Scientific Computing Department: <http://www.stfc.ac.uk/SCD/>
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- <sup>28</sup> All published work cited herein can be accessed from <https://epubs.stfc.ac.uk>
- <sup>29</sup> D. Ross, *SCARF Annual Report 2012-2013*, Rutherford Appleton Laboratory Technical Report RAL-TR-2013-014 (Didcot, 2013).
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- <sup>33</sup> SCARF cluster at the Rutherford Appleton Laboratory: <http://sct.esc.rl.ac.uk/SCARF/>

# Density Functional Theory for Experimentalists

## A Four-Lecture Primer

Felix Fernandez-Alonso

ISIS Facility, Rutherford Appleton Laboratory and  
Department of Physics & Astronomy, University College London

*e-mail:* [felix.fernandez-alonso@stfc.ac.uk](mailto:felix.fernandez-alonso@stfc.ac.uk)

## Outline of Course

1. **Fundamentals: Materials Modelling, Electronic Structure & DFT.**
2. The Practice of DFT calculations using the CASTEP code & Materials Studio.
3. A Closer Look under the Hood: from Structure to Properties.
4. Advanced Features.

# Lecture I

## Fundamentals

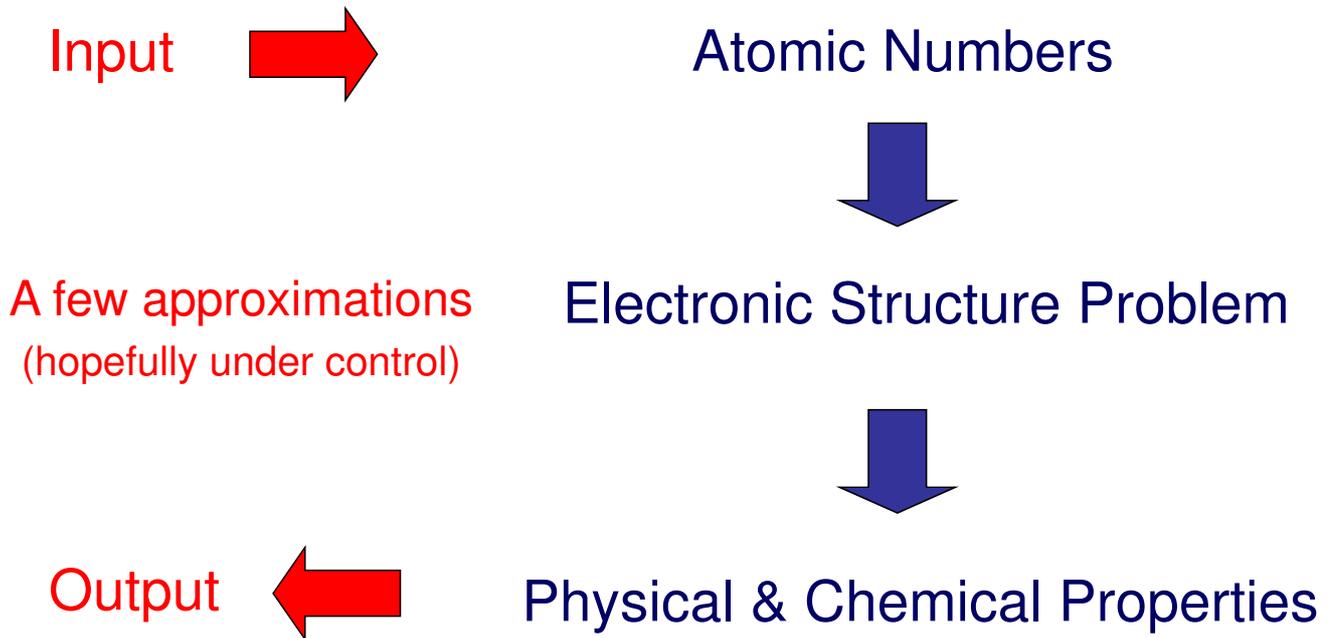
### Outline of Today's Lecture

- First-principles Materials Modelling: why should an experimentalist care?
- Electronic structure calculations: wavefunction vs. density-based methods.
- DFT basics, with an emphasis on terminology and some well-known limitations.

*People love jargon. It is so palpable, tangible, visible, audible; it makes so obvious what one has learned; it satisfies the craving for results. It is impressive to the uninitiated. It makes one feels one belongs. Jargon divides People into Us and Them.*

*M. Buber, "I and Thou"*

# The Goal of First Principles (“ab-initio”) Calculations



## The Use of First Principles (“ab-initio”) Calculations

- Predictive simulation
  - Accurate calculation of properties from first principles.
  - Model development (structure/property relationships).
  - An integral component of Materials Design – a full-time job in itself.
- Computational “Experiments”
  - Calculate experimental observables, virtually anything you can measure (X-ray, neutron, optical, etc).
  - Complement experimental data with sophisticated / detailed models.
  - Suggest new experiments.

Software packages have reached a level of sophistication whereby experimentalists can also enter the game (10 years ago, this task was much harder).

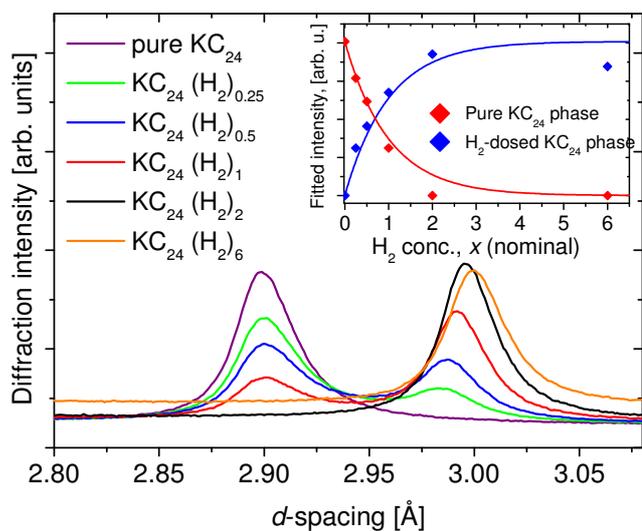
BASIC REQUIREMENTS (and objectives of this course):

- A certain level of understanding/appreciation for what is going on “under the hood” is a must, particularly so when one asks for help (e.g., talk to a theorist/modeller).
- Get your hands dirty with the codes: the more you do, the more you know.

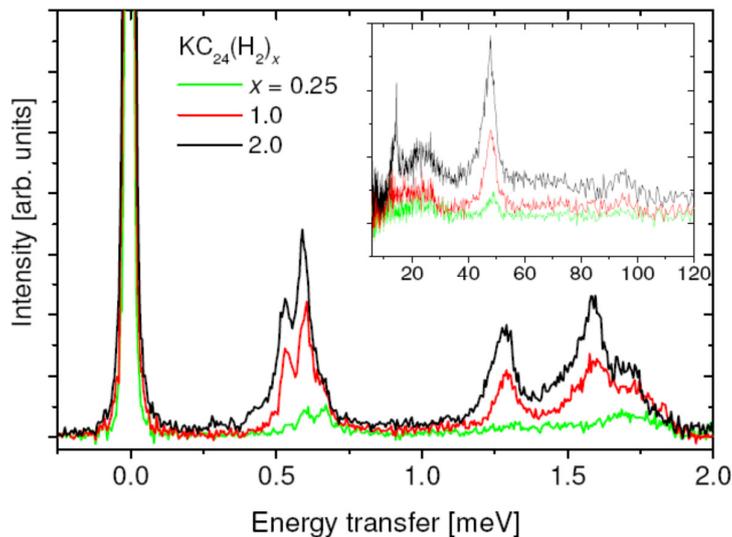
# What is Possible with CASTEP: An Illustrated Tour

## H<sub>2</sub> Uptake in Alkali-Graphite Intercalates Neutron Scattering Data

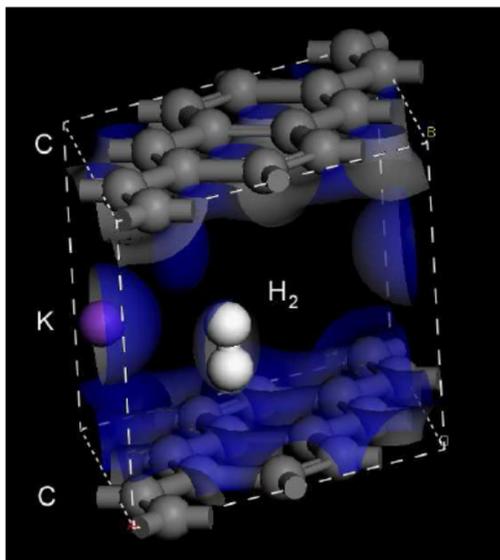
### Diffraction



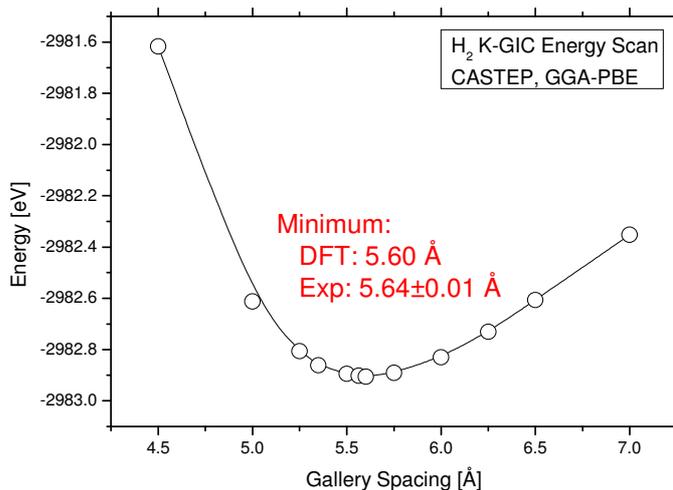
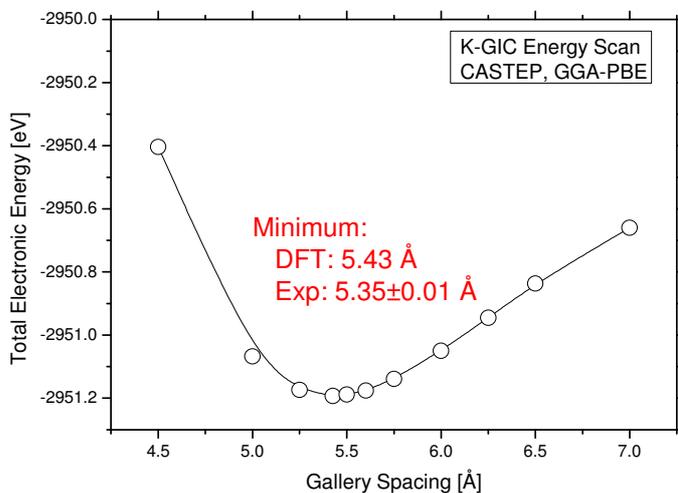
### Spectroscopy



## CASTEP Calculation

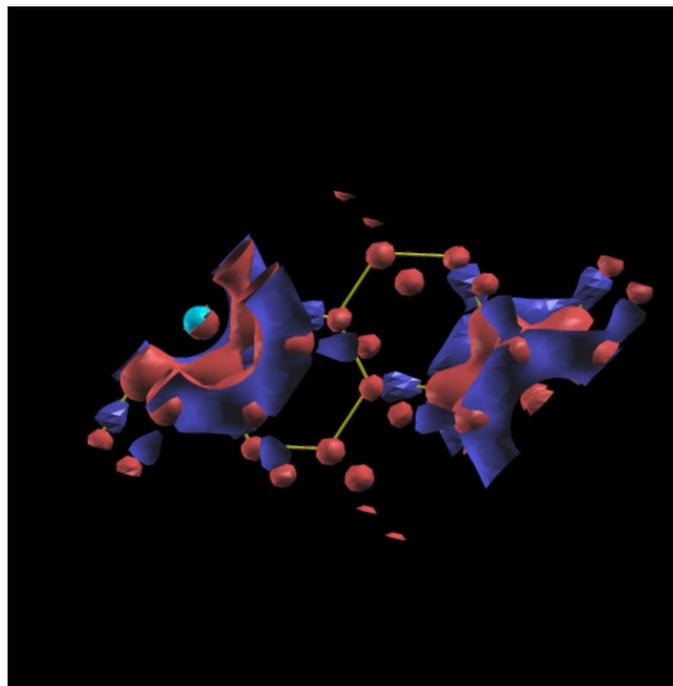
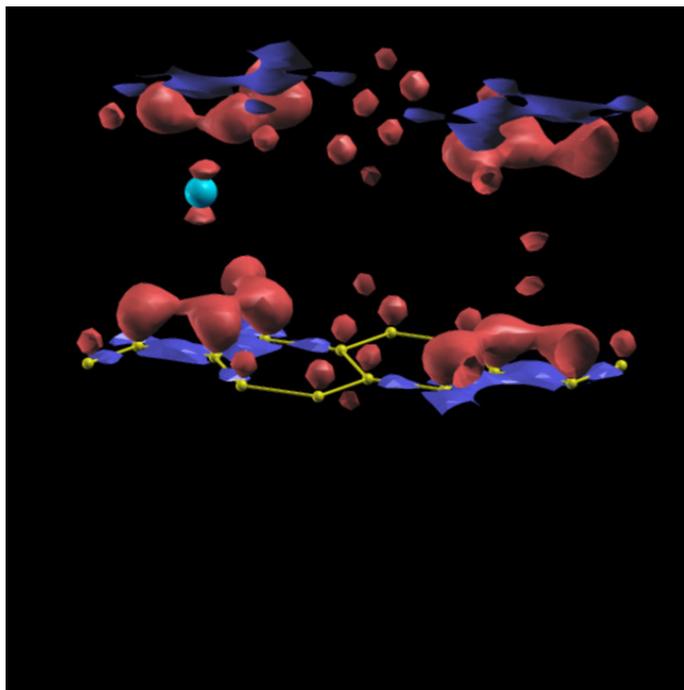


- Model validation: DFT can reproduce experimental data *quantitatively*.
- Expansion of graphite c-axis is significant: H<sub>2</sub> is too big to fit.



# Electron density difference map: +KGIC - K - Graphite

Legend: red / blue = e density gain / loss

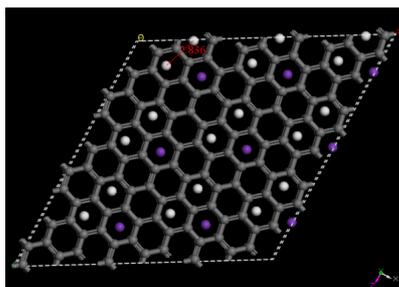


DFT does well at predicting electron transfer from alkali to graphite (this feature was not forced into the calculation). This extra electron now occupies LUMO (antibonding) graphite levels with a clear preference for the ring just above/below the alkali metal (as expected from simple electrostatics). Thus, binding of the graphene layers is mostly electrostatic in nature, with little back-donation (bonding) to the metal ion.

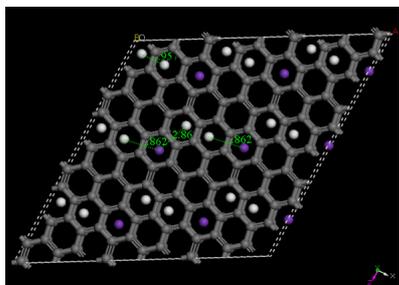
## Binding Energies vs H<sub>2</sub> Coverage

Addition of a 2<sup>nd</sup> H<sub>2</sub>: 3 distinct possibilities

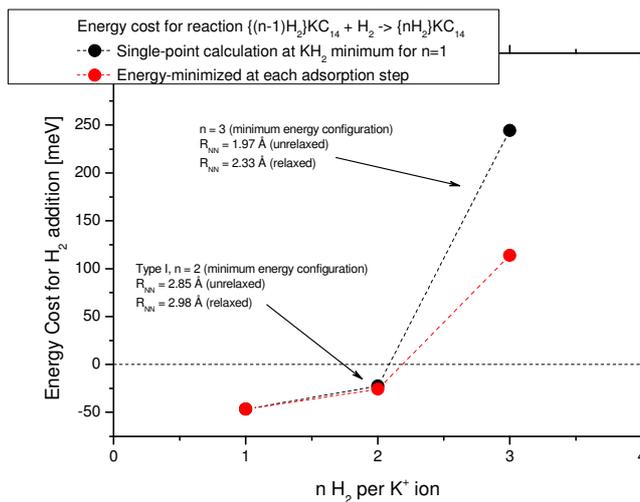
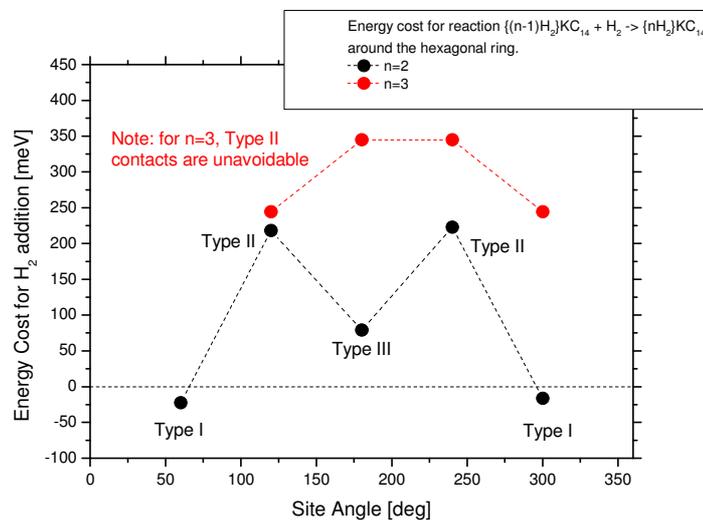
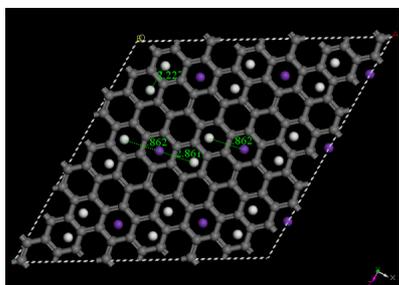
Type I  
Twofold degenerate  
 $R_{NN} = 2.85 \text{ \AA}$  (unrelaxed)  
 $R_{NN} = 2.98 \text{ \AA}$  (relaxed)



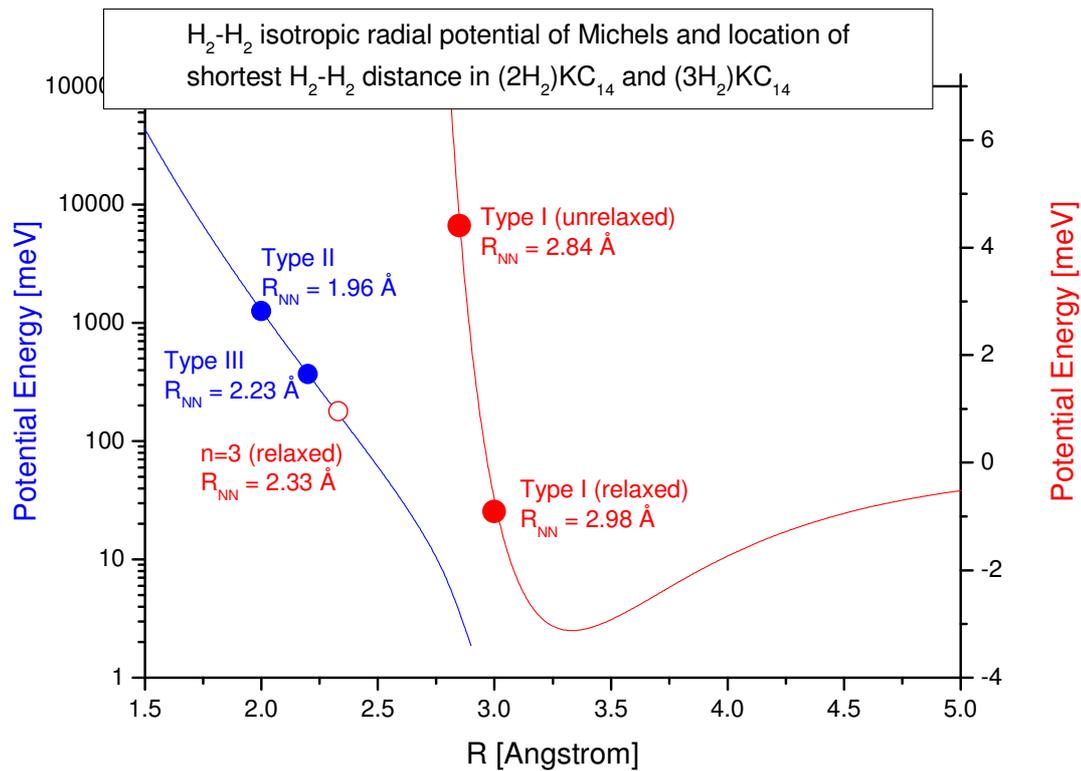
Type II  
Twofold degenerate  
 $R_{NN} = 1.96 \text{ \AA}$  (unrelaxed)  
 $R_{NN} = 2.33 \text{ \AA}$  (relaxed)



Type III  
Singly degenerate  
 $R_{NN} = 2.23 \text{ \AA}$  (unrelaxed)

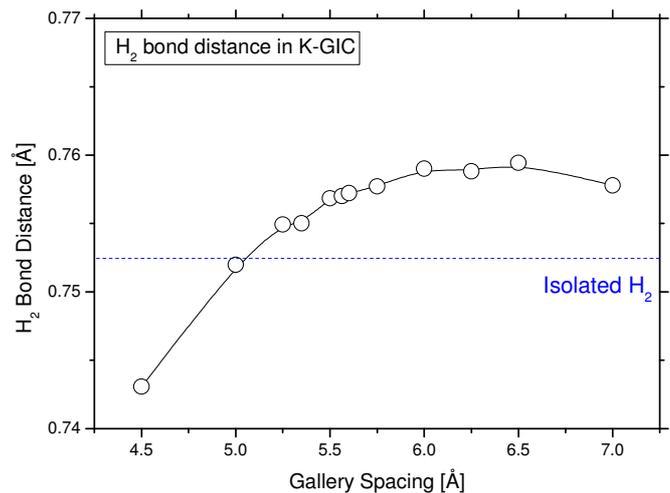
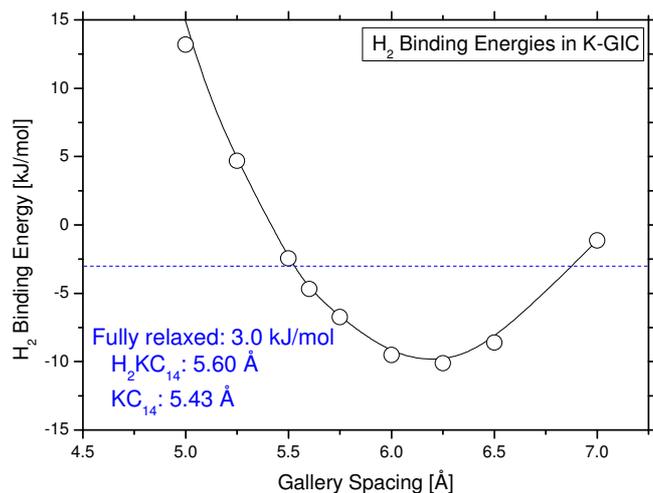


## H<sub>2</sub>-H<sub>2</sub> Intermolecular Potential and nearest-neighbour H<sub>2</sub>-H<sub>2</sub> distances in the intercalate.



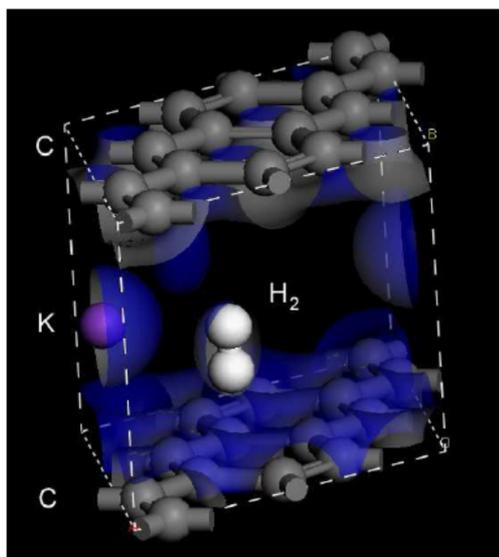
The distance between centers of two benzene rings in graphite is  $R=2.48$  Å. In terms of H<sub>2</sub>-H<sub>2</sub> interactions this distance will correspond to a REPULSIVE energy of ca. 61 meV. What does this tell us about the suitability of graphite for hydrogen storage?

## DFT Insights: Binding Energies & H<sub>2</sub> Bond Elongation

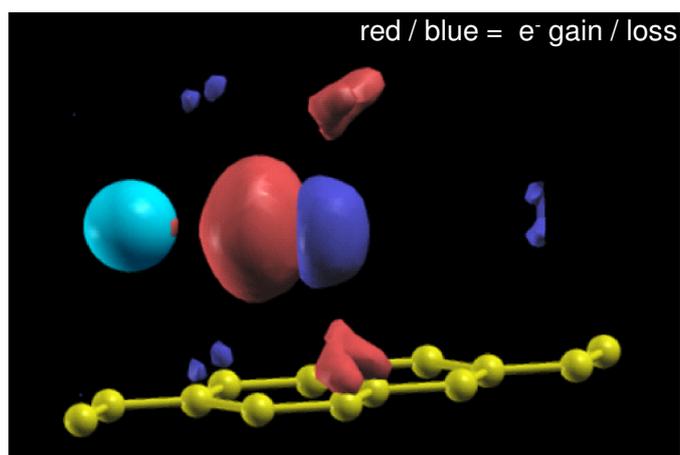


- Three-fold reduction in binding energy due to relaxation effects (but could be tuned, e.g., via mixed intercalation).
- Physisorptive nature: negligible bond elongation (H-H vibrational frequency softens by a modest 80 cm<sup>-1</sup>).

# H<sub>2</sub> Complexes in K-GIC



Electron density difference map



- T-shaped K-H<sub>2</sub> geometry: dominant interaction is with alkali.
- Small amount of charge redistribution on graphene sheets (in quantitative agreement with observed lattice expansion).



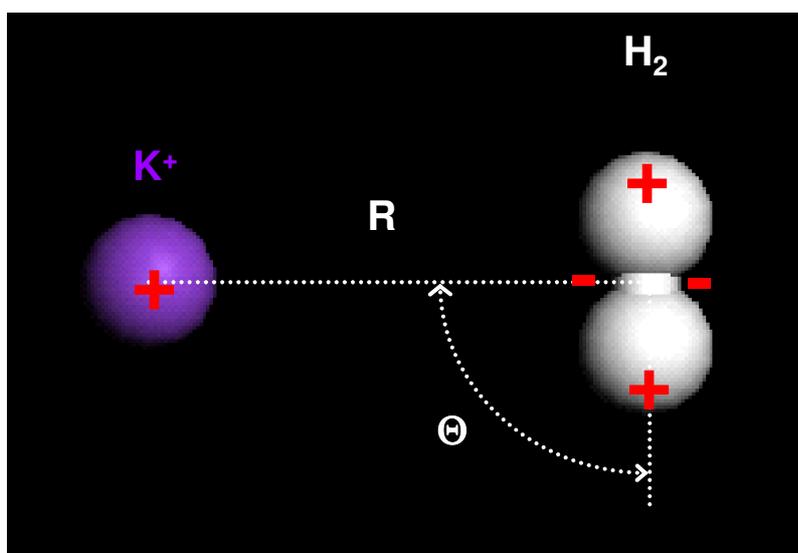
## Nature of the K<sup>+</sup>- H<sub>2</sub> Interaction

Ion-permanent quadrupole  
(T-shaped complex)

$$V_Q(R, \Theta) = \left[ \frac{Q_{H_2}}{R^3} \right] P_2(\cos \Theta)$$

Ion-induced dipole  
(linear complex)

$Q_{H_2} = 0.460 \text{ au}$ $\alpha = 5.179 \text{ au}$ $\alpha_{par} = 6.305 \text{ au}$ $\alpha_{per} = 4.578 \text{ au}$
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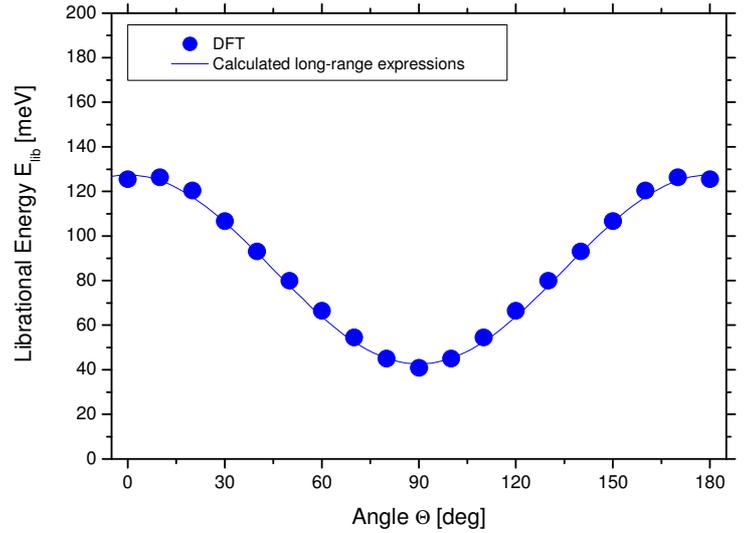
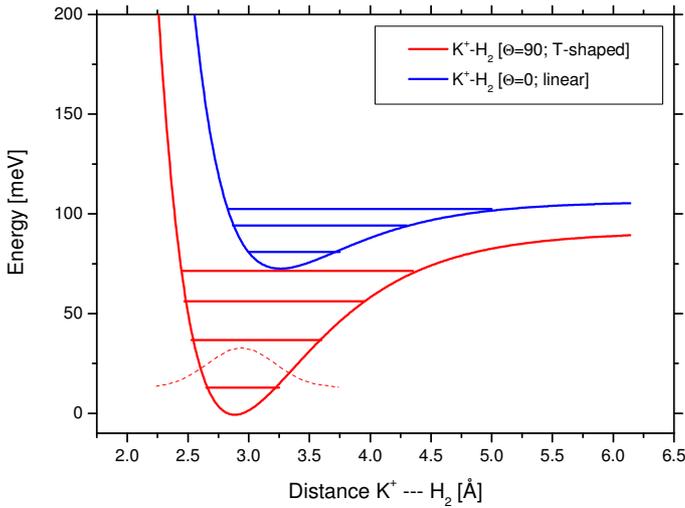


$$V_\alpha(R, \Theta) = - \left[ \frac{1}{R^4} \right] \left[ \frac{\alpha}{2} + \frac{1}{3} (\alpha_{par} - \alpha_{per}) P_2(\cos \Theta) \right]$$

For the H<sub>2</sub> molecule: quadrupole term dominates.

NOTE: free rotation about K<sup>+</sup>- H<sub>2</sub> symmetry axis.

# Benchmarking DFT Calculations with $K^+$ - $H_2$ Complex

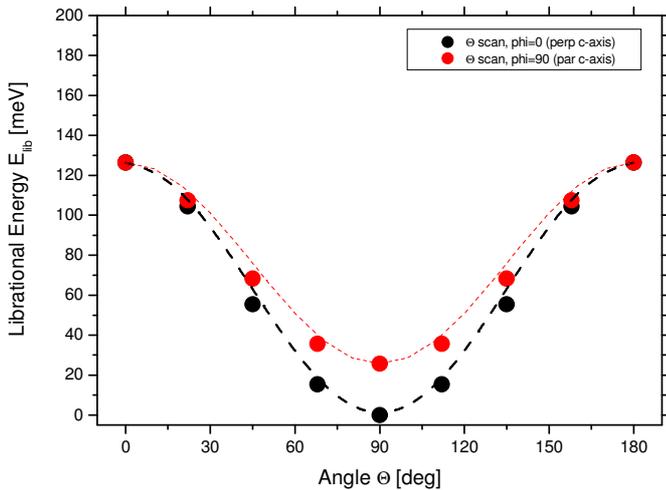
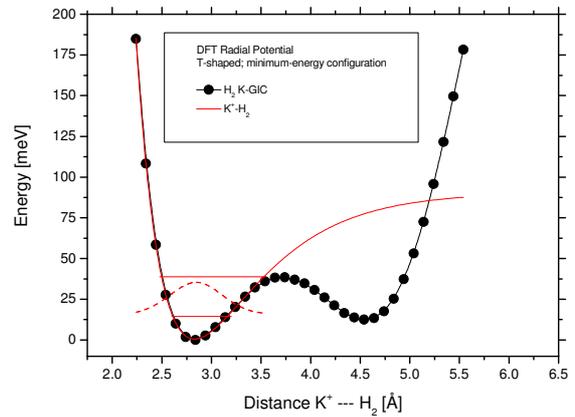
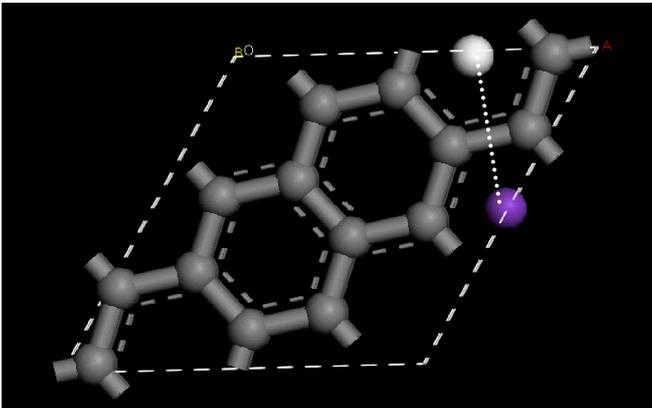


## Computational details:

- CASTEP PW code.
- GGA approximation.
- 300 eV PW cutoff.
- Vanderbilt ultrasoft pseudopotential.
- Eigenvalues/energies: Numerov algorithm.

Excellent agreement with known values in literature (geometry, ZPE's ...)

## Surveying the Potential Energy Landscape of $H_2$ in K-GIC



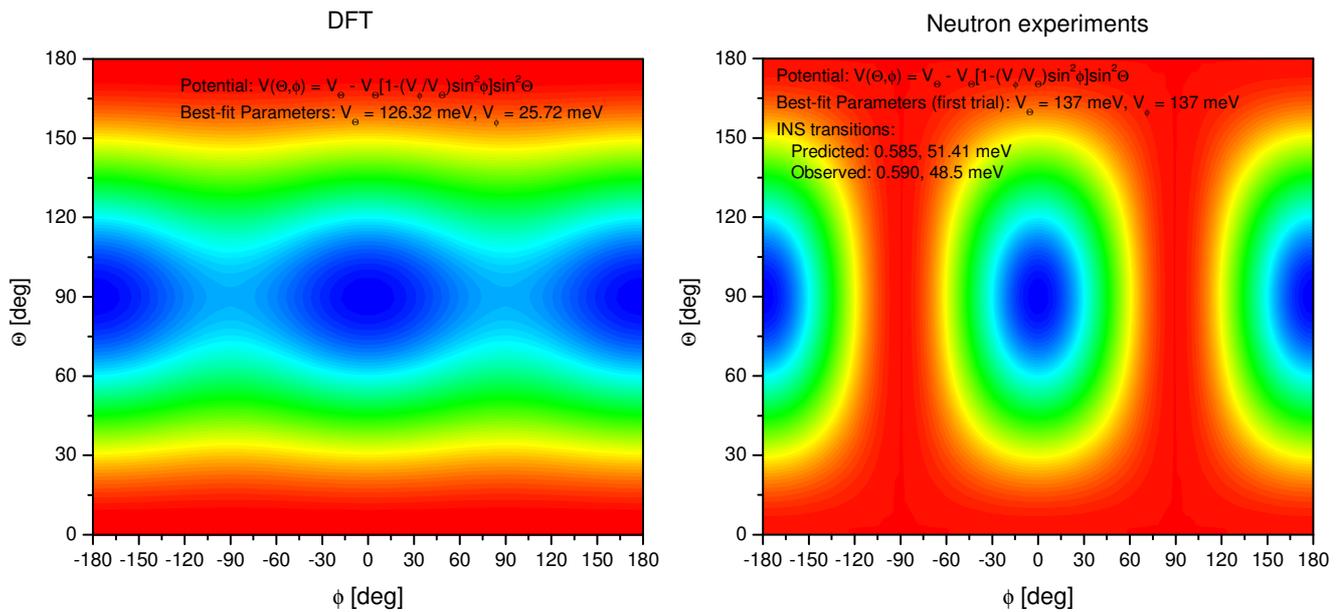
## Orientalional potential:

$$V(\Theta, \phi) = V_{\Theta} \left[ 1 - \left( 1 - \frac{V_{\phi}}{V_{\Theta}} \sin^2 \phi \right) \sin^2 \Theta \right]$$

Right barrier height towards ion ( $V_{\Theta}=125$  meV).

Small modulation ( $V_{\phi}=25$  meV) due to graphite planes.

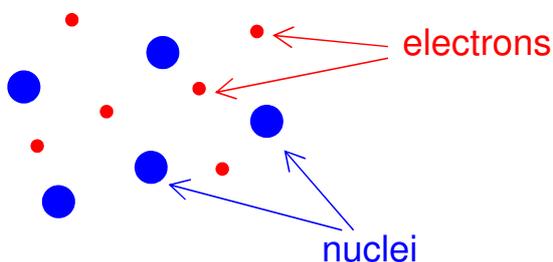
# DFT Orientational Potential vs Inelastic Neutron Experiments



DFT gives very sensible results in terms of interaction energies, except for the underlying symmetry of the adsorption site.

## Back to Square One: The Schrodinger Equation

Any material can be boiled down to a collection of electrons and nuclei



Obeying the celebrated (time-independent & non-relativistic) Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

Where electronic and nuclear variables include BOTH spatial coordinates and spin.

The Hamiltonian operator describes the total energy of the collection in the absence of external fields

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{N-N} + \hat{V}_{N-e} + \hat{V}_{e-e}$$

Including both kinetic and potential (Coulomb) energy terms

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_j^{all e} \nabla_j^2 = -\frac{\hbar^2}{2m_e} \sum_j^{all e} \frac{\partial^2}{\partial r_j^2}$$

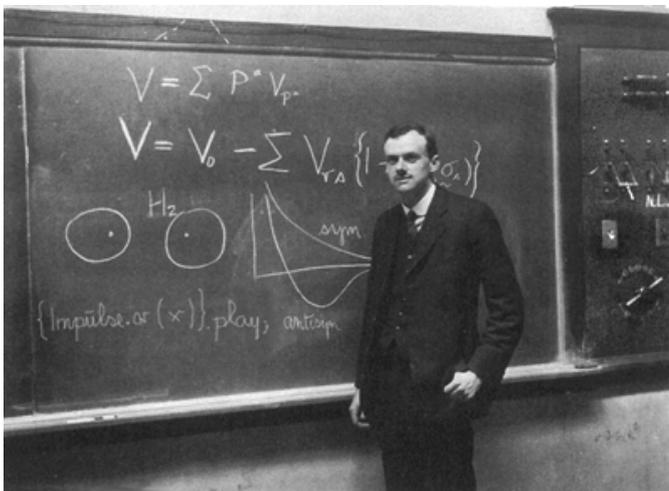
$$\hat{V}_{NN} = \frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_{j>i}^{all N} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_i^{all N} \frac{\nabla_i^2}{m_i} = -\frac{\hbar^2}{2} \sum_i^{all N} \frac{1}{m_i} \frac{\partial^2}{\partial R_i^2}$$

$$\hat{V}_{Ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{all e} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

$$\hat{V}_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_i^{all e} \sum_{j>i}^{all e} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Formally, this solves the problem.



*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.*

PAM Dirac (1929)

*Nobody understands quantum mechanics*  
RP Feynman



REALITY CHECK: with the exception of the H atom, the SE equation is a many-body problem (thus, unsolvable).

**DEFINITELY, WE NEED APPROXIMATIONS**

# Important Properties of the Total Wavefunction

- Wavefunction must be physical, e.g., normalizable (particles must be somewhere in space).
- Symmetric/Antisymmetric with respect to exchange of fermions/bosons (Pauli exclusion principle).
  - Most important case is the electron (antisymmetric).
  - Other examples include H (antisymm) or D (symm).
- Pauli Principle for electrons implies these are correlated regardless of other interactions (Coulomb repulsion) since

$$\Psi(\dots, r_1, \dots, r_1, \dots) = 0$$

## Understanding What All This Means

- Our goal: solve SE for the many-body wavefunction  $\psi$ .
- This object is a highly dimensional object and thus exceedingly complex:
  - $3N_e$  electron spatial coordinates.
  - $N_e$  electron spin coordinates.
  - $3N_N$  nuclear spatial coordinates (ignoring nuclear spin).
- Let's work out some numbers for a "simple" molecule such as benzene ( $C_6H_6$ ).

# The Benzene Wavefunction

- Total of 12 nuclei and 42 electrons.
- Dimensionality of  $\psi$  in Cartesian space is  $3 \times (12+42) = 162$ .
- Removing translations and rotations of the whole system (6 DOFs) does not help much:  $162-6=156$  (but still practicable)
- MUCH WORSE for the ELECTRONIC problem:  $42!$  distinct permutations or  $\sim 10^{51}$  terms.
- How BIG is this number?

## Unsurmountable Practicalities

- Try to store  $\sim 10^{51}$  terms as a numerical object for a SINGLE point in coordinate space (not much after all!!!).
- Just keeping modest single precision (4 bytes per number), a typical  $2 \text{ Gb/cm}^2$  storage capacity would require a surface of  $\sim 10^{42} \text{ Km}^2$ .
- For comparison, the Earth's surface is  $\sim 10^9 \text{ Km}^2$ .

THE PROMISED WISDOM HIDDEN IN THE SE IS NOT READILY ACCESSIBLE IF ONE LOOKS AT  $\psi$ .

WE MUST MAKE DO WITH MUCH, MUCH LESS ...

*Mathematically speaking, we are dealing with a problem like that of the "travelling salesman," still far from being solved due to its rather horrible size scaling (see K. Delvin, The Millennium Problems, Ch. 3).*

# The Born-Oppenheimer Approximation (or the “Dog-Fly” Problem)

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

- $m_N > 1800m_e$  thus nuclei move far more slowly than electrons (e.g., the dog vs. the fly).
- Electrons (the fly) thus follow nucleus (the dog) instantaneously.
- Mathematically one writes

$$\Psi(\{r_i\}, \{R_j\}) = \Psi_N(\{R_j\}) \Psi_e(\{r_i\})$$

- where electronic wavefunction only depends “parametrically” on nuclear coordinates.
- Procedure: “clamp” nuclei in place and solve the “electronic problem” (or forget about the dog!)

$$\hat{H} \Psi_e(\{r_i\}) = E \Psi_e(\{r_i\})$$

## The Electronic Problem (or the “Fly” Problem)

$$\hat{H} \Psi_e(\{r_i\}) = E \Psi_e(\{r_i\})$$

Nuclear-only terms are either zero or constant  $\hat{H} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee}$

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_j^{all e} \nabla_j^2 = -\frac{\hbar^2}{2m_e} \sum_j^{all e} \frac{\partial^2}{\partial r_j^2}$$

Electronic kinetic energy

$$\hat{V}_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_i^{all e} \sum_{j>i}^{all e} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Electron-electron repulsion

$$\hat{V}_{Ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{all e} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

“External” potential

Thus the EXTERNAL POTENTIAL (nuclear structure) and the number of electrons (chemical makeup) determine the problem (within the BO approx).

**THIS OBSERVATION IS IMPORTANT TO LAY THE FOUNDATIONS OF DFT**

# Molecular Structure and Physical Properties

- Structure problem: find nuclear coordinates for which the TOTAL energy is a minimum (the so-called ground-state energy).
- Once ground-state structure has been found, other properties follow, e.g., band structure, phonons, dielectric constant, dipole moment, polarizability, etc.
- To achieve the above, total wavefunction  $\psi$  needs to be obtained by solving the SE (almost always involving BO approx).

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

## Tackling the Problem

- USE OF FINITE “BASIS SETS” centered around each nucleus (e.g., start with atomic orbitals): choice of basis becomes a crucial point of departure but a hard one to control if not careful.
- Electron motion is highly correlated (we face a complicated many-body problem).
  - Those electrons with same spin are “kept away” by antisymmetry requirements from Pauli Exclusion Principle (also called “exchange correlation” or “Fermi correlation”).
  - Those with same spin are kept away due to repulsion (Coulomb correlation).
  - In practice we can only hope to do this APPROXIMATELY.

# Wavefunction-based Methods

- Simplest method of practical use: Hartree Fock (1950s)
- What is done (& assumed) in HF:
  - Electronic wavefunction is an antisymmetric combination of one-electron orbitals (so-called Slater determinant).
  - Replace exact Hamiltonian by that of a set of non-interacting electrons where each moves in an average field (Mean-field Theory).
  - One-electron “orbitals” obey a set of COUPLED differential equations, whose solution must be obtained ITERATIVELY (so-called SCF or “self-consistent-field” method).

Hartree-Fock and SCF: also important to understand DFT, thus we need to delve a bit into the details.

## The Hartree-Fock Method

Wavefunction is a “Slater determinant” of “spin-orbitals”

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) & \cdot & \chi_N(r_1) \\ \chi_1(r_2) & \chi_2(r_2) & \cdot & \chi_N(r_2) \\ \cdot & \cdot & \cdot & \cdot \\ \chi_1(r_N) & \chi_2(r_N) & \cdot & \chi_N(r_N) \end{vmatrix}$$

“Spin-orbitals” contain both spatial and spin wavefunctions  $\chi_i = \phi_i \alpha$

Simple example: two-electron system (the H<sub>2</sub> molecule)

$$\Psi_{HF}(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) \\ \chi_1(r_2) & \chi_2(r_2) \end{vmatrix} = \chi_1(r_1)\chi_2(r_2) - \chi_1(r_2)\chi_2(r_1) = -\Psi_{HF}(r_2, r_1)$$

Need second term to satisfy antisymmetry requirement (first term is not enough)

# The Hartree-Fock Method for Solving SE Equation

“Slater determinant” is our one-electron guess for

$$\hat{H} \Psi_{HF}(\{r_i\}) = E \Psi_{HF}(\{r_i\})$$

Variational Principle:  $E = \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$

To use this principle we vary spin orbitals to minimize E

Hartree-Fock Energy:  $E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle$

## The Hartree-Fock Method in Some Detail

Seek to solve:  $E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle$

Which for a Slater-type electronic wavefunction gives:

$$E_{HF} = \sum_{i=1}^N \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^N \sum_{j=1}^N \left\{ \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_j \chi_i \rangle \right\}$$

One-electron  
operator

Coulomb  
Exchange  
Self-interaction

cancels out exactly (i=j)

$$\hat{h}_i = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_j^{\text{all nuclei}} \frac{Z_j}{r_{ij}}$$

$$\langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_i \chi_j \rangle = \int \chi_i^*(r_1) \chi_j^*(r_2) \frac{1}{|r_1 - r_2|} \chi_i(r_1) \chi_j(r_2) dr_1 dr_2$$

$$\langle \chi_i \chi_j | \frac{1}{r_{12}} | \chi_j \chi_i \rangle = \int \chi_i^*(r_1) \chi_j^*(r_2) \frac{1}{|r_1 - r_2|} \chi_j(r_2) \chi_i(r_1) dr_1 dr_2$$

# The Hartree-Fock Equations

Apply Variational Theorem & use orthogonality of spin orbitals

$$E_{HF} = \sum_{i=1}^N \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^N \sum_{j=1}^N \left\{ \left\langle \chi_i \chi_j \left| \frac{1}{r_{12}} \right| \chi_i \chi_j \right\rangle - \left\langle \chi_i \chi_j \left| \frac{1}{r_{12}} \right| \chi_j \chi_i \right\rangle \right\}$$

and  $\langle \chi_i | \chi_j \rangle = \delta_{ij}$

To obtain a set of equations for each spin orbital

$$\left[ \hat{h}_i + \hat{V}_{HF} \right] \chi_i = \epsilon_i \chi_i \quad \text{with} \quad \hat{V}_{HF} = \sum_{k=1}^{alle} \hat{J}_k - \hat{K}_k$$

Coulomb  $\left[ \hat{J}_k(r_1) \right] \chi_i(r_1) = \left[ \int \chi_k^*(r_2) \chi_k(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_i(r_1)$

Exchange  $\left[ \hat{K}_k(r_1) \right] \chi_i(r_1) = \left[ \int \chi_k^*(r_2) \chi_i(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_k(r_1)$

## The Coulomb and Exchange Terms

Coulomb term related to electronic density

$$\left[ \hat{J}_k(r_1) \right] \chi_i(r_1) = \left[ \int \chi_k^*(r_2) \chi_k(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_i(r_1)$$

$$\sum_{k=1}^{alle} \hat{J}_k = \sum_{k=1}^{alle} \int \chi_k^*(r_2) \chi_k(r_2) \frac{1}{r_{12}} dr_2 = \int \frac{\rho(r_2)}{r_{12}} dr_2$$

Exchange term leads to NON-LOCAL EXCHANGE POTENTIAL

$$-\sum_{k=1}^{alle} \left[ \hat{K}_k(r_1) \right] \chi_i(r_1) = -\int \sum_{k=1}^{alle} \frac{\chi_k^*(r_2) \chi_k(r_1)}{r_{12}} \chi_i(r_2) dr_2 = \int v_X(r_1, r_2) \chi_i(r_2) dr_2$$

Such that

$$\left[ \hat{h}_i + \int \rho(r_2) \frac{1}{r_{12}} dr_2 \right] \chi_i + \int v_X(r_1, r_2) \chi_i(r_2) dr_2 = \epsilon_i \chi_i$$

Hartree term (electron density is important)

exchange potential (hard bit)

# Hartree Fock Recap

HF orbitals obey:

$$\left[ \hat{h}_i + \int \frac{\rho(r_2)}{r_{12}} dr_2 \right] \chi_i + \int v_X(r_1, r_2) \chi_i(r_2) dr_2 = \varepsilon_i \chi_i$$

HF one-electron spin orbitals describe a non-interacting system under the influence of a mean-field potential made up of a Coulomb term and a NON-LOCAL exchange potential.

To note:

- Electronic density plays a role from the outset.
- HF is a mean-field theory and thus breaks down very quickly:  $F_2$  is not a molecule, metallic state does not exist, ...
- Errors in HF approach are due to absence of electron correlation.

## Wavefunction-based Methods Beyond Hartree-Fock

- Better approximations (so-called “correlated methods”) exist but at a very high computational cost due to unfavourable scaling (e.g., need a sum of Slater determinants or “configurations,” or use of perturbation theory).
- Some examples are: MP2, CISD, CCSD, MRCI which scale as  $N^x$  where  $x > 5$  [1]. Be aware of these when reading the literature (they are quite common and useful to benchmark DFT calculations).
- Some problems:
  - Very flexible descriptions of wavefunction required – hard work.
  - A more expensive calculation or basis set does not guarantee better results (uncontrolled cancellation of errors, BSSEs, etc).
  - Case-by-case exploration is typically the norm.
  - Extension to large systems (a solid) of practical interest clearly beyond our reach now and in the foreseeable future.

[1] For an excellent account, see: A Szabo & NS Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, 1989).

*Is it, however, necessary to solve the SE and determine the wavefunction in order to compute the ground-state energy?*

*To what extent can we avoid it?*

*In a sense, the SE equation is quite misleading as it invites us to pay close attention to the wavefunction*

$$\hat{H} \Psi(\{r_i\}, \{R_j\}) = E \Psi(\{r_i\}, \{R_j\})$$

# The Two Theorems that Changed Everything [1]

## Theorem 1

The external potential  $V_{Ne}$  is *uniquely* determined by the density. The total energy is a unique functional of the electron density (written  $E[n]$ ).

$$\hat{V}_{Ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{alle} \frac{Z_i}{|\vec{R}_i - \vec{r}_j|}$$

## Theorem 2

The density which minimizes the energy corresponds to the ground-state density and the minimum energy is the ground state energy (yet another Variational Principle).

*In other words, there is a universal functional  $E[n]$  which can be minimised to obtain the exact ground state density and energy.*

[1] Hohenberg & Kohn, Phys. Rev. B 136, 864 (1964).

## What is a Functional?

- We are all familiar with functions, whereby one establishes a map or rule between one set of numbers and another, e.g.,  $y=f(x)$ .
- A functional extends this concept to create a map between a set of functions and a set of numbers, denoted  $y=F[f(x)]$ .
- In the context of DFT,  $y=E$  (the energy) and  $f(x)=n$  (the electronic density).
- In fact, you have all been dealing with functionals for quite a while (e.g., definite integrals)

$$F[g] = \int_a^b g(x) dx$$

where specification of an integrable function  $g(x)$  produces a number defined in terms of the constants  $a$  and  $b$ .

# The Energy Functional

Electronic SE  $\hat{H} \Psi_e(\{r_i\}) = E \Psi_e(\{r_i\})$

Electronic Hamiltonian  $\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne}$

Conventionally  $\hat{V}_{Ne} = \hat{V}_{ext}$  to emphasize its “external” character in the electronic problem

Total energy is given by  $E[n] = T[n] + E_{ee}[n] + E_{ext}[n]$

From SE equation, “external” part follows

$$E_{ext}[n] = \int \hat{V}_{ext} n(r) dr \quad \text{with} \quad \hat{V}_{ext} = -\frac{e^2}{4\pi\epsilon_0} \sum_i^{all N} \sum_j^{alle} \frac{Z_i}{|\bar{R}_i - \vec{r}_j|}$$

Kinetic and electron-electron functionals are a priori unknown.

Need to approximate them intelligently.

## The Kohn-Sham Approach [1]

First (and most popular) way to approximate unknown functionals.

Essence: introduce a *fictitious* system of N non-interacting electrons described by a single determinant (Slater-type) wavefunction in N “orbitals”. **FORMALLY IDENTICAL TO HARTREE-FOCK.**

In this non-interacting system, both kinetic energy and electron density can be obtained exactly from the orbitals.

$$\hat{T}_s = -\frac{\hbar^2}{2m_e} \sum_j^{alle} \langle \phi_j | \nabla^2 | \phi_j \rangle \quad \text{Note: this KE is fictitious}$$

$$\rho(r) = \sum_j^{alle} |\phi_j|^2 \quad \text{Note: this construction immediately ensures that it is “legal” (obeys Pauli Exclusion Principle)}$$

## Recall expression for Hartree-Fock energy

$$E_{HF} = \sum_{i=1}^N \langle \chi_i | \hat{h}_i | \chi_i \rangle + \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{i=1}^N \sum_{j=1}^N \left\{ \left\langle \chi_i \chi_j \left| \frac{1}{r_{12}} \right| \chi_i \chi_j \right\rangle - \left\langle \chi_i \chi_j \left| \frac{1}{r_{12}} \right| \chi_j \chi_i \right\rangle \right\}$$

Coulomb term is related to densities      Exchange is not

We thus treat Coulomb correlation separately (it is an important term)

$$E_H[n] = \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \int \frac{n(r_1)n(r_2)}{r_{12}} dr_1 dr_2 \quad \text{"Hartree" term}$$

And the energy functional  $E[n]$  is rewritten as

$$E[n] = T_s[n] + E_H[n] + E_{ext}[n] + E_{XC}[n]$$

where we have introduced the "exchange-correlation" functional  $E_{XC}$

$$E_{XC}[n] = [T[n] - T_s[n]] + [E_{ee}[n] - E_H[n]]$$

("exchange-correlation" is somewhat of a misnomer, but never mind)

## What is $E_{XC}$ ?

$$E_{XC}[n] = [T[n] - T_s[n]] + [E_{ee}[n] - E_H[n]]$$

The exchange correlation functional is the error made when using

- A non-interacting kinetic energy term.
- Assuming that electron-electron interactions are classical (no exchange).

IT CONTAINS ALL REMAINING UNCERTAINTIES

With this functional for the total energy in terms of the electronic density we can now

- Apply the Variational Theorem.
- Use the KS orbitals which minimise the total energy to construct the electronic density  $n$ .
- Formally identical to the HF approach where the non-local exchange potential is replaced by a local exchange-correlation potential.

# The Kohn-Sham Equations

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{ext} + \int \frac{n(r_2)}{r_{12}} dr_2 + \hat{V}_{XC} \right] \phi_i = \epsilon_i \phi_i$$

where  $V_{XC}$  is a local potential defined as the functional derivative of  $E_{XC}$  wrt to the density.

$$\hat{V}_{XC} = \frac{\delta E_{XC}[n]}{\delta n}$$

KS Equations are solved iteratively until self-consistency is reached.

The procedure does not involve approximations, EXCEPT for the precise form of  $E_{XC}$ .

Conversely, if we knew  $E_{XC}[n]$ , we could solve for the exact ground-state energy and density EXACTLY, FOR ANY SYSTEM .

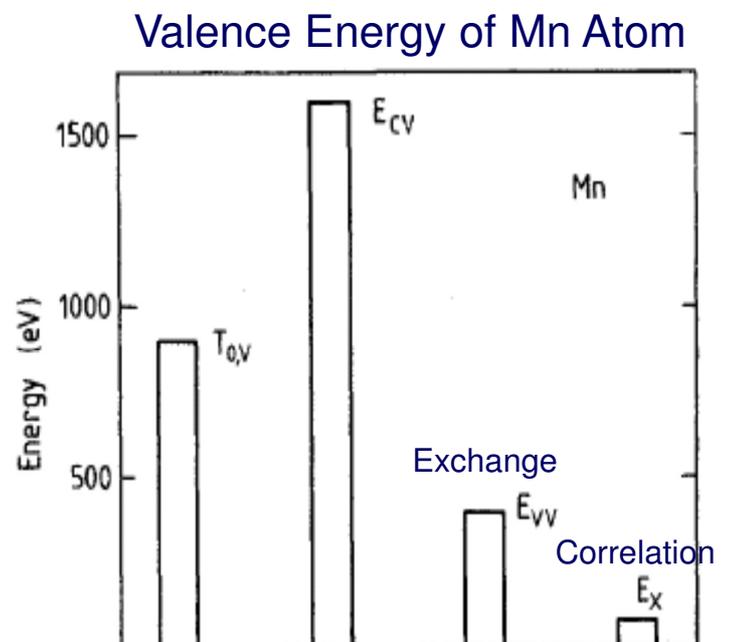
**THE KS Equations ARE AT THE HEART OF ALL DFT CODES**

## Hierarchy of Contributions to the Total Energy

Our ignorance about how to solve SE appears to have been swept into a single term  $E_{XC}$  accounting for the hard bits (e.g., electron exchange and correlation).

### Does this help?

- Exchange is small, correlation even smaller.
- Thus, a smart choice in most cases.
- A reasonable approx. to  $E_{XC}$  is likely to provide a good description of total energy.



Courtesy of Dr K Refson

# Remarks on DFT and KS Equations

- Correspondence between electron density and energy of the real vs. non-interacting system is ONLY EXACT if the exact functional is known.
- In this sense, KS Method is EMPIRICAL: need to guess  $E_{XC}$ .
  - We do not know it.
  - We do not know even know how to systematically approach it.
- However
  - We can work it out in a number of systems for which solutions are known.
  - From this, we can have good approximations to the functional.
  - And use it in an UNBIASED & PREDICTIVE manner.
- Computational cost: traditionally it has been  $N^3$  but recent progress is making it drop towards  $N$  (can do larger systems).

## Functionals: The Uniform Electron Gas

Collection of  $N$  electrons in a uniformly positive background (to keep things neutral).

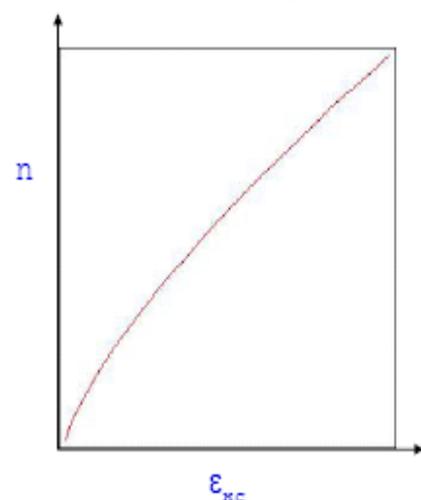
It is an old problem (uniform electron gas):

- Kinetic energy, Thomas & Fermi (1927).
- Exchange, Dirac (1930).
- Coulomb part (numerical, QMC [1])

KE and X terms suggest an ansatz for  $E_{XC}$  in inhomogeneous (real) systems as an integral over a **local function of the charge density**.

$$E_{xc}[n] = \int n(r) \epsilon_{xc}(n(r)) dr$$

$$T[n] = C_{KE} \int n^{\frac{5}{4}}(r) dr$$
$$E_x[n] = -C_x \int n^{\frac{4}{3}}(r) dr$$



# Functionals: The Local Density Approximation

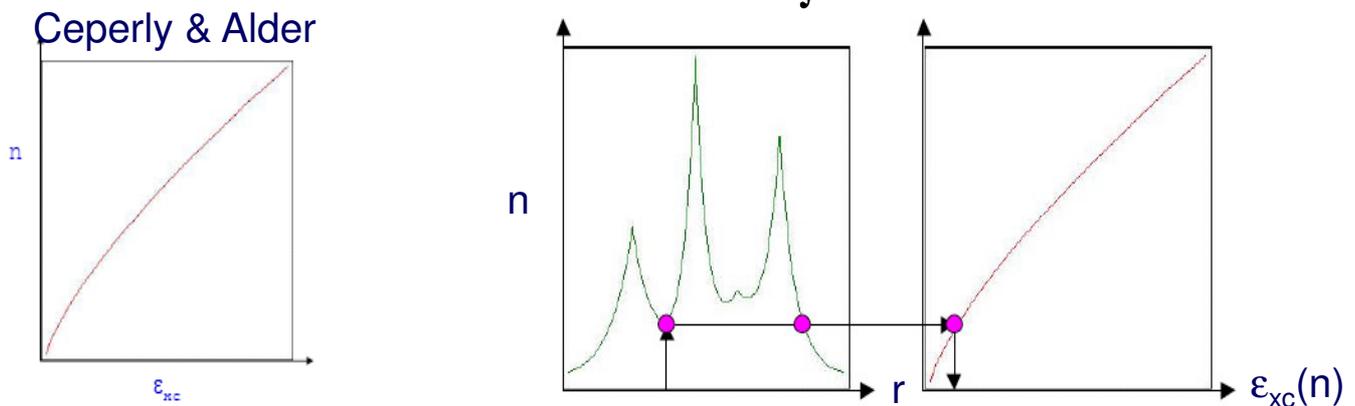
Simplest approximation: at every point in space, use the value of the density that the uniform gas would have (LDA).

$\epsilon_{xc}(n)$  can then be taken as a sum of exchange and Coulomb correlation terms

$$\epsilon_{XC}(n) = \epsilon_X(n) + \epsilon_C(n) \quad \text{with} \quad \epsilon_X(n) = -C_X n^{\frac{1}{3}} \quad (\text{Dirac})$$

and  $\epsilon_C(n)$

$$E_{xc}[n] = \int n(r) \epsilon_{xc}(n(r)) dr$$



## How Good is the LDA?

ORIGINAL PREDICTION (Kohn & Sham 1965): “We do not expect an accurate description of chemical bonding.”

Extensive computational experimentation in the past 30+ years shows **REMARKABLE SUCCESS:**

- Good description of covalent, metallic, and ionic bonds.
- Not adequate for:
  - Hydrogen bonds (relatively weak).
  - Van der Waals interaction (London dispersion): but this is a problem with DFT in general.

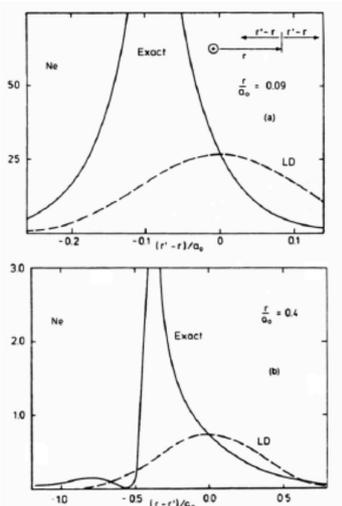
Common problems:

- Energy differences between very different structures.
- Binding energies are typically OVERESTIMATED.
- Energy barriers for diffusion/chemical reactions can be very small.

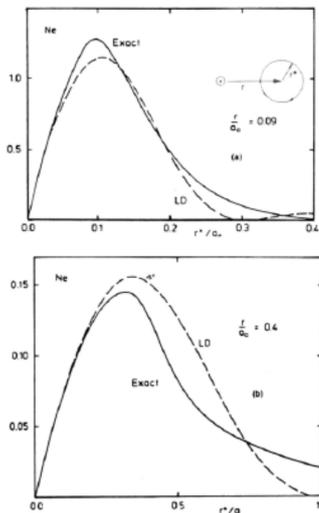
# Detour: Why the LDA Works so Well [1]

- To see this, need to look at the so-called “exchange-correlation” hole (ECH).
- ECH is the hole a given electron at position  $r$  digs for itself in the surrounding electronic density.
- ECH should normalize to unity (one electron): LDA ensures this (it is physically sound).

LDA: lousy for ECH



LDA: much better for  $V_{ee}$



The reasons why:

- $V_{ee}$  only depends on spherical average of ECH (due to its  $1/r$  character).
- LDA provides a good estimate of this averaged property.

*For a more detailed account see Koch & Holthausen in the Refs.*

[1] Jones & Gunnarson, *Rev. Mod. Phys.* 61, 689 (1979)

## Functionals Beyond LDA: GGA

LDA is the zeroth approximation to the density (sort of a 80-for-20 answer).

To go beyond, need to account for the spatial variation of the density.

Generalized Gradient Approximation (GGA) is the most popular of these approaches.

GGA functional is of the form:

$$E_{xc}[n] = \int n(r) \varepsilon_{xc}(n, \nabla n) dr$$

Approximations are made separately for Exchange & Coulomb terms, usually involving empirical parameters from fits to large sets of accurate calculations on atoms. Some examples are:

- Coulomb: LYP (1988), PW91 (1991), P86 (1986) ...
- Exchange: BPW91, BLYP, ...

# Functionals Beyond GGA: Meta-GGA

Simply, include the second derivatives in your description

$$E_{xc}[n] = \int n(r) \varepsilon_{xc}(n, \nabla n, \nabla^2 n, \tau) dr$$

where  $\tau$  is the “kinetic energy density”

$$\tau = \frac{1}{2} \sum_i |\nabla \phi_i|^2$$

## Hybrid Functionals

If electron-electron interactions are switched off from the problem, one recovers the Hartree-Fock answer.

The above suggests that the GGA functional can be used to improve our ansatz for the exact exchange-correlation functional.

A reasonable, first-order approximation is given by

$$E_{xc}[n] = \alpha E_{HF} + \beta E_{xc}^{GGA}$$

With  $\alpha$  and  $\beta$  determined by reference to exact results (e.g., fit to a data set including ionization potentials, proton affinities, total energies).

B3LYP is the most popular one (particularly amongst chemists): binding energies, geometries, and frequencies are systematically improved with respect to GGA.

# The Performance of DFT Functionals

“Functional Design:” two schools of thought

- Puristic: use the properties of the functional to determine its form and shape (including parameters).
- Pragmatic: come up with a functional form, introduce lots of parameters to be fitted against experimental data or accurate calculations (empirical).

**THIS IS A USEFUL DISTINCTION IN ASSESSING PERFORMANCE FOR A PARTICULAR PROBLEM.**

Characteristics of some popular functionals:

- BLYP, PBE, PKZB: virtually “ab-initio.”
- HCTH, VS98: heavily parameterised (large molecular training sets).

Recent tabulations/benchmarks:

- Kurth, Perdew & Blaha, *Int. J. Quantum Chemistry* 75, 889 (1999).
- Adamo, Ernzerhof & Scuseria, *J. Chem. Phys.* 112, 2643 (2000).

## DFT Functionals: Benchmarking (I)

KURTH, PERDEW, AND BLAHA

*International Journal of Quantum Chemistry*, Vol. 75, 889–909 (1999)  
© 1999 John Wiley & Sons, Inc.

TABLE I  
Exchange energies ( $-E_x$  in hartree) for some spherically symmetric atoms.<sup>a</sup>

	$E_x^{\text{exact}}$	$E_x^{\text{LSD}}$	$E_x^{\text{PBE}}$	$E_x^{\text{RPBE}}$	$E_x^{\text{BLYP}}$	$E_x^{\text{HCTH}}$	$E_x^{\text{PKZB}}$	$E_x^{\text{VS98}}$	$E_x^{\text{FT98}}$
H	0.3125	0.2680	0.3059	0.3112	0.3098	0.3055	0.3081	0.3148	0.3120
He	1.0258	0.8840	1.0136	1.0313	1.0255	1.0063	1.0202	1.0399	1.0302
Li	1.7807	1.5379	1.7572	1.7876	1.7753	1.7454	1.7682	1.7893	1.7852
Be	2.6658	2.3124	2.6358	2.6801	2.6578	2.6114	2.6482	2.6579	2.6707
N	6.6044	5.9008	6.5521	6.6252	6.5961	6.5145	6.5255	6.5968	6.6045
Ne	12.1050	11.0335	12.0667	12.1593	12.1378	12.0114	11.9514	12.1404	12.1260
Na	14.0131	12.7859	13.9506	14.0528	14.0304	13.9009	13.8115	14.0374	14.0177
Mg	15.9884	14.6117	15.9147	16.0260	16.0005	15.8596	15.7448	15.9967	15.9862
P	22.6341	20.7931	22.5028	22.6369	22.6221	22.5016	22.2475	22.6365	22.6089
Ar	30.1747	27.8632	29.9961	30.1494	30.1535	30.0751	29.6437	30.1918	30.1429
Kr	93.8330	88.6245	93.4257	93.6645	93.8721	95.1802	92.2949	94.8248	93.8407
Xe	179.0635	170.5660	178.2450	178.5649	179.0427	183.2130	176.2574	181.6907	179.0636
mare (in %)		9.8	0.8	0.3	0.2	1.4	1.3	0.5	0.1

<sup>a</sup>All functionals were evaluated with self-consistent exchange-only OEP orbitals and densities [47]. Exact values,  $E_x^{\text{exact}}$ , were obtained by evaluating Eq. (11) with these orbitals. The “mare” is the mean absolute value of the relative error.

Mean absolute value of the average error

- LDA overbinds by 20-30%
- GGA: significant improvements.
- Highly parameterized HCTH a bit better than PBE and BLYP.
- Meta-GGA: 2-3% error (3-5 kcal/mol, thus “chemical” accuracy)
- Maximum errors can be large (30-40 kcal/mol for “difficult systems”).

- LDA or GGA bond lengths in solids at the few % level.
- Heavily parameterised functionals biased towards isolated molecules (training sets).
- Lightly parameterized functionals are more transferable.
- Bulk modulus and vib freq.: GGA (~10%) better than LDA. VG98 > PBE-GGA.

TABLE VIII  
Equilibrium unit cell volumes  $V_0$  (in bohr<sup>3</sup>) for bulk solids, using self-consistent LSD-xc orbitals and densities for LSD, and self-consistent PBE-GGA-xc orbitals and densities for the other functionals.<sup>a</sup>

Solid	$V_0^{\text{expt}}$	$V_0^{\text{LSD}}$	$V_0^{\text{PBE}}$	$V_0^{\text{RPBE}}$	$V_0^{\text{BLYP}}$	$V_0^{\text{HCTH}}$	$V_0^{\text{PKZB}}$	$V_0^{\text{KCIS}}$	$V_0^{\text{VS98}}$	$V_0^{\text{FT98}}$
Na	255.4	224.4	249.8	267.8	250.1	275.6	272.0	271.0	229.1	194.0
NaCl	302.7	276.1	313.1	338.3	324.3	353.6	296.6	312.5	240.0	321.0
Al	112.1	106.6	111.2	113.3	116.5	108.4	109.3	108.0	101.8	106.0
Si	270.0	266.2	276.3	282.1	285.6	278.3	274.5	280.4	270.6	268.1
Ge	305.9	301.4	322.1	331.0	343.1	328.9	314.6	319.9	318.1	325.4
GaAs	304.3	298.3	320.5	330.2	340.1	329.0	314.0	319.4	315.8	323.0
Cu	78.7	73.5	80.6	83.5	85.7	82.5	78.5	79.9	82.7	78.7
W	106.5	104.0	108.9	110.2	112.7	106.1	107.1	108.1	108.9	106.9
Fe	79.5	70.5	76.7	79.1	80.3	—	75.9	77.0	—	75.5
Pd	99.3	95.5	103.2	106.1	110.1	104.3	100.9	102.9	110.0	106.9
Pt	101.3	99.7	105.7	107.5	112.4	104.4	103.0	104.4	110.2	106.8
Au	112.8	111.9	121.1	124.6	131.0	123.5	117.8	120.6	129.2	120.8
mare (in %)	—	4.8	3.6	6.0	8.0	6.3	2.6	3.8	8.1	6.2

<sup>a</sup>The calculations were done with the WIEN code [99]. The experimental values are from Refs. [52] (for most of the solids), [113] (for Pd), and [55] (for Pt and Au). For Fe, the HCTH and VS98 energies oscillate near the minimum.

# DFT Functionals: Benchmarking (II)

TABLE I. Electronic atomization energies (in kcal/mol) for the molecules in the extended G2 set (Ref. 38–40). The MP2/6-31G(d) geometries of Refs. 38–40 and 6-311+G(3d/2p) basis sets are used.

Molecule	Exp.	PBE*	PBE1PBE*	MGGA
LiH	57.8	-4.5	-5.3	1.3
BeH	49.8	5.8	6.0	3.7
CH	83.8	1.0	-0.6	1.8
CH <sub>2</sub> ( <sup>1</sup> B <sub>1</sub> )	190.0	4.5	3.7	2.7
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	180.7	5.0	3.1	0.7
CH <sub>3</sub>	306.6	3.4	1.8	3.9
CH <sub>4</sub>	419.2	0.9	-1.5	2.9
NH	83.5	5.0	1.7	3.6
NH <sub>2</sub>	181.5	7.2	1.7	5.7
NH <sub>3</sub>	297.5	4.6	-2.4	2.3
OH	106.4	3.6	-0.7	1.7
H <sub>2</sub> O	232.2	2.2	-5.2	-1.7
HF	140.8	1.3	-4.1	-2.1
SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	151.3	-2.7	-4.2	4.3
SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	131.2	1.8	1.5	8.3
SiH <sub>3</sub>	225.1	-2.0	-1.7	8.3
SiH <sub>4</sub>	321.4	-7.3	-6.3	6.5
PH <sub>2</sub>	152.9	1.9	0.5	7.2
PH <sub>3</sub>	241.8	-2.3	-3.9	5.9
SH <sub>2</sub>	182.4	-0.3	-2.4	4.2
HCl	106.3	1.1	-1.1	3.3
Li <sub>2</sub>	24.4	-4.0	-4.8	-0.5
LiF	137.5	1.7	-5.3	-8.2
C <sub>2</sub> H <sub>2</sub>	405.3	9.7	-1.3	-3.1
C <sub>2</sub> H <sub>4</sub>	562.6	9.2	1.3	-0.1
C <sub>2</sub> H <sub>6</sub>	710.8	6.1	1.2	0.8
CN	180.9	14.8	-2.6	0.5
HCN	312.6	13.7	-2.2	0.4
CO	259.3	10.3	-3.8	-1.8
HCO	278.7	17.3	2.3	3.9
H <sub>2</sub> CO	373.6	13.1	-0.7	1.4
H <sub>2</sub> COH	511.9	8.8	-1.5	-1.4
N <sub>2</sub>	228.6	13.9	-5.8	1.1
N <sub>2</sub> H <sub>4</sub>	437.8	15.5	0.4	2.7

TABLE III. Bond lengths (Å) for diatomic molecules in the G2-1 set (Ref. 42). All values are computed using 6-311G(d,p) basis sets.

Molecule	PBE	PBE1PBE	MGGA	Exp.
H <sub>2</sub>	0.749	0.745	0.750	0.741
LiH	1.604	1.597	1.634	1.595
BeH	1.355	1.347	1.372	1.343
CH	1.140	1.126	1.150	1.120
NH	1.053	1.040	1.060	1.045
OH	0.983	0.971	0.986	0.971
HF	0.928	0.916	0.928	0.917
Li <sub>2</sub>	2.734	2.732	2.781	2.670
LiF	1.569	1.559	1.592	1.564
CN	1.177	1.163	1.186	1.172
CO	1.138	1.125	1.146	1.128
N <sub>2</sub>	1.105	1.093	1.113	1.098
NO	1.160	1.143	1.167	1.151
O <sub>2</sub>	1.221	1.194	1.225	1.207
F <sub>2</sub>	1.420	1.401	1.434	1.417

Unfortunately, the geometries and frequencies calculated with the meta-GGA are worse than PBE and PBE hybrid results.

Useful rule of thumb: *PBE-GGA is always a good starting point (but always check!). But before delving into the unknown ...*

- *Be aware of common features of a particular functional.*
- *If possible, compare to experiment.*

## DFT Functionals: Some Suggestions

- LDA:
  - Covalent systems.
  - Simple metals.
- GGA:
  - Molecules.
  - Hydrogen-bonded materials.
  - Highly varying electronic densities (d and f orbitals).
  - Complex metals.
  - Most magnetic systems.
- Non-local sX / empirical LDA+U (recently implemented in MS)
  - Band gaps (with care).
  - Complex magnetic systems.
- **PLEASE NOTE: VdW materials not listed!!!**

# Advantages of DFT

- It is quite forgiving to the uninitiated or non-dedicated person (e.g., an experimentalist):
  - Choice of functional largely determines quality of calculation
  - Parameters: relatively few; easy to ascertain convergence.
- Good scaling with system size (more next lecture with plane-wave basis sets).
- Allows calculations on large systems (particularly if periodic; more next lecture)
- Large data base to compare with / benchmark your calculation (first thing to do is to check the literature for similar systems; DFT publication rate at present +4000 papers/year).

Efficient & unbiased tool to model materials properties.

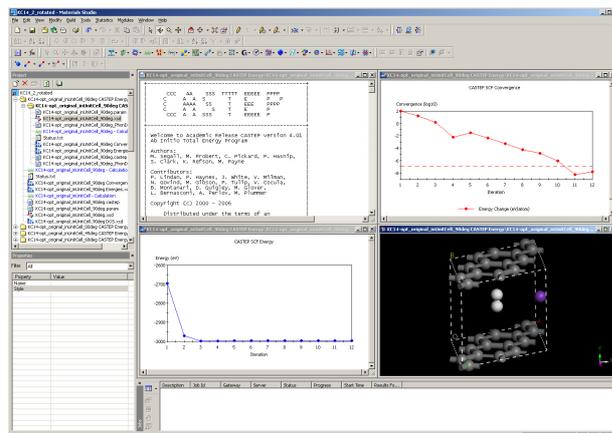
## What is missing in DFT?

- Van der Waals interactions (mutual electronic polarization due to induced-dipole-induced-dipole interactions): very weak. These are not included in ANY existing approximation to  $E_{xc}$ .  
**VERY CAREFUL WITH MOLECULAR SOLIDS AND SOFT MATERIALS (e.g., graphite)**
- Excited states:
  - DFT, as explained today, is a ground-state theory.
  - Time-dependent DFT can overcome this limitation (in its infancy but watch out for progress in this area)
- Non-adiabatic processes (breakdown of the BE approx; a universal limitation):
  - Non-radiative electronic transitions.
  - Jahn-Teller systems (symmetry forces electron-nuclear coupling).
  - Superconductivity (electron-phonon coupling)
- Self-interaction problem: each electron lives in field created by all electrons, including itself (need so-called SIC-DFT methods). This is not a problem in HF Theory where cancellation is exact.
- Still somewhat hard: extended magnetism & associated magnetic excitations (magnons).

# A Glimpse at Next Lecture

## The Practice of DFT calculations: CASTEP & Materials Studio.

- **CASTEP: plane-wave pseudopotential DFT code**
  - Many features, increasing by the day thanks to a dedicated (UK-based) development team.
  - Very efficient for solid-state problems.
  - Free to UK Academics (including a few nice utilities & tools)
- **Materials Studio: easy-to-use interface to**
  - Build molecular models.
  - Run calculations.
  - Analyse output.
  - But you have to pay for it.



## Further Reading & General References

### Recent:

- *J Kohanoff, "Electronic Structure Calculations for Solids & Molecules: Theory & Computational Methods," Cambridge University Press (2006). Relatively concise & quite informative*
- *RM Martin, "Electronic Structure: Basic Theory and Practical Methods," Cambridge University Press (2004). Comprehensive & extensively documented.*

### Useful & Didactical:

- *W Koch & MC Holthausen, "A Chemist's Guide to Density Functional Theory," Wiley-VCH (2002). Theory behind DFT covered in some detail; quite some emphasis on isolated molecules (quantum chemical applications).*
- *AP Sutton, "Electronic Structure of Materials," Oxford Science Publications (1996). Excellent introductory book to the electronic structure of materials.*

### A Bit Outdated but Still Authoritative:

- *RM Dreizler and EKH Gross, "Density Functional Theory," Springer Verlag (1990).*
- *RG Parr and W Yang, "Density Functional Theory of Atoms and Molecules," Oxford University Press (1989).*
- *A Szabo & NS Ostlund, "Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory," McGraw-Hill (1989). The "Bible" of wavefunction-based electronic structure methods (Hartree-Fock and beyond).*

# Outline of Course

1. Fundamentals: Materials Modelling, Electronic Structure & DFT.
2. The Practice of DFT calculations using the CASTEP code & Materials Studio.
3. A Closer Look under the Hood: from Structure to Properties.
4. Advanced Features.

## Lecture II

### The Practice of DFT Calculations

# Outline of Today's Lecture

- Periodic DFT calculations in a nutshell.
- The tools in a flash: Materials Studio & CASTEP.
- Some simple (yet hopefully instructive) examples.

*"Every ab-initio calculation is an approximate one."*

## The Kohn-Sham Equations (Recap)

Single-particle equations: 
$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{eff} \right] \phi_i = \epsilon_i \phi_i$$

Effective potential:

$$\hat{V}_{eff} = \hat{V}_{ext} + \hat{V}_H + \hat{V}_{XC}$$

External potential: 
$$-\frac{e^2}{4\pi\epsilon_0} \sum_i^{allN} \sum_j^{alle} \frac{Z_j}{|\vec{R}_i - \vec{r}_j|}$$

Hartree term: 
$$\int \frac{n(r_2)}{r_{12}} dr_2$$

Exchange-correlation  
The big unknown:  
LDA, GGA, meta-GGA, ...

Single-particle orbitals can *always* be represented in a convenient BASIS SET.

# Periodic DFT Calculations with CASTEP: Basic Ingredients

- BASIS sets
- Pseudopotentials.
- Grids and FFTs.
- k points and Brillouin-zone sampling.

## Basis Sets

- The traditional choice: start with atomic orbitals, so-called “LCAO basis” (linear combination of atomic orbitals).
  - It makes “physical sense.”
  - Expected to describe well core electrons (those not participating in chemical bonding).
  - But it is an ARBITRARY choice after all.
- Mathematically, we can use ANY complete (orthonormal) basis set as starting point.
- For solid-state problems with translational invariance (well-defined  $k$ ), **PLANE WAVES** are a convenient choice.

# Plane Waves

For a given electronic orbital

$$\phi_i(\vec{r}) = \int \phi_i(\vec{k}) e^{i\vec{k}\cdot\vec{r}} d\vec{r} \quad \text{where } \phi(k) \text{ is the Fourier transform of } \phi(r).$$

Very familiar expression to many, e.g., diffraction, image or signal processing, or FT-IR if  $r$  is replaced by *time* ...

Fourier transformation is computationally efficient (FFT algorithms).

Also, certain operations are easier to do in  $k/r$  space.

In addition, for a periodic system:

$$\phi_{i,k}(r) = u_{i,k}(r) e^{ik\cdot r} \quad \text{BLOCH's THEOREM}$$

$u(r)$  has periodicity of unit cell

## Plane Waves: How Many?

Plane-wave basis functions are of the form:

$$\phi_{i,k}(r) = \sum_G u_{i,k}(G) e^{i(k+G)r} \quad \text{for reciprocal lattice vectors } G, k \text{ spanning 1st Brillouin zone.}$$

E.g.,  $\phi_{i,k}(G)$  is the  $k$  component of the  $i^{\text{th}}$  electronic orbital.

$u_{i,k}(G)$  are simply expansion coefficients (constants).

In principle, we need an infinite number of terms.

**PLANE-WAVE ENERGY CUTOFF (a convergence parameter)**

$$E_{\text{cutoff}} \geq \frac{\hbar^2 (k^2 + G^2)}{2m_e} \quad \text{or length scale: } \lambda_{\text{cutoff}} = \frac{h}{\sqrt{2m_e E_{\text{cutoff}}}}$$

# Choosing $E_{\text{cutoff}}$

- The theory:
  - PW cutoff energy defines the “spatial resolution” of resulting (computed, numerical) wavefunction.
  - It behaves VARIATIONALLY: the larger the cutoff the lower the ENERGY.
- The practice:

*Converge calculation for a given property (total energy, lattice parameters, bond lengths ...).*

*Cutoff is system independent but not property-independent.*

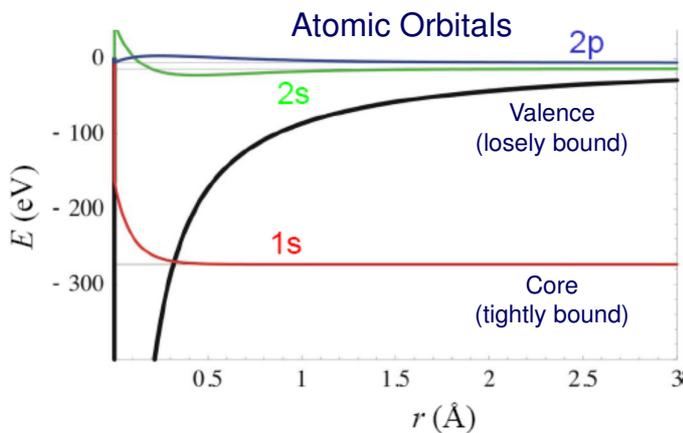
*Note: relative energy differences typically converge faster than total energies.*

## Plane Waves: Pros & Cons

- Advantages:
  - Complete & unbiased: they fill space without prejudice.
  - Mathematically simple and numerically efficient (FFT).
  - Do not depend of atomic positions (they are “originless”).
  - Can be used for periodic, non-periodic & isolated systems (with the addition of an extra convergence parameter – **which one?**)
  - Energy differences not affected by basis-set superposition errors (as in atom-centered basis sets).
  - Single convergence parameter: cutoff energy.
- Disadvantages:
  - Filled & empty space are treated equally: this can be costly (e.g., calculation of isolated molecules).
  - Maximum number of PWs determined by steepest curvature of wavefunction: this is a problem for “tight orbitals” (core electrons).

# Core vs Valence Electrons: Pseudopotentials

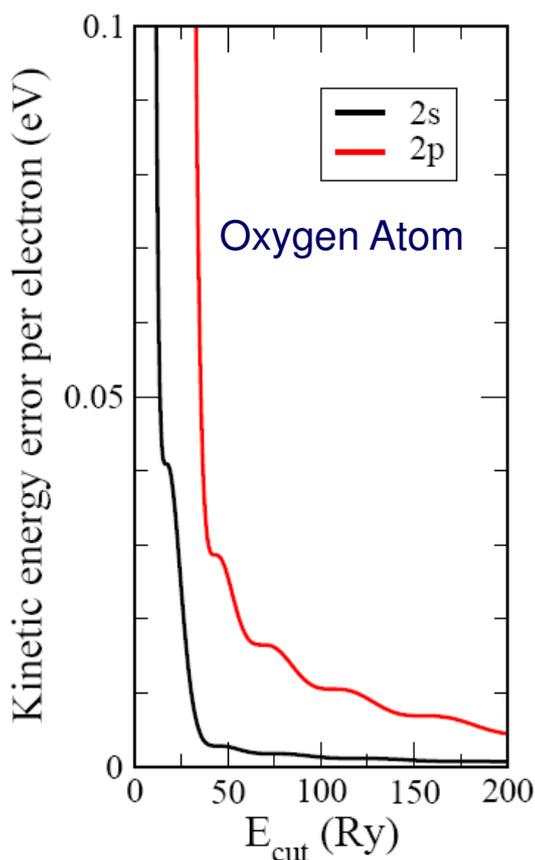
- Motivation: representing core electrons would require a HUGE plane-wave basis set.
- Is this necessary?
  - Chemical binding mostly involves valence shells.
  - Could try to replace nucleus & core with a “pseudopotential” within a specified region of a given radius
  - Then, PW basis set is of reasonable size.
  - NOTE: core features can be “reconstructed” (to calculate properties such as NMR shielding tensors).



*The pseudopotential mimics how the valence electrons see cores (nuclei + tightly bound electrons).*

*CASTEP provides built-in pseudopotentials (but you can also build your own, if need be)*

## Pseudopotentials & $E_{\text{cutoff}}$



- Convergence with cutoff is not necessarily smooth (plateau behaviour).
- Choose energy from most difficult element (inspect pseudopots to find this number).
- Particularly problematic elements: fluorine.

# Types of Pseudopotentials

- **NORM-CONSERVING**: they normalize to unity.
  - In practice, larger basis-set & cutoff energies than necessary, particularly for transition metals.
  - Less flexible.
  - Transferability can always be an issue.
- **ULTRASOFT**: normalization condition relaxed [1].
  - More efficient: smaller basis set required.
  - They are transferable (as practice shows): generation of pseudopotential from neutral atom typically suffices.

[1] D. Vanderbilt, *Phys. Rev. B* 41, 7892 (1990); CY Lee et al., *Phys. Rev. B* 47, 4863 (1993).

## Recap

*So far, we have described the two major ingredients of a “PWP DFT Calculation” as implemented in CASTEP*

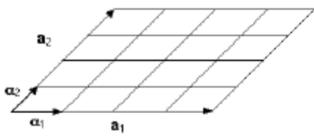
***PWP = Plane-Wave Pseudopotential.***

*Other important ingredients: GRIDS in real & reciprocal space, k-point sampling.*

# Grids and FFTs

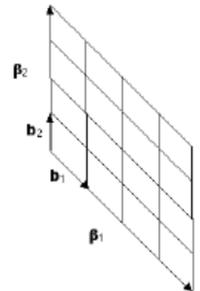
## Motivation:

- Use of plane waves as basis set (well-defined  $k$ ) leads to concept of a reciprocal-space GRID.
- Reciprocal space grid capped by PW Energy cutoff.
- But real-space representation (GRID) is also necessary, e.g., to represent wavefunctions, charge densities, etc. **What determines the real-space grid?**
- FFT's: an efficient means of swapping between  $r$  and  $k$  GRIDS, depending on what needs to be calculated.



Real space

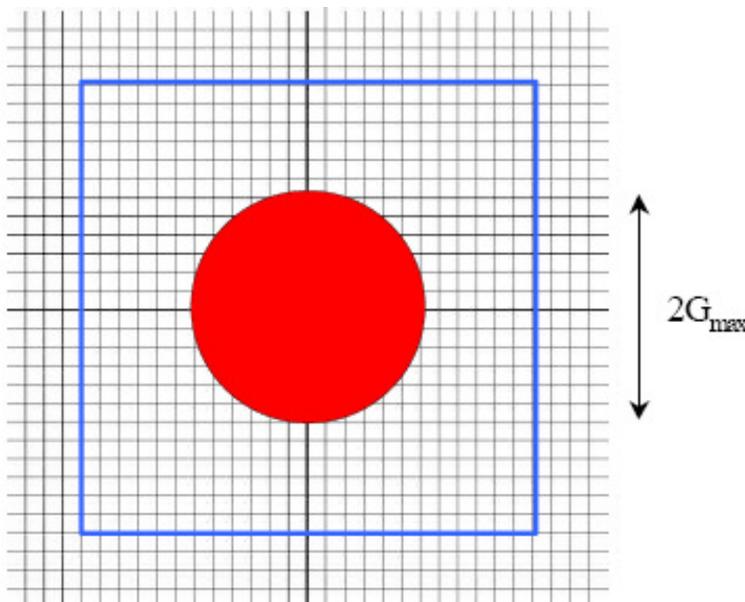
$$u_{i,k}(G) = \frac{1}{N} \sum_r \phi_{i,k}(r) e^{-i(k+G)r}$$



Reciprocal space

## Defining the FFT Grid

- Related to energy cutoff.
- Defined as twice maximum grid (to store charge density as orbitals).



$$E_{cutoff} = \frac{\hbar^2 G_{max}^2}{2m_e}$$

# Grids: Important Remarks

- Transformation between G and r grids are exact at the points we evaluate them.
- Example: kinetic energy is diagonal in reciprocal space thus it is done in G grid, not on r grid.

The above is true because FFT algorithms are cheap (scale as  $N \log N$ ), whereas KE calculation in real space would go as  $N^2$ .

Illustration: typical grid size  $N \sim 10^{+6}$  (say, 100 points along each axis)

- » Brute force in real space ( $N^2$ ):  $\sim 10^{+12}$
- » FFT + reciprocal-space calculation ( $N \log N$ ):  $\sim 10^{+7}$ .

## k points and BZ Integration

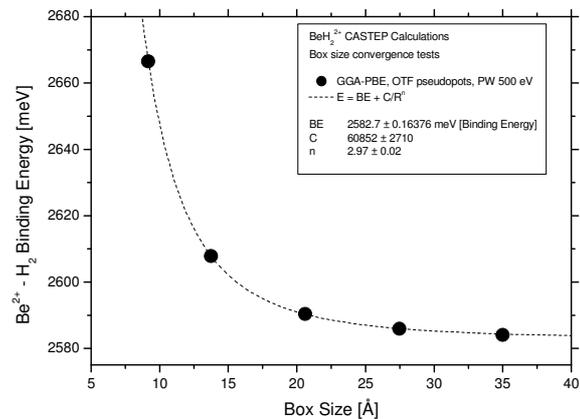
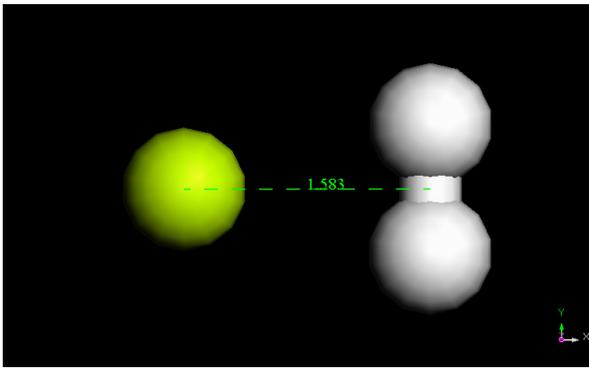
- For a periodic system, many observables are calculated by integration over 1<sup>st</sup> Brillouin Zone [1].
- Examples: total energy or density.
$$E_{tot} = \frac{1}{V_{BZ}} \int_{BZ} E(\vec{k}) d\vec{k} \quad n(\vec{r}) = \frac{1}{V_{BZ}} \int_{BZ} n_{\vec{k}}(\vec{r}) d\vec{k}$$
- Standard method: Monkhorst-Pack grid [2], regular in k-space. It is a CONVERGENCE parameter (inversely proportional to cell volume) but it is NON-VARIATIONAL (thus, be careful)
- Symmetry of unit cell VERY USEFUL to reduce number of k points (calculation time).
- Origin shifts can be used to improve k-point convergence.
- Metals (partially filled bands): require fine k-point grids to represent Fermi surface.
- **Food for thought: how would you deal with an isolated atom/molecule?3**

[1] See any solid-state physics book, e.g., C Kittel, *Introduction to Solid State Physics 6<sup>th</sup> Edition*, John Wiley & Sons (1986).

[2] HJ Monkhorst and JD Pack, *Phys. Rev. B* 13, 5188-5192 (1976).

# Isolated Molecules and Cell Size

- Periodic calculations: can be used to calculate properties of isolated molecules, including ions.
- Requirement: periodic images are sufficiently far away from each other not to affect desired property: not necessarily monotonic, particularly for smallish boxes (try with an H atom, starting with a 5 Å box).
- Need to converge calculation with box size: important parameter is distance, not volume.
- Similar considerations apply to surfaces separated by vacuum gap.



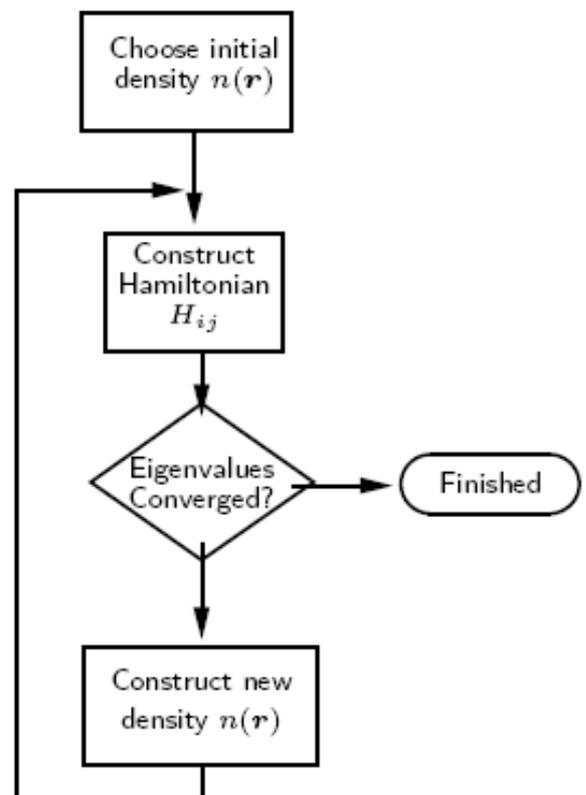
## Finding Electronic Ground State: The Basics

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{eff} \right] \phi_i = \epsilon_i \phi_i$$

$$\phi_{i,k}(r) = \sum_G u_{i,k}(G) e^{i(k+G)r}$$

where G-sum is over reciprocal lattice vectors below cutoff energy.

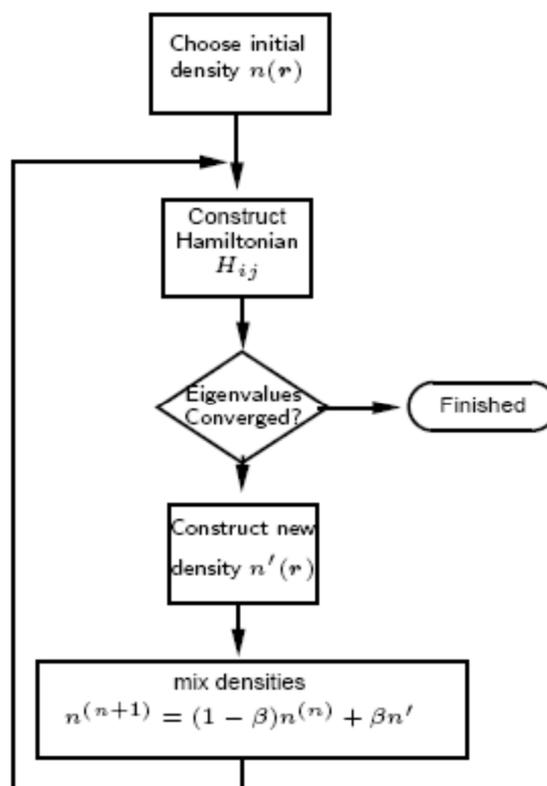
- KS Equations: energy depends on density, density depends on orbitals, energy depends on orbitals.
- Self-consistent-field cycle to find plane-wave coefficients is a must.
- But brute-force SCF is not practical.



Courtesy of Dr K Refson

# SCF and “Density Mixing”

- Need to stabilize SCF convergence (so-called density/spin “sloshing instabilities”).
- Basic idea: mix new electron densities with old ones. Initial density is that of the atoms (not a bad guess).
- Algorithms: linear, Pulay, Broyden, Kerker ... Quite effective (quick) but can be unstable.
- ALWAYS CHECK FOR CONVERGENCE.
- In practice:
  - Default values are quite robust.
  - Only worry about this if poor or no SCF convergence is encountered.
- Above method is not variational: variational methods include EDFT (ensemble DFT) which is more stable but slower. Use it if DM fails.



*Courtesy of Dr K Refson*

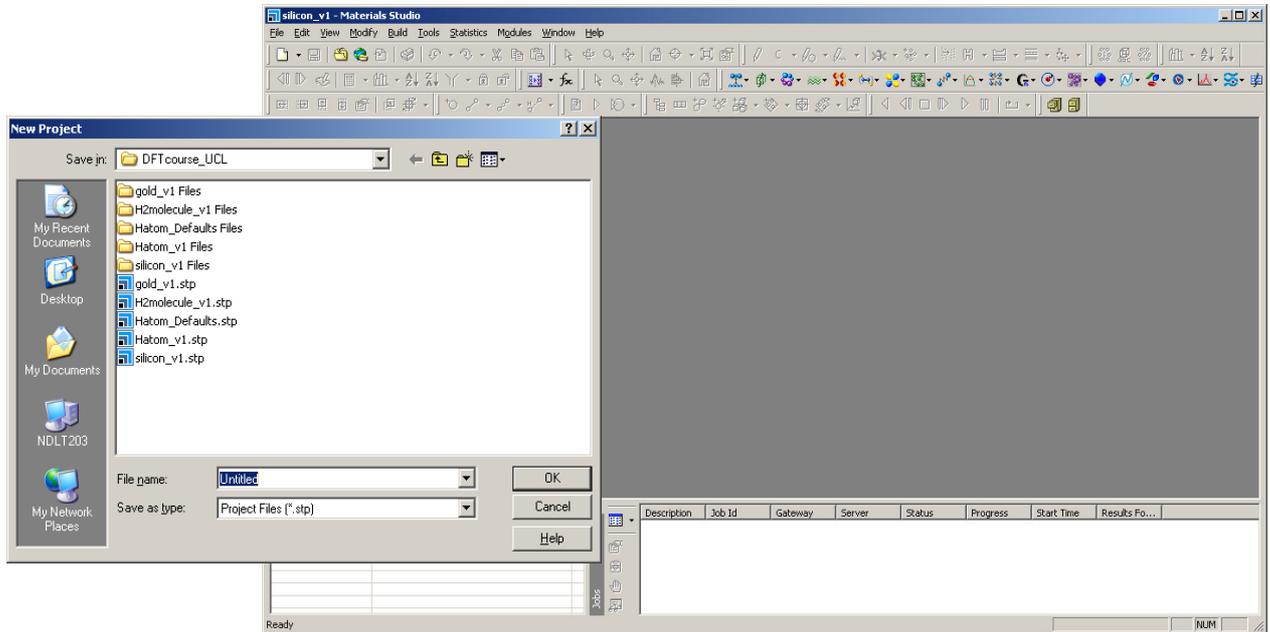
## The Tools in a Flash: The Hydrogen Atom

### First Dive into Materials Studio & CASTEP:

- We will use Materials Studio to create a 10 Angstrom cubic box.
- Insert a hydrogen atom at the cell/box centre.
- Run CASTEP for the first time.

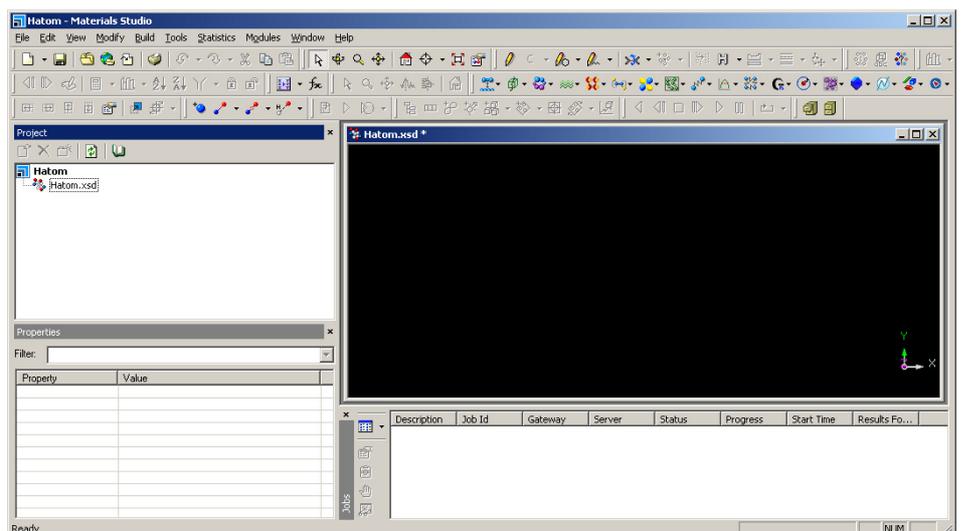
# Materials Studio: Create a Project

- Create a new “project”.
- Call it, say, “Hatom”



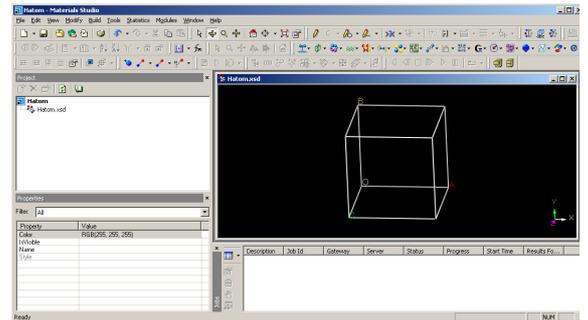
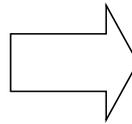
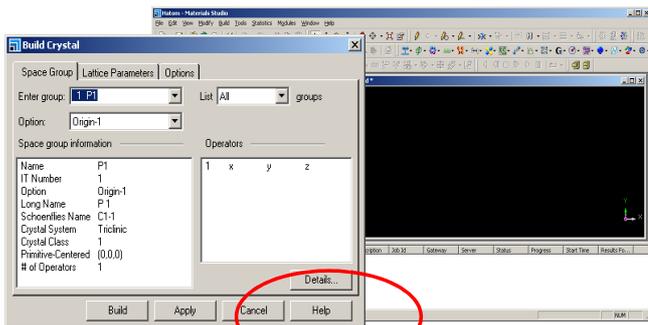
# Materials Studio: Create Atomistic File

- In Hatom project, create a new “3D atomistic” file.
- Rename it “Hatom.”
- Tip: as you do all this, have a look at contents of “Hatom” directory in your computer. Materials studio is acting as a sort of “file manager,” thus lots of cleaning up can be done in the background.



# Materials Studio: Create Box

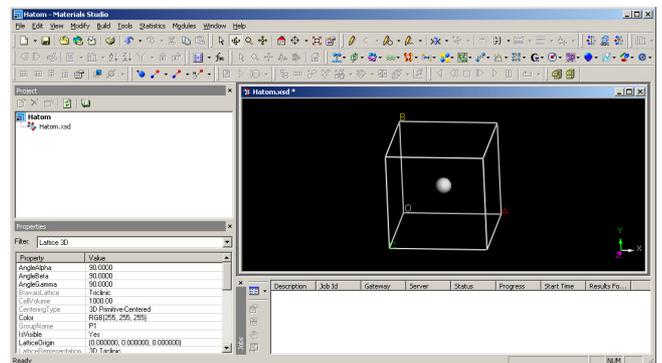
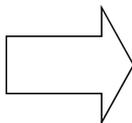
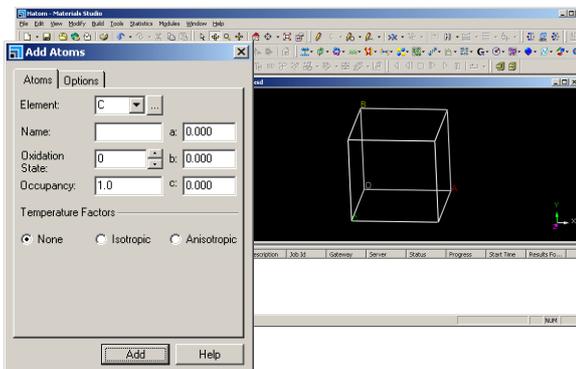
- Build → Crystal → Build Crystal.
- Space group: 1 P1 (default)
- Lattice parameters: 10 Å, 10 Å, 10 Å (default values)
- Click “Build”



**Loads of “Help” buttons: use them!**

# Materials Studio: Add Atom

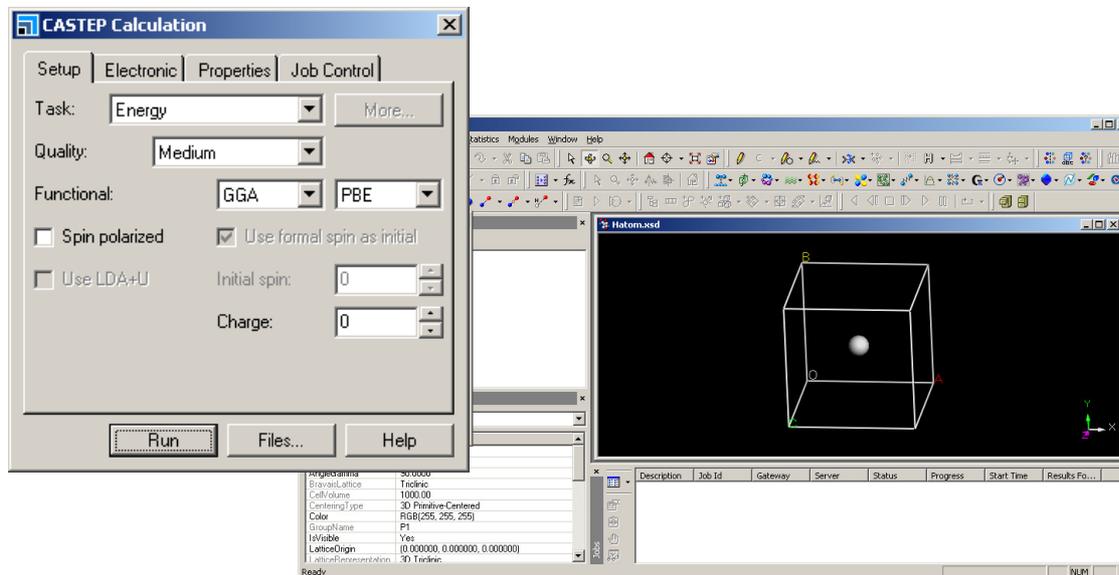
- Build → Add Atoms.
- Element: H
- (a,b,c) = (0.5, 0.5, 0.5) – centre of the box (reduced units)
- Click “Add”



Tip: default appearance is a bit odd (a cross). Use “View → Display Style” to change it to what you like.

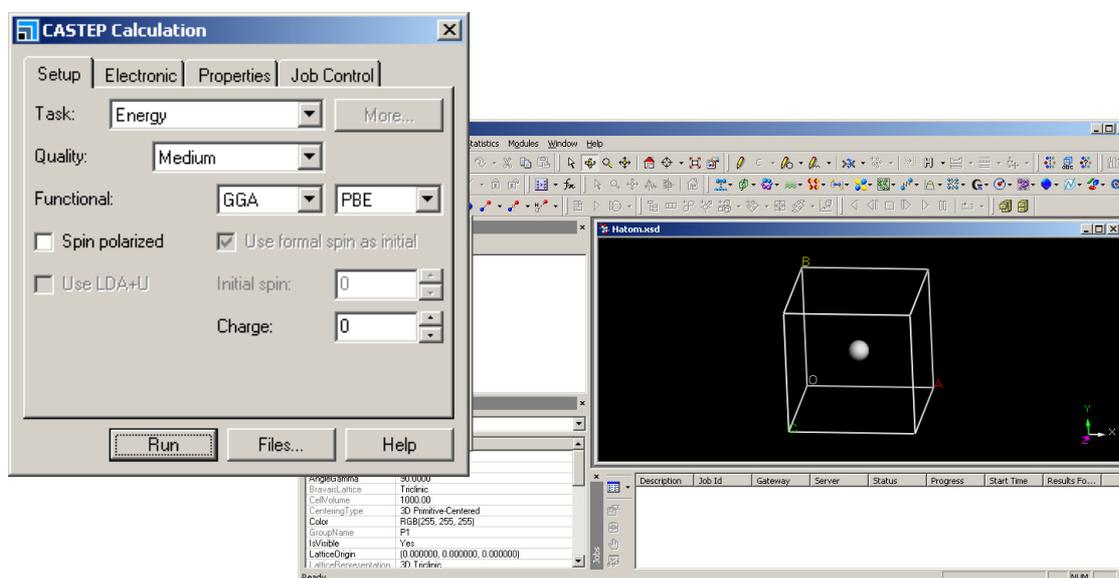
# Materials Studio: Invoking CASTEP

- Ensure your atom-in-a-box is active window.
- Modules → CASTEP → Calculation
- Note: most of these options can be easily accessed by activating the toolbars on “View → Toolbars.”



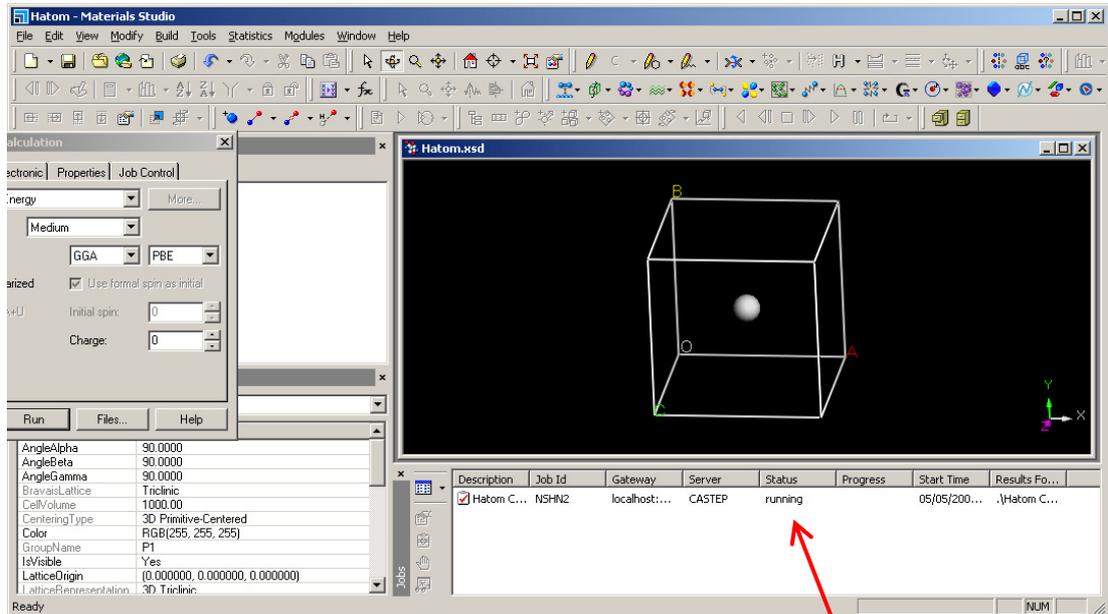
# Materials Studio: Running CASTEP

- Be brave: just press “Run”!
- And wait for a few moments to see what happens ...



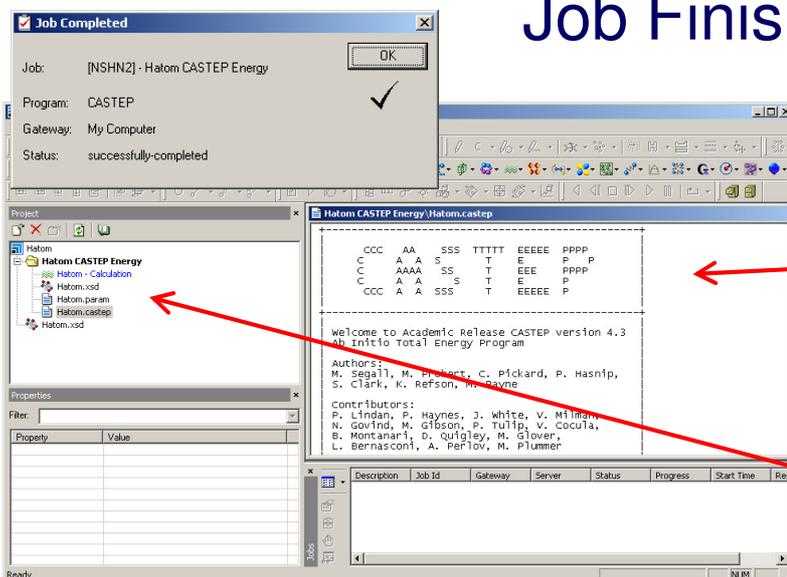
Note: a nice feature of MS (and CASTEP) is that they contain built-in default values for calculations, thus do not be afraid to try things out (but do test them).

# CASTEP: Calculating Away



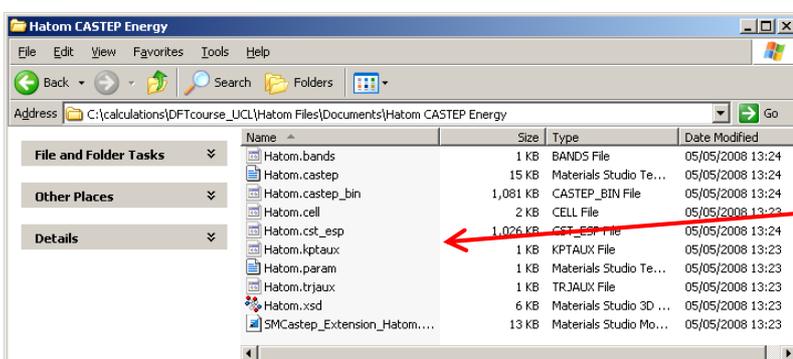
Job is running in background ("gateway")

## Job Finished



CASTEP Output File for inspection

File Manager updated with new folder



A bunch of new files have been generated (careful: some are hidden!)

# The CASTEP file

Beginning: Header Info

End: Whether Calc “Worked”

```
CCC AA SSS TTTT EEEE PPPP
C A A S T E P P
C AAAA SS T EEE PPPP
C A A S T E P
CCC A A SSS T EEEEE P

Welcome to Academic Release CASTEP version 4.3
Ab Initio Total Energy Program

Authors:
M. Segall, M. Probert, C. Pickard, P. Hasnip,
S. Clark, K. Refson, M. Payne

Contributors:
P. Lindan, P. Haynes, J. White, U. Milman,
N. Govind, M. Gibson, P. Tulip, V. Cocula,
B. Montanari, D. Quigley, M. Glover,
L. Bernasconi, A. Perlov, M. Plummer

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Zeitschrift fuer Kristallographie
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S. J. Clark, M. D. Segall, C. J. Pickard,
P. J. Hasnip, M. J. Probert, K. Refson,
M. C. Payne

in all publications arising from
your use of CASTEP
```

```
Initial 3.14016514E+001 5.18965189E+001 3.55954724E+001
1 -4.19382097E+000 3.08730478E+000 3.55954724E+001
2 -1.21581452E+001 -6.11730094E+000 7.94432420E+000
3 -1.23967791E+001 -6.41297099E+000 2.38633887E+000
4 -1.24068713E+001 -6.44713030E+000 1.00922620E+000
5 -1.24081077E+001 -6.44825368E+000 1.23641031E+000
6 -1.24083274E+001 -6.43318820E+000 2.19704901E+000
7 -1.24084593E+001 -6.42892906E+000 1.31862742E+000
8 -1.24084861E+001 -6.42591919E+000 2.68504789E+000
9 -1.24084832E+001 -6.42571285E+000 -2.94668061E+000
10 -1.24085208E+001 -6.42372260E+000 4.06325726E+000
11 -1.24085146E+001 -6.42467773E+000 -9.27100557E+000
12 -1.24085199E+001 -6.42460473E+000 5.34837615E+000
13 -1.24085173E+001 -6.42405529E+000 -2.65167187E+000
14 -1.24085259E+001 -6.42333039E+000 8.62924150E+000
15 -1.24085247E+001 -6.42337039E+000 -1.18105723E+000
16 -1.24085260E+001 -6.42350877E+000 1.29440869E+000

Final energy, E = -12.35210703959 eU
Final free energy (E-TS) = -12.40852599795 eU
(energies not corrected for finite basis set)

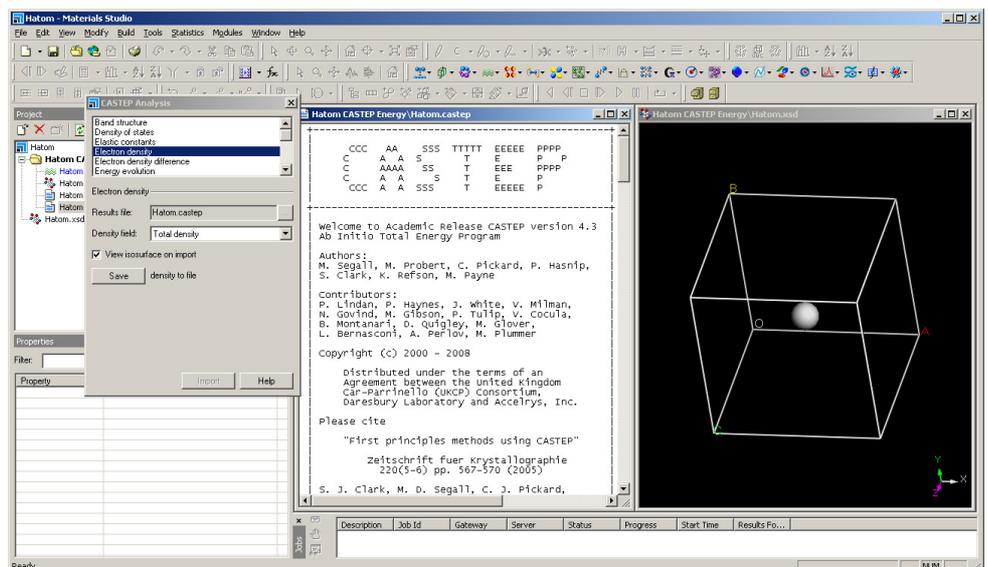
NB est. OK energy (E-0.5TS) = -12.38031651877

***** Forces *****
* Cartesian components (eU/A) *
* x y z *
* H 1 0.00000 0.00000 0.00000 *
*****

Writing model to Hatom.check
Writing analysis data to Hatom.castep_bin
Initialisation time = 0.19 s
Calculation time = 21.22 s
Finalisation time = 0.28 s
Total time = 21.68 s
```

## Further Analysis in Materials Studio

- Ensure your atom-in-a-box is active window.
- Modules → CASTEP → Analysis
- Surf thru different menu items to see what you find or can do.
- More on this later.



# Back to the CASTEP file: Electronic Energy

```
Programmer's File Editor
File Edit Options Template Execute Macro Window Help
C:\calculations\DF\course_UCL\Hatom Files\Documents\Hatom C...
Initial 3.14016514E+001 5.18965189E+001
1 -4.19382097E+000 3.03730478E+000 3.55954724
2 -1.21581452E+001 -6.11738094E+000 7.96432420
3 -1.23967791E+001 -6.41297099E+000 2.38633887
4 -1.24068713E+001 -6.44713089E+000 1.08922620
5 -1.24081077E+001 -6.44895368E+000 1.23641031
6 -1.24083274E+001 -6.43318828E+000 2.19709011
7 -1.24084593E+001 -6.42892066E+000 1.31862742
8 -1.24084861E+001 -6.42591919E+000 2.68504789
9 -1.24084832E+001 -6.42571285E+000 -2.94668601
10 -1.24085238E+001 -6.42372260E+000 4.06325726
11 -1.24085146E+001 -6.42467773E+000 -9.27100557
12 -1.24085199E+001 -6.42409473E+000 5.34837615
13 -1.24085173E+001 -6.42405529E+000 -2.65167187
14 -1.24085259E+001 -6.42333039E+000 8.62924150
15 -1.24085247E+001 -6.42337039E+000 -1.18105723
16 -1.24085260E+001 -6.42350877E+000 1.29408694
-----
Final energy, E = -12.35210703959 eV
Final free energy (E-TS) = -12.40852599795 eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS) = -12.38031651877

***** Forces *****
* Cartesian components (eV/A) *
*-----*
* x y z *
*-----*
* H 1 0.00000 0.00000 0.00000 *
*-----*
Writing model to Hatom.check
Writing analysis data to Hatom.castep_bin
Initialisation time = 0.19 s
Calculation time = 21.22 s
Finalisation time = 0.28 s
Total time = 21.68 s
```

Electronic energy of H atom [1]:  $E_H = -13.6$  eV

CASTEP says -12.352... eV which is a bit off.

**WHAT NEXT?**

**Volunteers, please ...**

*ASIDE:  $2 E_H = 1$  hartree, common energy unit in electronic structure calculations.*

[1] C Kittel, Introduction to Solid State Physics 6<sup>th</sup> Edition, John Wiley & Sons (1986).

## What's Wrong with CASTEP's Hydrogen? A Few Tips

- Inspect CASTEP output file.
- Has anything gone (or is) wrong?
- How can we make it better?

# Second Dive: The Hydrogen Molecule

## Group Exercise:

- Use Materials Studio to create a 10 Angstrom cubic box.
- Insert two hydrogen atoms separated by 0.74 Å.
- Run CASTEP using same convergence parameters as for H atom.
- Have a look at what has happened (CASTEP output file)
- Some data for ground state H<sub>2</sub> [1]:
  - Dissociation energy: D = 4.478 eV.
  - Internuclear separation: r = 0.741 Å

[1] KP Huber & G Herzberg, *Molecular Spectra & Molecular Structure IV: Constants of Diatomic Molecules*, Van Nostrand (1979).

## Refined Figures for H Atom & Molecule

- Electronic energy of H atom [1]:  $E_H = -13.6$  eV

*NOTE:  $2 E_H = 1$  hartree, common energy unit.*
- Ground state H<sub>2</sub> [2]:
  - Dissociation energy: D = 4.478 eV.
  - Internuclear separation: r = 0.741 Å
- **CASTEP: 10-Angstrom box, GGA-PBE, ultrasoft pseudopotentials, 800 eV energy cutoff, gamma-point.**
  - **$E_H = -13.5921$  eV (0.05 % error).**
  - **D = 4.526 eV (1% overbinding; meV differences)**
  - **r = 0.752 Å (1.5%)**

[1] C Kittel, *Introduction to Solid State Physics 6<sup>th</sup> Edition*, John Wiley & Sons (1986).

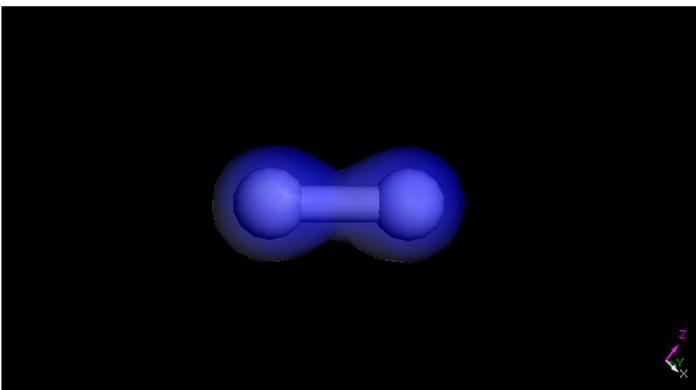
[2] KP Huber & G Herzberg, *Molecular Spectra & Molecular Structure IV: Constants of Diatomic Molecules*, Van Nostrand (1979).

# Visualization & Analysis with Materials Studio

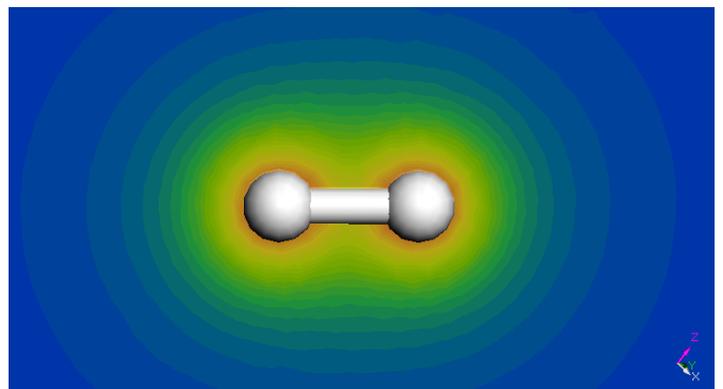
## The Hydrogen Molecule

### The Hydrogen Molecule: SCF Local Potential

Isosurface

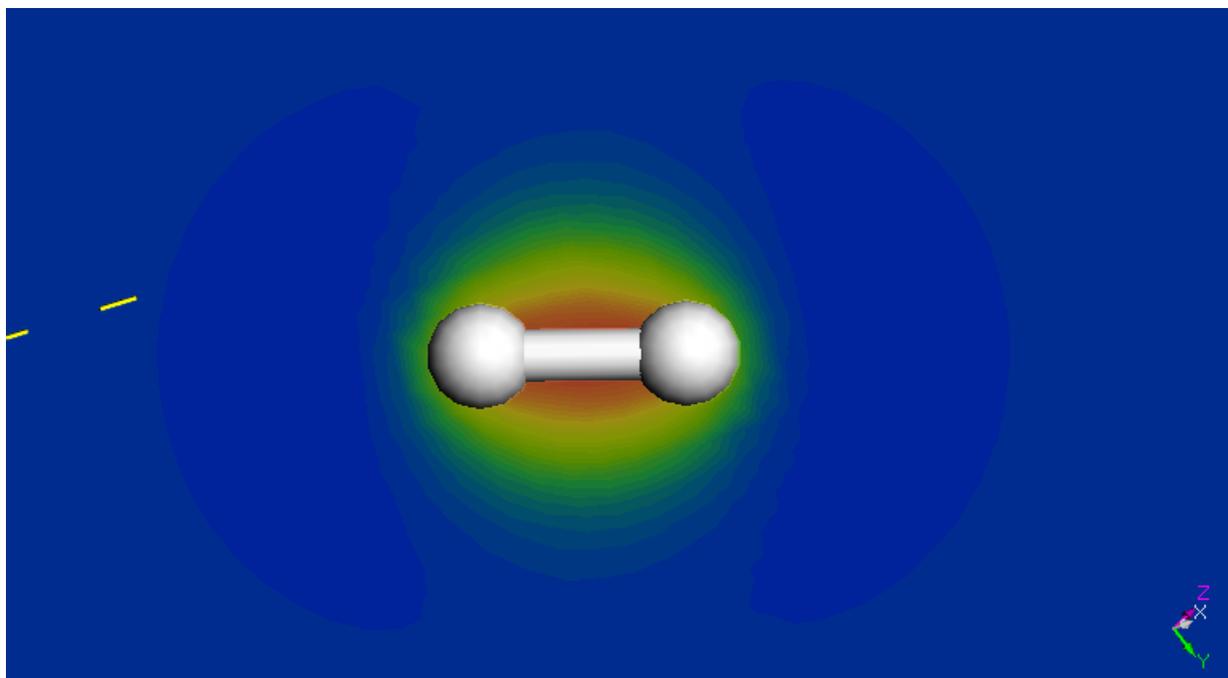


Slice



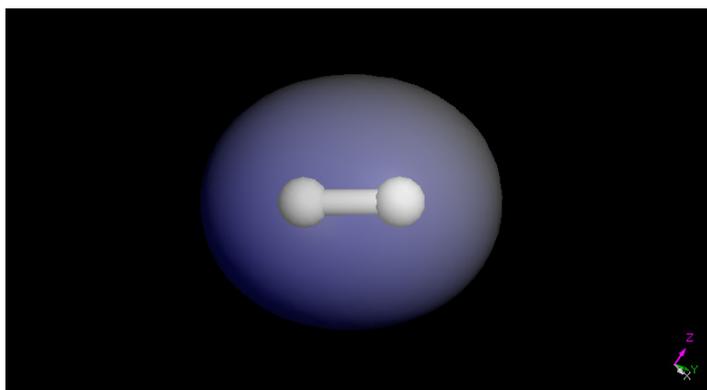
# The Hydrogen Molecule: Electron Energy Difference

Slice

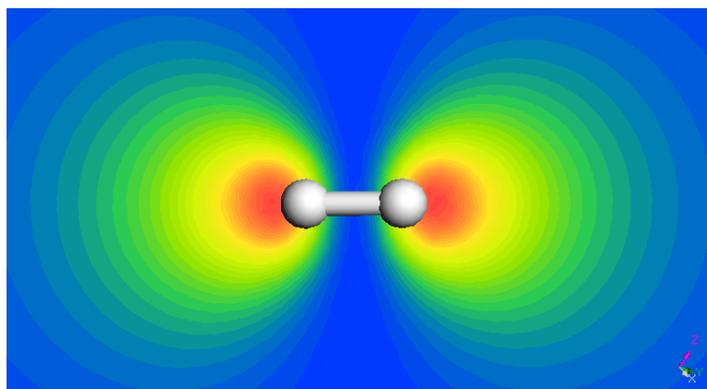
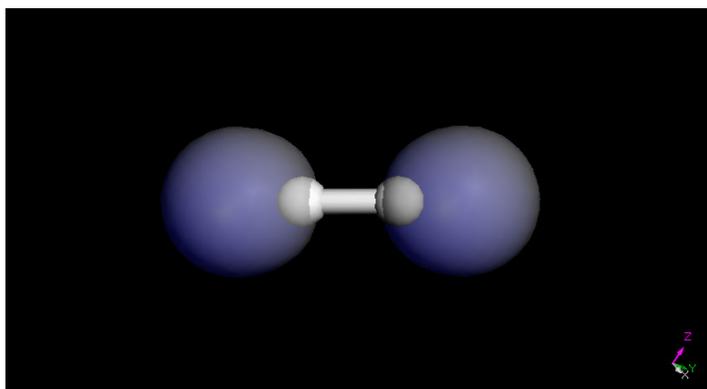
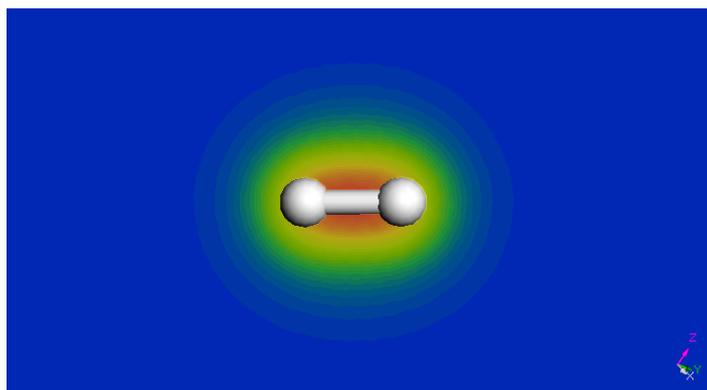


# The Hydrogen Molecule: KS Orbitals

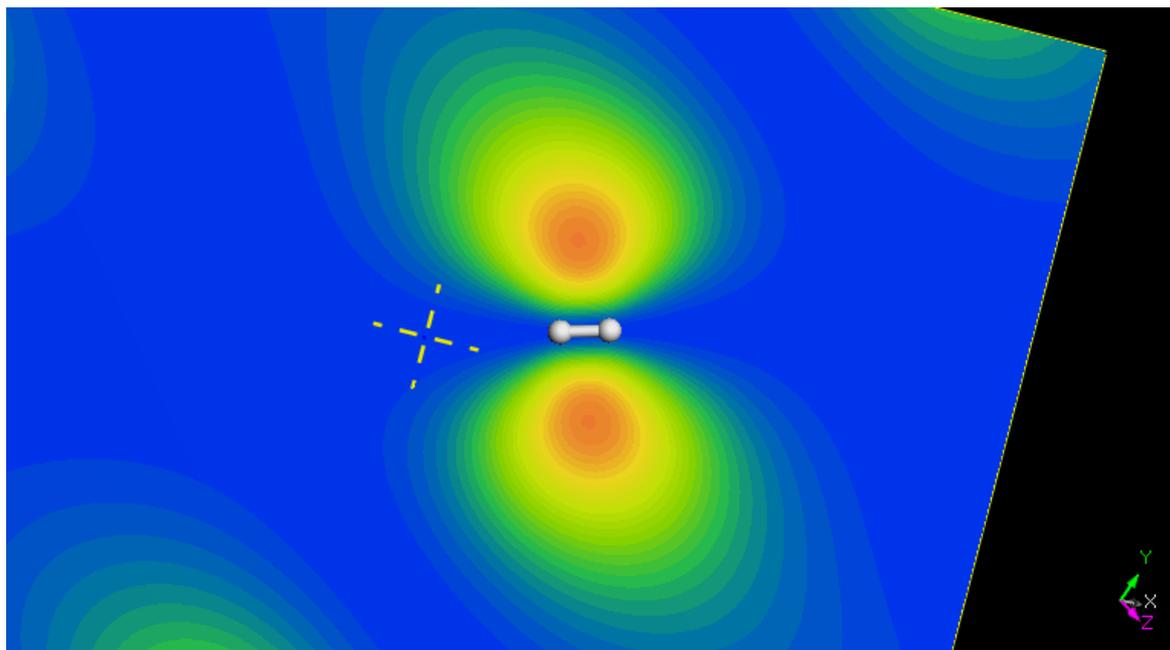
Isosurfaces



Slices

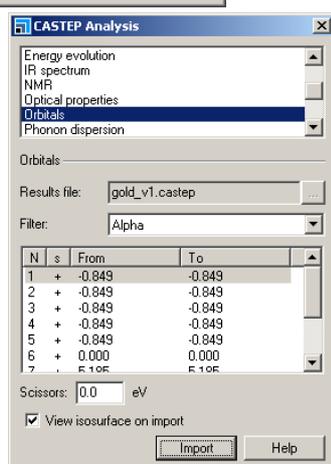
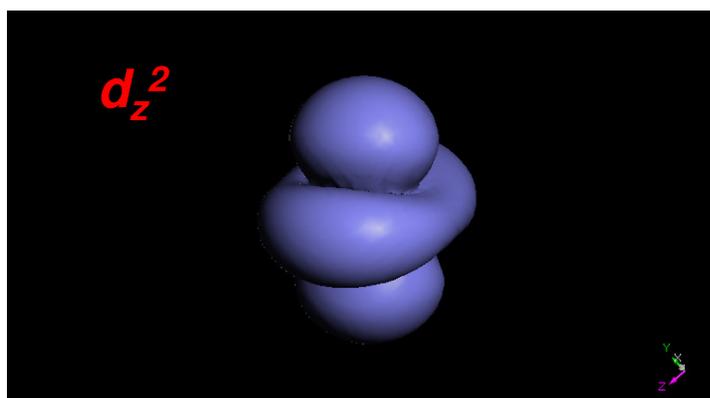
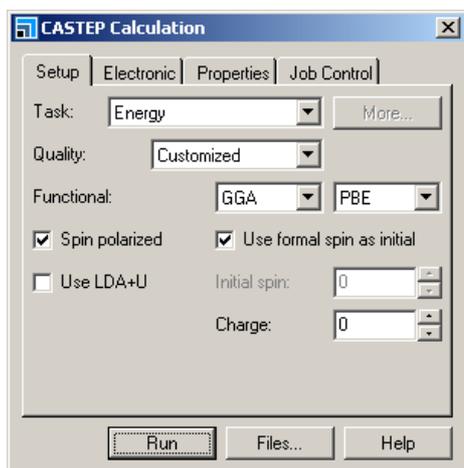


# The Hydrogen Molecule: High-lying KS Orbitals

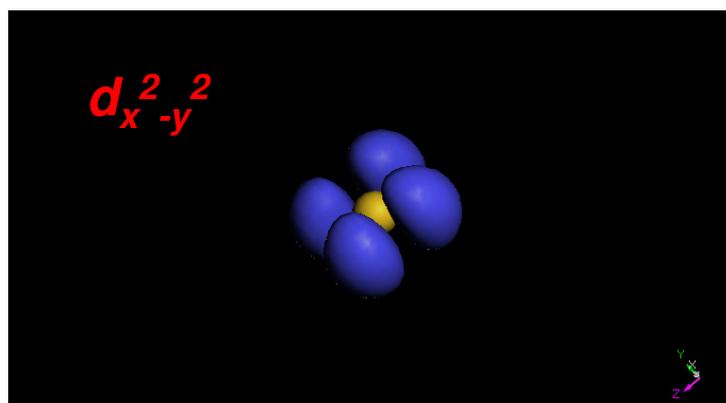


Can you notice that something is a bit odd?

## KS d-orbitals: Isolated Gold Atom



Fivefold  
degeneracy  
(as expected)

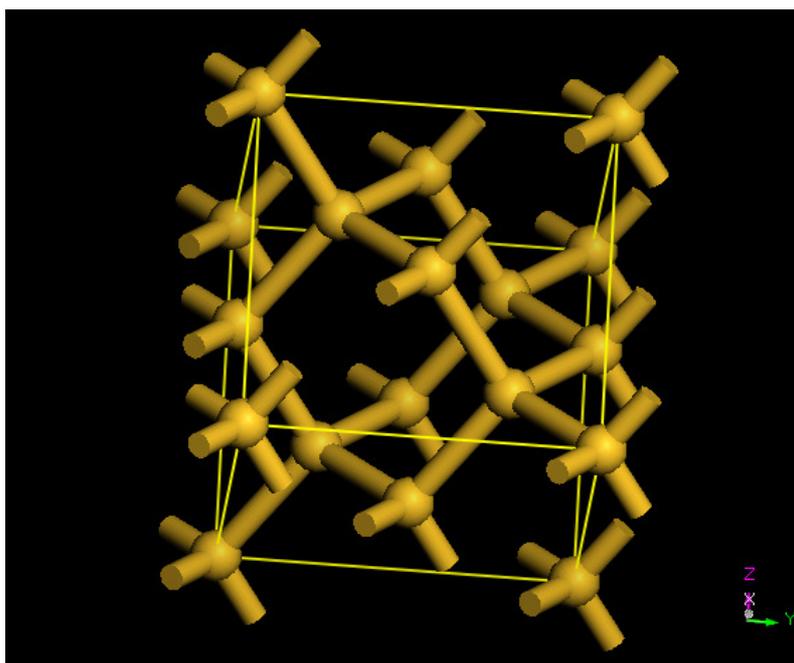


# Periodic Solids: Silicon

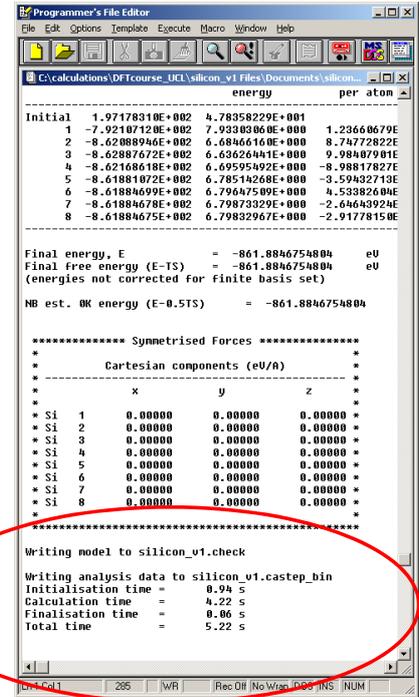
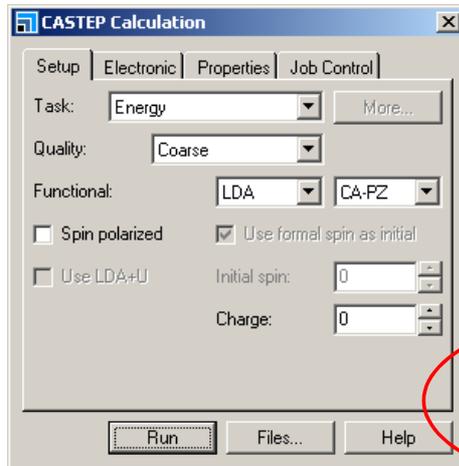
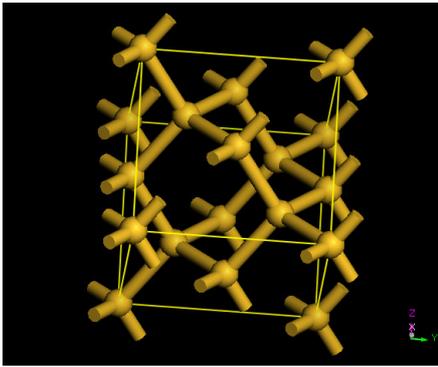
## Outline of Steps:

- Create a new project in Materials Studio.
- Generate a Silicon crystal using following info:
  - Space group: FD-3M (227)
  - Lattice parameter: 5.4 Å
  - Place a single Si atom at cell origin.
- Run CASTEP using
  - Task: "Energy."
  - Quality: "Coarse."
  - Functional: LDA-CAPZ

## The Silicon Crystal



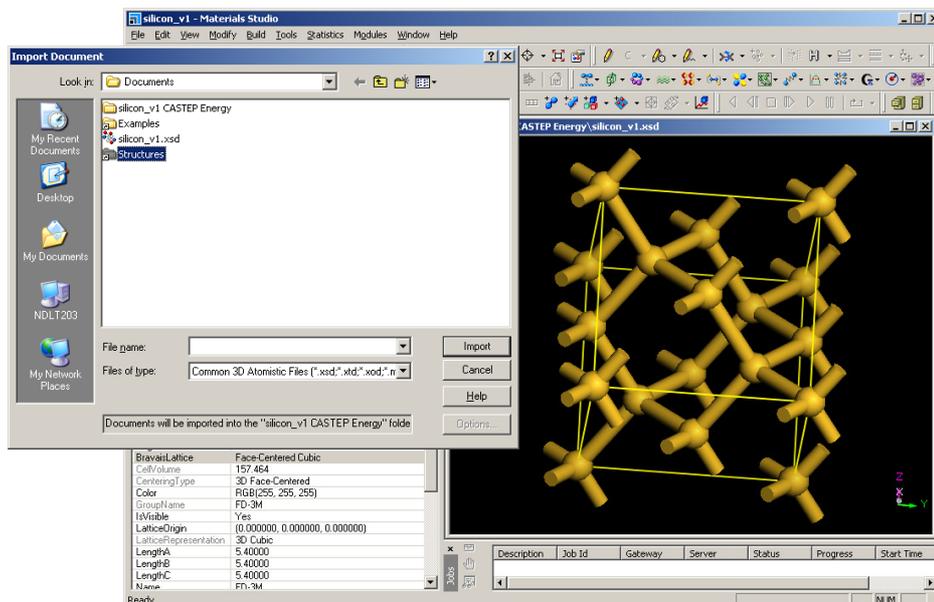
# The CASTEP Calculation



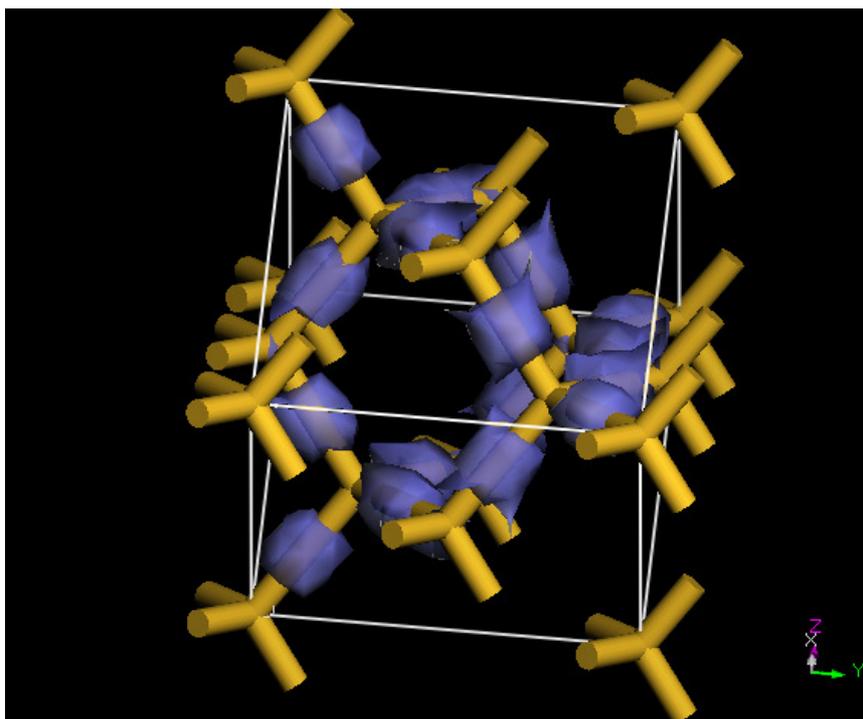
Quite quick: why?

## Useful Shortcut for Model Building

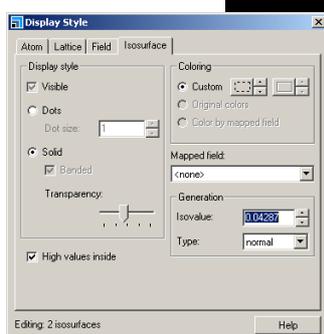
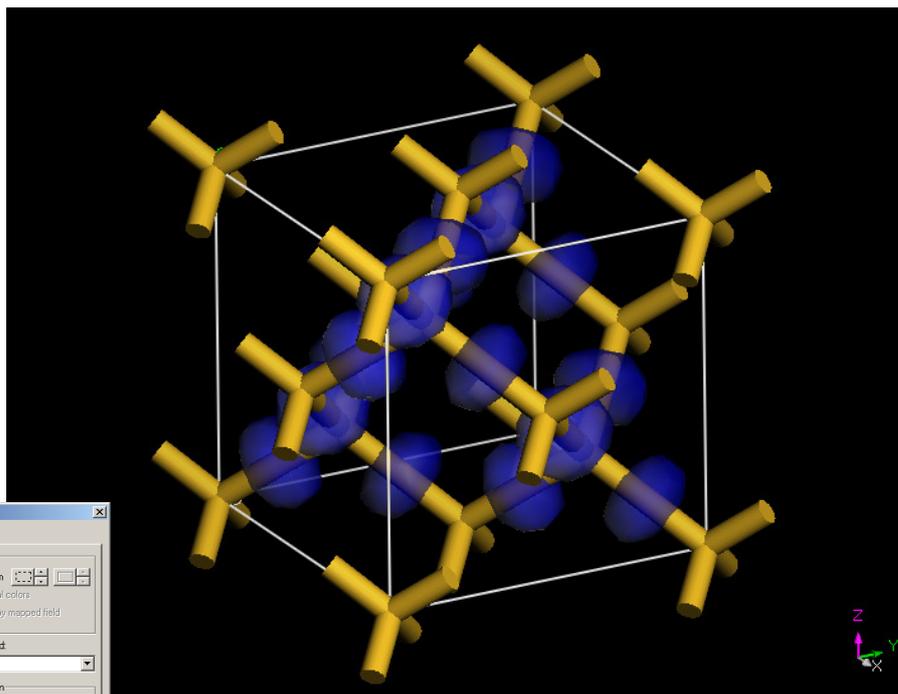
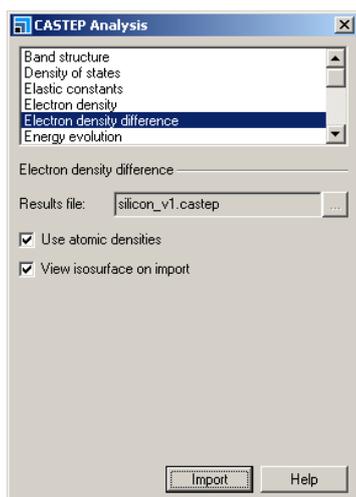
- Materials Studio comes with a nice library of structures.
- File → Import → Structures
- Silicon is in the “Semiconductors” sub-folder.
- Tip: surf thru this library before doing too much work (e.g., graphite is located in the “Ceramics” folder).



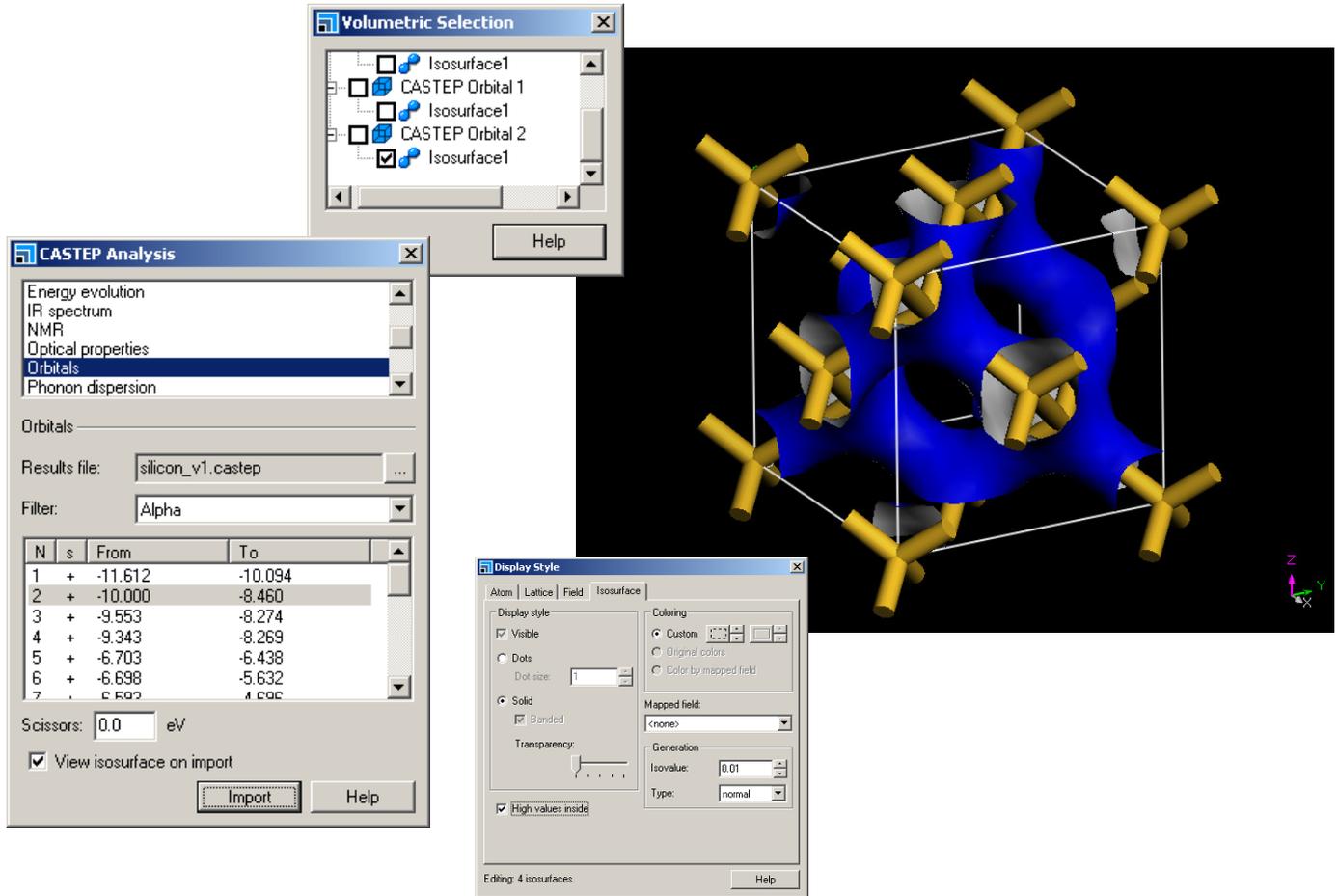
# CASTEP Analysis: Total Electron Density



# CASTEP Analysis: Electron Energy Difference



# CASTEP Analysis: KS Bands



## Other Systems You May Want to Play With

- Molecular
  - Water monomers & dimers: hydrogen bonds.
  - Graphite's building block: benzene.
- Solids
  - Insulators: diamond
  - Semimetals: graphite
  - Metals: sodium
- Magnetic:
  - The oxygen molecule.
  - Ferromagnetic iron (see Materials Studio Tutorial).

# A Glimpse at Next Lecture

## A Closer Look under the Hood: from Structure to Properties.

- Today
  - We “clicked” our way through MS (and CASTEP).
  - Materials Studio provides a very convenient platform to analyze data – a true time-saver.
- But there is a LOT going on in the background with CASTEP
- Thus we need to understand better:
  - CASTEP input/output.
  - Common keywords.
  - Beyond electrons: taking into account nuclear positions (energy minimization) & properties.

## References & Further Reading

### DFT Calculations: General & Quite Useful

- *AE Mattsson et al., “Designing Meaningful Density Functional Theory Calculations in Materials Science,” Modelling Simul. Mater. Sci. Eng. 13, R1-R31 (2005).*
- *MD Segall et al., “First-principles Simulation: Ideas, Illustrations, and the CASTEP Code,” J. Phys.: Condens. Matter 14, 2717-2744 (2002).*
- *MC Payne et al., “Iterative Minimization Techniques for Ab Initio Total Energy Calculations: Molecular Dynamics and Conjugate Gradients”, Rev. Mod. Phys. 64, 1045-1097 (1992).*

### CASTEP-specific:

- *The CASTEP Website: [www.castep.org](http://www.castep.org). Excellent source of info.*
- *CASTEP Newsgroup: <http://www.jiscmail.ac.uk/lists/CASTEP.html> . Very useful, does not hurt at all to subscribe.*
- *Castep Project on CCPForge: <http://ccpforge.cse.rl.ac.uk/projects/castep/> . This is where you could get the code.*
- *SJ Clark et al., “First Principles Methods using CASTEP,” Z. Krystallogr. 220, 567 (2005). Brief description of the CASTEP program. Also the one you should cite if you use it in your research.*

### Materials Studio:

- *Website <http://accelrys.com/products/materials-studio/> (see also Materials Studio Forum & Script Libraries).*
- *MS Program Help: quite comprehensive and helpful on graphical interface. Also good source of info for CASTEP, but a bit hard to surf through at the beginning (hopefully not so after this course).*

# Supplementary Material

## Beyond the LDA: Basic Considerations

- In many systems, exchange contribution dominates over correlation energy thus it makes sense to
  - Compute non-local exchange potential as in Hartree-Fock theory.
  - Use LDA to get the correlation energy.
- Consequences:
  - Greater difficulty in computing exchange potential might be justified if better results are obtained.
  - However, LDA performance is partially based on a rather delicate cancellation between these two interaction terms
  - Reality: use of this “exact-exchange” approach can lead to very poor results.
  - Extreme example: metals where Hartree-Fock fails miserably (non-local exchange potential is of infinite range).

# Exchange-correlation Functionals in CASTEP v4.3

## BASIC ONES

- Local Functionals (LDA):
  - Only one: PZ parameterization (Purdue & Zunger, 1981).
  - Regarded as most accurate LDA functional.
- Gradient-corrected (GGA): total of four parameterizations.
  - PW91 (Perdew & Wang, 1991).
  - PBE (Perdew-Burke-Ernzerhof, 1996). Similar to classic PW91 but more robust for systems with rapidly varying electron density.
  - RPBE (revised PBE, 1999). Designed to improve adsorption energies of molecules on metallic surfaces [see Marlo and Milman, PRB 62, 2899 (2000)]
  - WC (Wu and Cohen, 2006). Based on diffuse radial cutoff of exchange hole and analytical gradient expansion of exchange energy. Supposed to be a more accurate GGA functional (yet to be tested).

# Exchange-correlation Functionals in CASTEP v4.3

## ADVANCED: non-local exchange-correlation functionals

- Motivation: LDA & GGA underestimate band gaps, thus poor description of electronic structure of insulators & semiconductors (but not structure).
  - One approach is to rigidly shift conduction band wrt to valence band (but one loses predictive power).
  - A more robust solution involves the so-called sX-LDA scheme in the generalized Kohn-Sham procedure (total energy is split into screened, nonlocal and local components).
- Generalized Kohn-Sham schemes in CASTEP:
  - HF: exact exchange, no correlation.
  - HF-LDA: exact exchange, LDA correlation.
  - sX: screened exchange, no correlation.
  - sX-LDA: screened exchange, LDA correlation.
  - PBE0: PBE functional with predefined amount of exact exchange.

# Exchange-correlation Functionals in CASTEP v4.3

## ADVANCED: non-local exchange-correlation functionals

- Motivation: LDA & GGA underestimate band gaps, thus poor description of electronic structure of insulators & semiconductors (but not structure).
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  - A more robust solution involves the so-called sX-LDA scheme in the generalized Kohn-Sham procedure (total energy is split into screened, nonlocal and local components).
- Generalized Kohn-Sham schemes in CASTEP (expect a expensive calc!)
  - HF: exact exchange, no correlation.
  - HF-LDA: exact exchange, LDA correlation.
  - sX: screened exchange, no correlation.
  - sX-LDA: screened exchange, LDA correlation.
  - PBE0: PBE functional with predefined amount of exact exchange.

NOTE: only norm-conserving pseudopotentials allowed.

# Exchange-correlation Functionals in CASTEP v4.3

## ADVANCED: Electronic Excitations & Strongly Correlated Systems.

- Motivation:
  - Correlated systems: as found in transition/rare-earth metal compounds, leading to strong d/f localization.
  - Need to go beyond Kohn-Sham formalism (Hubbard model & DFT).
- LDA+U Approach [1,2]: recently implemented in CASTEP (v4.3, 2008)
  - Reproduces qualitative behaviour of Mott-Hubbard insulators (strong correlations lead to energy gaps).
  - Requires an effective value of on-site Coulomb parameter U (on-site repulsion term proportional to orbital occupancy).
  - Complications:
    - » U varies depending on property to be calculated.
    - » YOU have to choose U (not easy!): empirically or from LDA energy calculations with variable d/f occupancy.
  - Has been extended to include dynamical mean-field correlations (LDA+DMFT).
  - For a recent & informative study see [3] below.

[1] VI Anisimov et al., *Phys. Rev. B* 44, 943 (1991). [Original paper]

[2] VI Anisimov et al., *J. Phys.: Condens. Matter* 9, 767 (1997). [REVIEW]

[3] M Cococcioni et al., *Phys. Rev. B* 71, 035105 (2005).

# Computational Cost - Scaling

- For any calculation, we deal with a set of  $N_{PW}$  plane waves and  $N_B$  bands/orbitals.
- Computational costs is different for different operations:
  - Diagonalization of Hamiltonian  $\sim N_{PW}^3$
  - Kinetic energy in reciprocal space  $\sim N_{PW}N_B$
  - $r \leftrightarrow k$  FFT transform to construct density, etc:  $\sim N_B N_{PW} \ln N_{PW}$
  - Band orthogonalization  $\sim N_B^2 N_{PW}$ .
- Thus cost will scale as
  - Number of atoms  $N$   $\sim N^3$
  - PW energy cutoff  $\sim (E_{cutoff})^{3/2}$
  - For a periodic system symmetry can help in a BIG way (use primitive cells).
  - Optimal scaling in parallel machines (linear with number of processors).

## Outline of Course

1. Fundamentals: Materials Modelling, Electronic Structure & DFT.
2. The Practice of DFT calculations using the CASTEP code & Materials Studio.
3. **A Closer Look under the Hood: from Structure to Properties.**
4. Advanced Features.

# Lecture III

## A Closer Look Under the Hood

### Outline of Today's Lecture

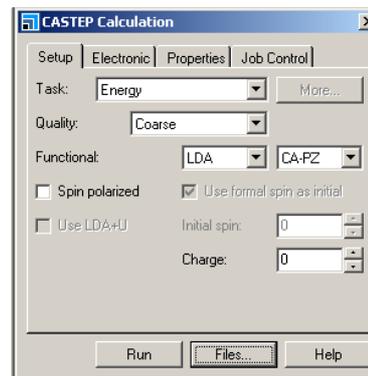
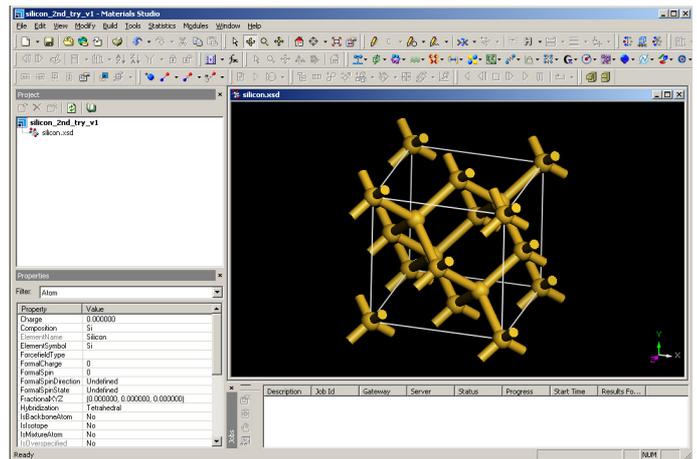
- CASTEP input/output: bulk silicon revisited.
- Common keywords (& a few shortcuts).
- Beyond electrons:
  - Geometry optimization.
  - First look at properties.

*The greatest obstacle to discovering the shape of the Earth, the continents  
and the Ocean was not ignorance, but the illusion of knowledge.  
D. Boorstin, "The Discoveries."*

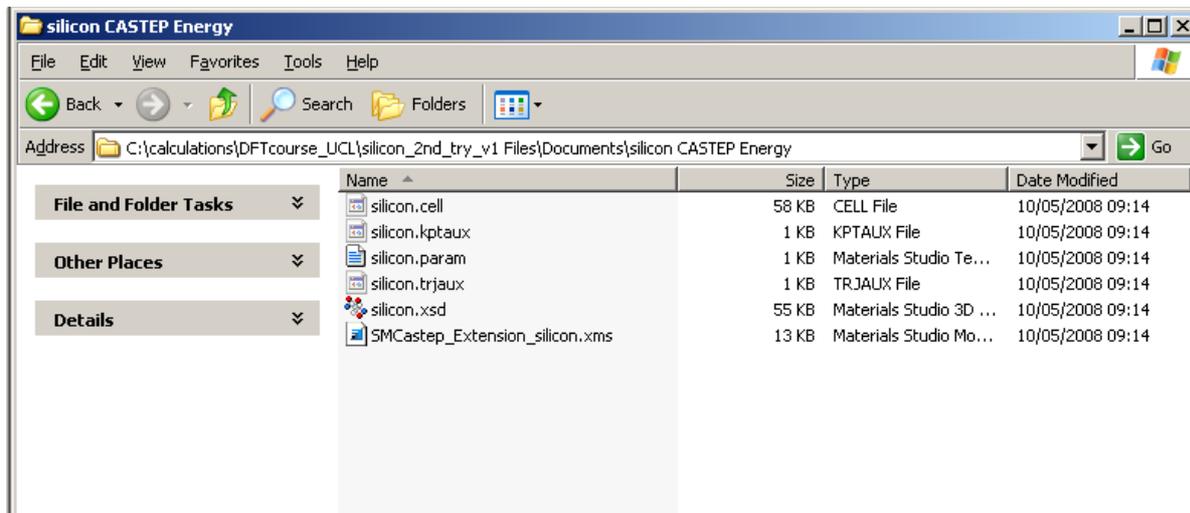
# Recap & Warm-up: Bulk Silicon

Need one volunteer to:

- Create a new project in Materials Studio.
- Generate a Silicon crystal using following info:
  - Space group: FD-3M (227)
  - Lattice parameter: 5.4 Å
  - Place a single Si atom at cell origin.
- Setup CASTEP calc using
  - Task: "Energy."
  - Quality: "Coarse."
  - Functional: LDA-CAPZ
  - **Save these files, do not run them (yet).**



## Files Generated by Materials Studio

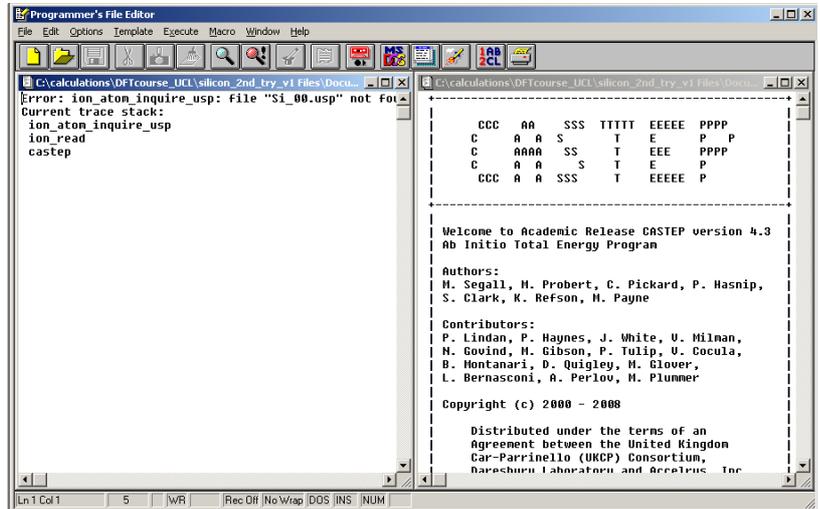


- Materials studio (of secondary importance for the time being):
  - .xsd: the model (geometry, chemical composition)
  - .xms: details of calculation (very verbose!).
  - Auxiliary: .kptaux (k-points) and .trjaux (trajectory).
- CASTEP: just two files (and they are important)
  - .cell
  - .param



# What Went Wrong: .err & .castep Files

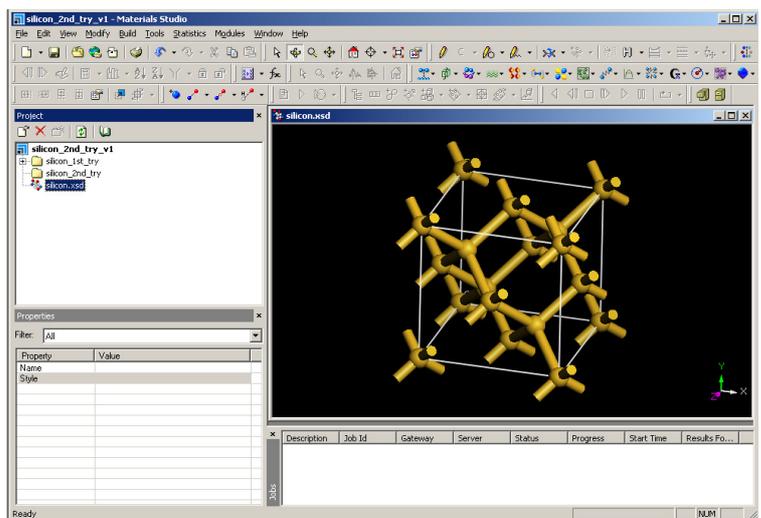
- Inspect .err and .castep files.
- Where is the problem?
- What is the fix?



- Hint: have a cursory look at silicon.cell file

## Interlude: Tips for File Management

- Can rename & create new directories within project at will.
- Only caveat: do not do this as you run a calculation!
- Create a second directory and copy .cell, .param, and .xsd files from first (see figure).





# The .cell file (input)

- Contains your model, i.e., what you want to do a calculation on.
- Subdivided into BLOCKS:
  - Definition of your unit cell.
  - Contents of your unit cell (elements and positions).
  - k-point grid.
  - Symmetry (if any).
  - Constraints (cell or else).
  - Pseudopotential info (see previous slide).
  - LCAOs for each species (more on this later).
- Want to know more? use `-help`.

```

%BLOCK LATTICE_CART
5.400000000000000 0.000000000000000 0.000000000000000
0.000000000000000 5.400000000000000 0.000000000000000
0.000000000000000 0.000000000000000 5.400000000000000
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
Si 0.000000000000000 0.000000000000000 0.000000000000000
Si 0.000000000000000 0.500000000000000 0.500000000000000
Si 0.500000000000000 0.000000000000000 0.500000000000000
Si 0.500000000000000 0.500000000000000 0.000000000000000
Si 0.750000000000000 0.250000000000000 0.750000000000000
Si 0.250000000000000 0.250000000000000 0.250000000000000
Si 0.250000000000000 0.750000000000000 0.750000000000000
Si 0.750000000000000 0.750000000000000 0.250000000000000
%ENDBLOCK POSITIONS_FRAC

%BLOCK KPOINTS_LIST
0.375000000000000 0.375000000000000 0.375000000000000 0.125000000000000
0.375000000000000 0.375000000000000 0.125000000000000 0.375000000000000
0.375000000000000 0.125000000000000 0.125000000000000 0.375000000000000
0.125000000000000 0.125000000000000 0.125000000000000 0.125000000000000
%ENDBLOCK KPOINTS_LIST

%BLOCK SYMMETRY_OPS
1.000000000000000 -0.000000000000000 -0.000000000000000

```

# The .param file (input)

- Contains what you want to do with your .cell file.
- *Freeform file format* specifying the TASK you want to achieve (including convergence criteria).
  - Single-point energy.
  - Geometry optimization.
  - Molecular Dynamics.
  - A bunch of properties including:
    - Band structure.
    - Phonons.
    - NMR.
    - Optical properties.
    - Thermodynamics.
    - etc.

```

comment : CASTEP calculation from Materials Studio
task : SinglePoint
xc_functional : LDA
spin_polarized : false
opt_strategy : Default
page_wfnns : 0
basis_precision : Coarse
grid_scale : 1.750000000000000
finite_basis_corr : 0
elec_energy_tol : 1.000000000000000e-005
max_scf_cycles : 100
fix_occupancy : false
metals_method : dm
mixing_scheme : Pulay
mix_charge_amp : 0.500000000000000
mix_charge_gmax : 1.500000000000000
mix_history_length : 20
nextra_bands : 4
smearing_width : 0.100000000000000
calculate_stress : false
popn_calculate : false
calculate_densdiff : false
pdos_calculate_weights : false
num_dump_cycles : 0

```

# The .castep file (human-readable output)

“head”

“tail”

- Summary of the calculation (and some results).
- Layout in order of appearance:
  - Header: version numbers, etc.
  - Parameters used.
  - Structure/cell used.
  - Summary of calculation.

```
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silic...
File Edit Options Template Execute Macro Window Help
-----
CCC AA SSS TTTT EEEE PPPP
C A A S S T E P P
C AAAA SS T EEE PPPP
C A A S T E P
CCC A A SSS T EEEE P

Welcome to Academic Release CASTEP version 4.3
Ab Initio Total Energy Program

Authors:
M. Segall, M. Probert, C. Pickard, P. Hasnip,
S. Clark, K. Refson, M. Payne

Contributors:
P. Lindan, P. Haynes, J. White, U. Nilman,
M. Govind, M. Gibson, P. Tully, U. Cocula,
B. Montanari, D. Quigley, M. Clover,
L. Bernasconi, A. Perlov, M. Plummer

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Daresbury Laboratory and Accelrys, Inc.

Please cite

"First principles methods using CASTEP"
Zeitschrift fuer Kristallographie
220(5-6) pp. 567-570 (2005)

S. J. Clark, H. D. Segall, C. J. Pickard,
P. J. Hasnip, M. J. Probert, K. Refson,
M. C. Payne

in all publications arising from
your use of CASTEP
```

```
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silic...
File Edit Options Template Execute Macro Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silic...
-----
energy per aton
Initial -7.14254911E+002 3.39036820E+001
1 -1.29277488E+003 8.21790415E+000 7.23149967E+001
2 -1.32888276E+003 6.94668348E+000 4.51348491E+000
3 -1.32994328E+003 7.00775589E+000 -1.32564473E-001
4 -1.32895543E+003 6.98913367E+000 -1.22481139E-001
5 -1.32862883E+003 6.98377070E+000 -4.08245096E-002
6 -1.32862915E+003 6.98537886E+000 3.96829652E-005
7 -1.32862877E+003 6.98624958E+000 -4.78306558E-005
8 -1.32862877E+003 6.98639634E+000 5.10211069E-007
9 -1.32862877E+003 6.98638597E+000 -5.71232652E-007

Final energy, E = -1328.62876884 eV
Final free energy (E-TS) = -1328.62876884 eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS) = -1328.62876884 eV

***** Symmetrised Forces *****
*
* Cartesian components (eU/A) *
*
* x y z *
* Si 1 0.00000 0.00000 0.00000 *
* Si 2 0.00000 0.00000 0.00000 *
* Si 3 0.00000 0.00000 0.00000 *
* Si 4 0.00000 0.00000 0.00000 *
* Si 5 0.00000 0.00000 0.00000 *
* Si 6 0.00000 0.00000 0.00000 *
* Si 7 0.00000 0.00000 0.00000 *
* Si 8 0.00000 0.00000 0.00000 *
*
*****
Writing model to silicon.check
Writing analysis data to silicon.castep_bin
Initialisation time = 6.70 s
Calculation time = 2.06 s
Finalisation time = 0.03 s
Total time = 8.80 s
```

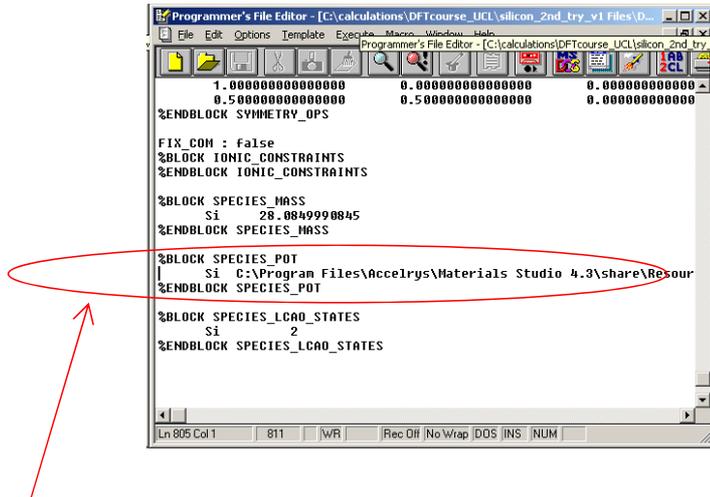
## Input Files: Useful Facts

- ALL input parameters have defaults.
- Exception: structural (model) parameters.
- Only necessary to specify what is *NOT* a default.
- Beware: MS defaults are not necessarily the same as CASTEP (Example: Pulay DM scheme)..
- Program output is controlled via the use of *keywords* (two types: cell & parameter).

Check PDFs with a (rather long & exhaustive) list of cell and param keywords taken from the [castep.org](http://castep.org) website.

# How Defaults Work: Pseudopotentials

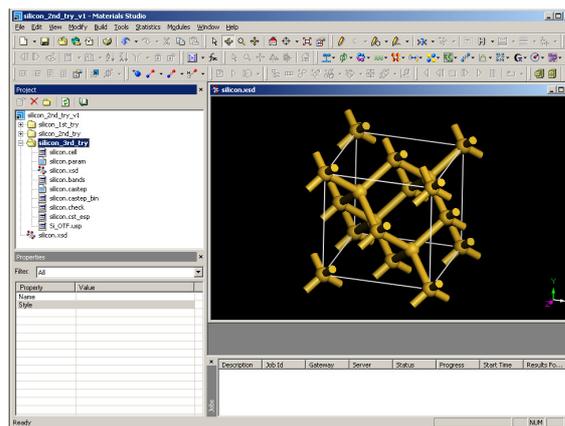
- Let's be forgetful about the inclusion of pseudopotential block in cell file.
- What happens?



delete this bit

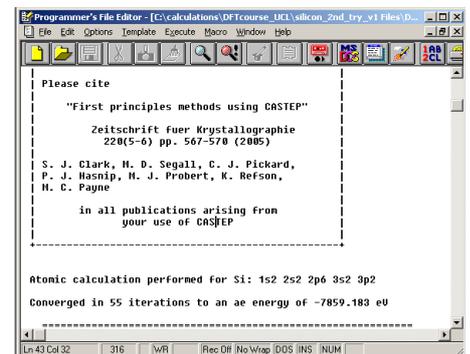
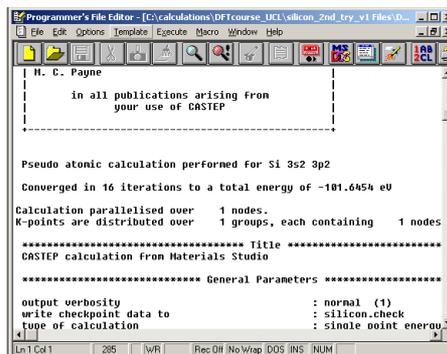
## Default (On-the-fly) Pseudopotentials

- Si\_OTF.usp file generated.
- Check .castep file for more details.
- Note: total electronic energies change.
- Why?



Before

Now



# Pseudopotentials: Explicit Definition

- Allows full control over electronic structure.
- Try defining your pseudopotential by using the **red circled bit** (i.e., hack cell file).
- More on what all these symbols mean later ...

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Docum...
File Edit Options Template Execute Macro Window Help
-----
Atomic calculation performed for Si: 1s2 2s2 2p6 3s2 3p2
Converged in 55 iterations to an ae energy of -7859.183 eV

-----
| Pseudopotential Report - Date of generation 10-05-2008 |
-----
Element: Si Ionic charge: 4.00 Level of theory: LDA

Reference Electronic Structure
Orbital      Occupation      Energy
3s           2.000           -0.400
3p           2.000           -0.153

Pseudopotential Definition
Beta 1 e Rc scheme norm
1 0 -0.400 1.797 qc 0
2 0 0.250 1.797 qc 0
3 1 -0.153 1.797 qc 0
4 1 0.250 1.797 qc 0
loc 2 0.000 1.797 pn 0

Augmentation charge Rinner = 1.298
Partial core correction Rc = 1.298

| "2|1.8|1.8|1.3|2|3|4|30:31:32L66(qc=4)" |
-----
Author: Chris J. Pickard, Cambridge University
-----

Pseudo atomic calculation performed for Si 3s2 3p2
Converged in 16 iterations to a total energy of -155.1585 eV
    
```

## Explicit Definition of Pseudopotentials: Outcome

*Before (default, OTF)*

*Now (explicit)*

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon_3rd_try...
File Edit Options Template Execute Macro Window Help
-----
SCF loop      Energy      Fermi energy      Energy gain      Timer
              (eV)          (eV)              per atom         (sec)
-----
Initial      -7.14254911E+002  3.39036820E+001  7.23149967E+001  7.09
1            -1.29277488E+003  8.21790415E+000  7.23149967E+001  7.26
2            -1.32888276E+003  6.94668348E+000  4.51348491E+000  7.44
3            -1.32994328E+003  7.00775583E+000  1.32564473E-001  7.59
4            -1.32895543E+003  6.98911367E+000  -1.23481139E-001  7.78
5            -1.32862883E+003  6.98377707E+000  -4.08245096E-002  7.97
6            -1.32862915E+003  6.98537866E+000  3.96829652E-005  8.17
7            -1.32862877E+003  6.98624958E+000  -4.78306550E-005  8.33
8            -1.32862877E+003  6.98639634E+000  5.10211063E-007  8.45
9            -1.32862877E+003  6.98638597E+000  -5.71232652E-007  8.59
-----
Final energy, E = -1328.628768844 eV
Final free energy (E-TS) = -1328.628768844 eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS) = -1328.628768844 eV
    
```

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon_4th_try...
File Edit Options Template Execute Macro Window Help
-----
SCF loop      Energy      Fermi energy      Energy gain      Timer
              (eV)          (eV)              per atom         (sec)
-----
Initial      -7.15496534E+002  3.34827842E+001  7.28373204E+001  6.51
1            -1.29819510E+003  7.94264253E+000  7.28373204E+001  6.70
2            -1.32877664E+003  6.94366483E+000  3.82267231E+000  6.86
3            -1.32994332E+003  7.00801408E+000  1.45835502E-001  7.01
4            -1.32895542E+003  6.98917446E+000  -1.23487087E-001  7.20
5            -1.32862883E+003  6.98376707E+000  -4.08237656E-002  7.41
6            -1.32862916E+003  6.98536294E+000  4.13955679E-005  7.61
7            -1.32862877E+003  6.98625037E+000  -4.94068552E-005  7.75
8            -1.32862877E+003  6.98639487E+000  5.20529686E-007  7.89
9            -1.32862877E+003  6.98638414E+000  -5.71947099E-007  8.03
-----
Final energy, E = -1328.628768866 eV
Final free energy (E-TS) = -1328.628768866 eV
(energies not corrected for finite basis set)
NB est. 0K energy (E-0.5TS) = -1328.628768866 eV
    
```

# Symmetry Made Simple (cell file)

cell input

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon...
File Edit Options Template Execute Macro Window Help
0.1250000000000000 0.1250000000000000 0.1250000000000000 0.1250000000000000
%ENDBLOCK KPOINTS_LIST

%BLOCK SYMMETRY_OPS
1.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.0000000000000000 1.0000000000000000 -0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.0000000000000000 0.0000000000000000 0.0000000000000000
1.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.0000000000000000 1.0000000000000000 -0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.0000000000000000 0.0000000000000000 0.0000000000000000
1.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.0000000000000000 1.0000000000000000 -0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.5000000000000000 0.0000000000000000 -0.0000000000000000
1.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.0000000000000000 1.0000000000000000 -0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.5000000000000000 0.5000000000000000 0.0000000000000000
-1.0000000000000000 0.0000000000000000 -0.0000000000000000
0.0000000000000000 -1.0000000000000000 -0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.0000000000000000 0.5000000000000000 0.5000000000000000
-1.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.0000000000000000 -1.0000000000000000 -0.0000000000000000
0.0000000000000000 0.0000000000000000 1.0000000000000000
0.0000000000000000 0.0000000000000000 0.0000000000000000
Ln 1 Col 1 807 |wR| Rec Off |No Wrap| DOS |INS| NUM
    
```

castep output

```

Programmer's File Editor
File Edit Options Template Execute Macro Window Help
C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon_4th_try\silicon.castep

----- Symmetry and Constraints -----
Number of symmetry operations = 192
There are no ionic constraints specified or generated for this cell
Set iprint > 1 for details on symmetry rotations/translations

Centre of mass is NOT constrained

Number of cell constraints= 5
Cell constraints are: 1 1 1 0 0 0

External pressure/stress (GPa)
0.00000 0.00000 0.00000
0.00000 0.00000 0.00000
1.00000 0.00000 0.00000

----- MEMORY AND SCRATCH DISK ESTIMATES PER NODE -----
Model and support data Memory Disk
Electronic energy minimisation requirements 22.3 MB 0.5 MB
Approx. total storage required per node 23.2 MB 0.7 MB
    
```

a long list of symmetry operations

- Can we make it a bit less terse?
- Hint: *castep –help basic*
- Look for cell keywords related to symmetry.

# SYMMETRY\_GENERATE (cell file)

SYMMETRY\_GENERATE  
 If present, then the crystal symmetry rotations/translations will be generated automatically.  
 This is often used, and the much easier option, than the symmetry\_ops block.  
 Default value: If not present, no symmetry elements are generated.

cell input

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon...
File Edit Options Template Execute Macro Window Help
Si 0.7500000000000001 0.2500000000000000 0.7500000000000000
Si 0.2500000000000000 0.2500000000000000 0.2500000000000000
Si 0.2500000000000000 0.7500000000000001 0.7500000000000000
Si 0.7500000000000001 0.7500000000000000 0.2500000000000000
%ENDBLOCK POSITIONS_FRAC

%BLOCK KPOINTS_LIST
0.3750000000000000 0.3750000000000000 0.3750000000000000 0.1250000000000000
0.3750000000000000 0.3750000000000000 0.1250000000000000 0.3750000000000000
0.3750000000000000 0.1250000000000000 0.1250000000000000 0.3750000000000000
0.1250000000000000 0.1250000000000000 0.1250000000000000 0.1250000000000000
%ENDBLOCK KPOINTS_LIST

symmetry_generate

FIX_CON : false
%BLOCK IONIC_CONSTRAINTS
%ENDBLOCK IONIC_CONSTRAINTS

%BLOCK SPECIES_MASS
Si 28.084999845
%ENDBLOCK SPECIES_MASS

%BLOCK SPECIES_POT
Si 2|1.8|1.8|1.3|2|3|4|30:31:32LG6(qc=4)
%ENDBLOCK SPECIES_POT
    
```

castep output

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon...
File Edit Options Template Execute Macro Window Help
+ 4 0.125000 0.125000 0.125000 0.125000 +
----- Symmetry and Constraints -----
Number of symmetry operations = 48
There are no ionic constraints specified or generated for this cell
Set iprint > 1 for details on symmetry rotations/translations

Centre of mass is NOT constrained

Number of cell constraints= 5
Cell constraints are: 1 1 1 0 0 0

External pressure/stress (GPa)
0.00000 0.00000 0.00000
0.00000 0.00000 0.00000
0.00000 0.00000 0.00000

----- MEMORY AND SCRATCH DISK ESTIMATES PER NODE -----
Model and support data Memory Disk
Electronic energy minimisation requirements 22.2 MB 0.5 MB
Approx. total storage required per node 23.1 MB 0.7 MB
    
```

Not all have been included but almost ...

# Fancy Different Units?

```
%BLOCK LATTICE_CART
nm
0.5400000000000000 0.0000000000000000 0.0000000000000000
0.0000000000000000 0.5400000000000000 0.0000000000000000
0.0000000000000000 0.0000000000000000 0.5400000000000000
%ENDBLOCK LATTICE_CART
....
```

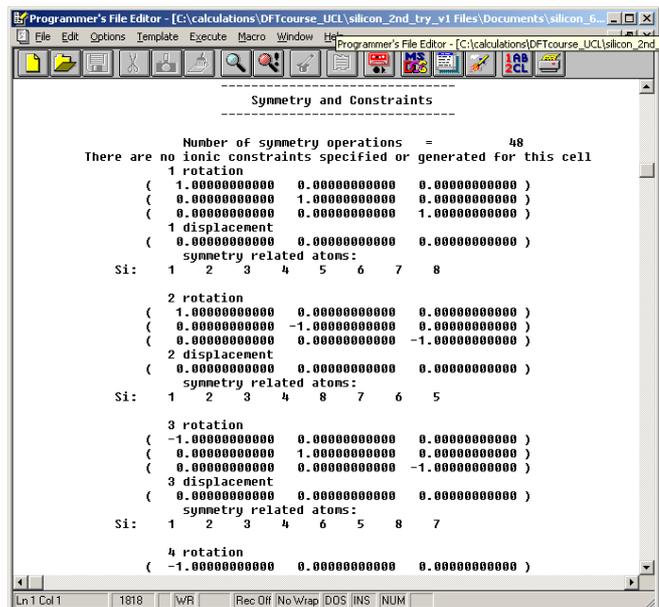
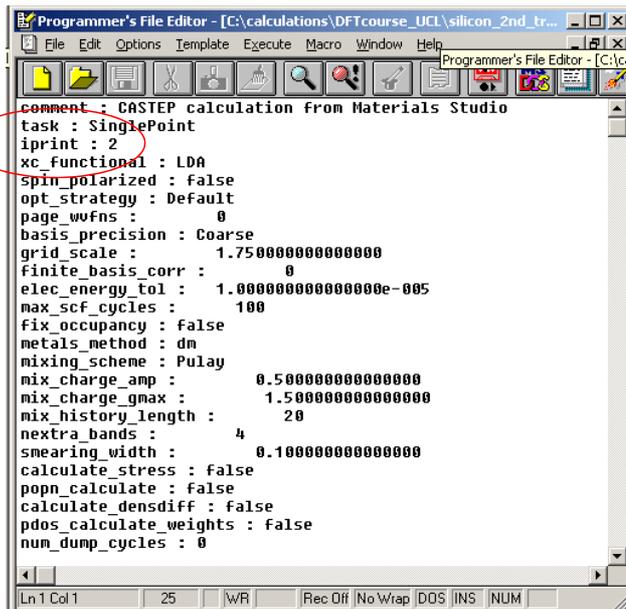
Default is Angstrom.

If unit is wrong/unknown, CASTEP will complain.

## Output Verbosity: IPRINT (param file)

*param file*

*castep output*



- IPRINT : 2 gives lots of detail on calculation.
- Useful to find out where a calculation might be problematic.
- Exercise: look at the differences between implicit symmetry generation with SYMMETRY\_OPS vs SYMMETRY\_GENERATE in previous examples.

# SYMMETRY\_OPS vs SYMMETRY\_GENERATE

CASTEP output

*symmetry\_ops*

```
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon_7_...
-----
Symmetry and Constraints
-----
Number of symmetry operations = 192
There are no ionic constraints specified or generated for this cell
1 rotation
( 1.0000000000 0.0000000000 0.0000000000 )
( 0.0000000000 1.0000000000 0.0000000000 )
( 0.0000000000 0.0000000000 1.0000000000 )
1 displacement
( 0.0000000000 0.0000000000 0.0000000000 )
Si: 1 2 3 4 5 6 7 8
symmetry related atoms:
2 rotation
( 1.0000000000 0.0000000000 0.0000000000 )
( 0.0000000000 1.0000000000 0.0000000000 )
( 0.0000000000 0.0000000000 1.0000000000 )
2 displacement
( 0.0000000000 0.5000000000 0.5000000000 )
Si: 2 1 4 3 8 7 6 5
symmetry related atoms:
3 rotation
( 1.0000000000 0.0000000000 0.0000000000 )
( 0.0000000000 1.0000000000 0.0000000000 )
( 0.0000000000 0.0000000000 1.0000000000 )
3 displacement
( 0.5000000000 0.0000000000 0.5000000000 )
Si: 3 4 1 2 6 5 8 7
symmetry related atoms:
Ln 1 Col 1 3110 |wR |Rec Diff |No Wrap |DOS |INS |NUM
```

*symmetry\_generate*

```
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_2nd_try_v1 Files\Documents\silicon_6_...
-----
Symmetry and Constraints
-----
Number of symmetry operations = 48
There are no ionic constraints specified or generated for this cell
1 rotation
( 1.0000000000 0.0000000000 0.0000000000 )
( 0.0000000000 1.0000000000 0.0000000000 )
( 0.0000000000 0.0000000000 1.0000000000 )
1 displacement
( 0.0000000000 0.0000000000 0.0000000000 )
Si: 1 2 3 4 5 6 7 8
symmetry related atoms:
2 rotation
( 1.0000000000 0.0000000000 0.0000000000 )
( 0.0000000000 -1.0000000000 0.0000000000 )
( 0.0000000000 0.0000000000 -1.0000000000 )
2 displacement
( 0.0000000000 0.0000000000 0.0000000000 )
Si: 1 2 3 4 8 7 6 5
symmetry related atoms:
3 rotation
( -1.0000000000 0.0000000000 0.0000000000 )
( 0.0000000000 1.0000000000 0.0000000000 )
( 0.0000000000 0.0000000000 -1.0000000000 )
3 displacement
( 0.0000000000 0.0000000000 0.0000000000 )
Si: 1 2 3 4 6 5 8 7
symmetry related atoms:
4 rotation
( -1.0000000000 0.0000000000 0.0000000000 )
Ln 1 Col 1 1818 |wR |Rec Diff |No Wrap |DOS |INS |NUM
```

## A Few Additional (& important) *Cell* Keywords

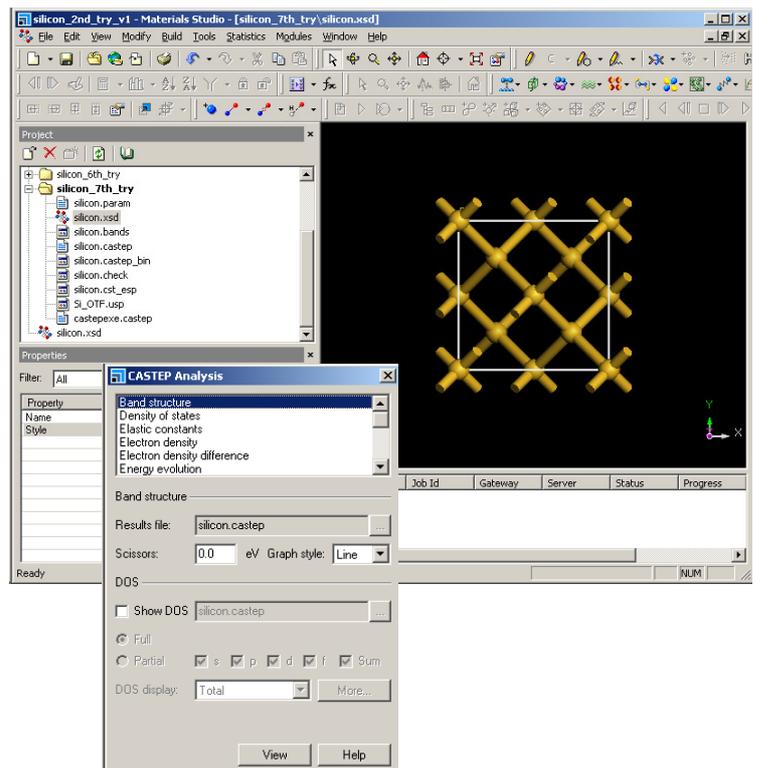
- `kpoints_mp_grid` & `kpoints_mp_spacing`.
- `*_kpoints_mp_grid`, where `*` = BS, PHONON, MAGRES ...
- `species_lcao_states` (block): default given by pseudopotential; used to calculate partial (Mulliken) charges
- Have a look in the documentation to familiarize yourself with these.

# A Few Additional (& important) *Parameter* Keywords

- Task.
- xc\_functional.
- cut\_off\_energy, grid\_scale, and fine\_grid\_scale.
- charge, spin & spin\_polarised.
- n\_extra\_bands.
- Note: each task will have an associated number of keywords, e.g., bs\_\* (band structure), phonon\_\* (phonon), magres\_\* (magnetic resonance), ...

## Output in More Detail: Back to Materials Studio

- CASTEP output (e.g., check file) can be analysed in MS
- Otherwise, you can use a multitude of utilities provided along with CASTEP (or write your own).
- Try seeing what you can (and can't) do with MS
- Steps & hints:
  - Activate your model file in MS.
  - Go to CASTEP ANALYSIS.
  - Play a bit with it.
  - Note: if you cannot do much, investigate how you can hack the param file to ask for more.



# “Cheap” Ground-state Properties

- Some properties are relatively cheap to compute: orbitals, density difference, KS orbitals – accessible from MS.

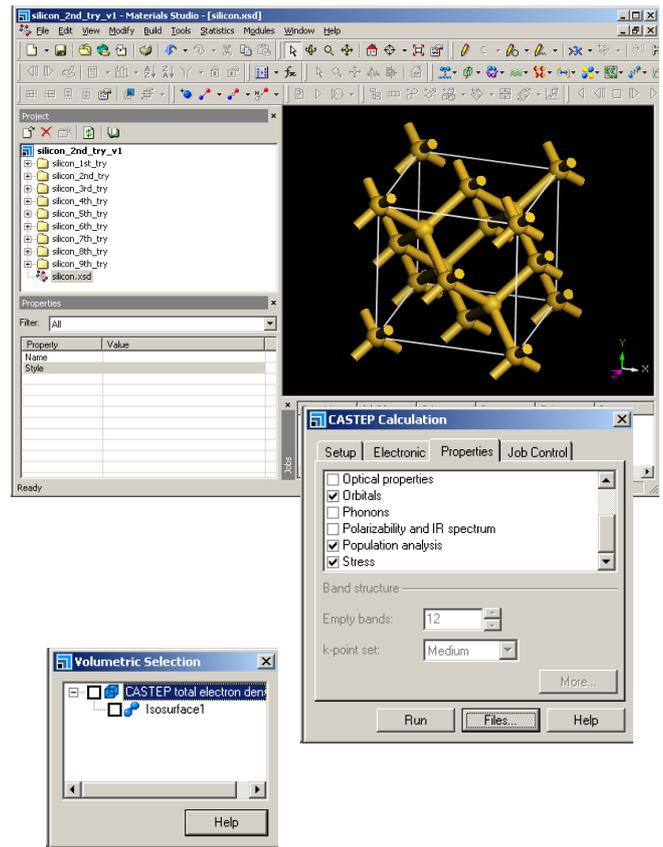
- Or directly in *param* file:

```
calculate_stress : true  
popn_calculate : true  
calculate_densdiff : true  
write_orbitals : true
```

- Optimize calculation parameters: speed or memory.

- Exercise:

- Explore analyzing results in MS
- Hints:
  - “Volume Visualization” tools are quite handy.
  - Band structure / density of states: these are allowed to be analyzed but careful, they correspond to the SCF calculation, not a proper calculation.



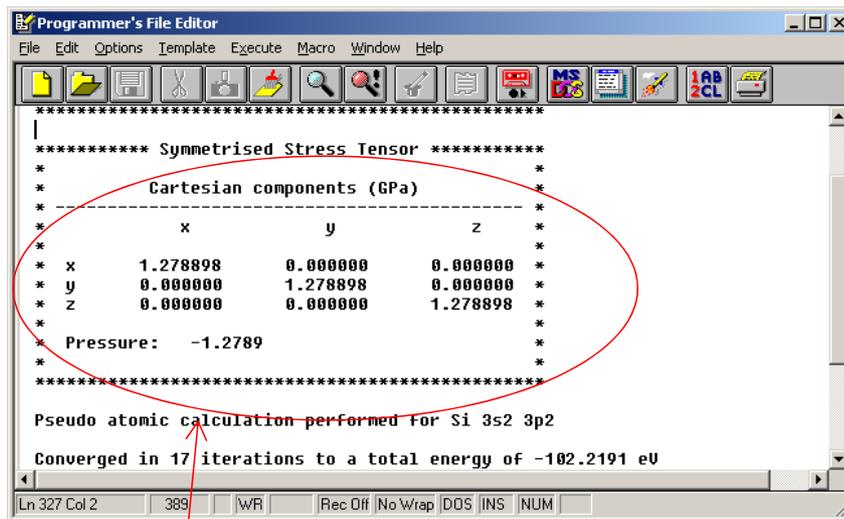
## Convergence Tests: Exercise

Electronic-energy convergence: essential ingredient to any serious calculation.

Exercise: explore how total electronic energy varies with cutoff energy and k-point sampling.

Also have a look at documentation for *basis\_precision* and how this is related to the information given in the pseudopotential library.

# A Closer Look at Our Silicon Structure



```
***** Symmetrised Stress Tensor *****
*
* Cartesian components (GPa)
*-----*
* x      y      z
* x  1.278898  0.000000  0.000000
* y  0.000000  1.278898  0.000000
* z  0.000000  0.000000  1.278898
*
* Pressure:  -1.2789
*
*****
Pseudo atomic calculation performed for Si 3s2 3p2
Converged in 17 iterations to a total energy of -102.2191 eV
```

Quite a bit of pressure (about 12.8 kbar).

## Geometry Optimization

- All our work so far assumed a given structure (e.g., as obtained from experimental data).
- However, the DFT ground state does not necessarily correspond to the true ground state, e.g., this ground state will also change with the level of theory (and convergence parameters).
- Thus, it is likely we have been doing calculations on a strained sample!
- The way out of this problem:
  - Calculate electronic energy for an initial (guess) structure.
  - Modify ionic positions (and/or unit-cell parameters).
  - Recalculate energy.
  - Iterate till minimum is found (usually closest minimum, not necessarily the absolute minimum).
- Agreement with experiment is typically on the order of a percent or better.

# Geometry Optimization: What One Gets

- Cell dimensions, bond lengths & angles
- Which structure is most stable (phase diagrams)
- Bulk moduli & elastic constants.
- A gateway to materials' properties: phonons, dielectric constants, etc on the GROUND-STATE structure.

## Geometry Optimization: How It Works

- Within the Born-Oppenheimer approximation (frozen nuclei), need to find global energy minimum dictated by geometry of ions → *Multidimensional optimization Problem*.

How to do it:

- Simplest approach: Steepest-Descent Methods.
- More sophisticated: Damped Molecular Dynamics, Conjugate Gradients, BFGS.
- Caveat: all of above will find minima, but not necessarily the ABSOLUTE minimum. Always need to check for this (and this might not be easy).

# Steepest Descents

- Conceptually, the simplest of all.
- How it is done:
  - Follow direction of largest local gradient using a trial step.
  - Find the optimal step (so-called “line minimization”).
  - Continue till energy starts rising, switch to an orthogonal direction.
  - Repeat till converge.
- What you get:
  - Ease of implementation, robust, and reliable.
  - Slow convergence, easily stuck in local minima.

## Damped MD (available on CASTEP)

- An improved steepest-descent method.
- How it is done:
  - Move ions using velocities & forces: more efficient than steepest descents.
  - Include a “friction” or damping term proportional to velocity: this damping term must be obtained by trial & error.
- What you get:
  - More efficient than classic steepest-descent method.
  - Speed of convergence depends on damping factor & can also get stuck in local minima.
  - CASTEP implementation does not allow cell minimization

# Conjugate Gradients

- How it is done:
  - Initial search: steepest descents.
  - Subsequent search directions: orthogonal to ALL prior search directions, not just previous step → big time saver.
- What you get:
  - Rapid rate of convergence.
  - More complex to code & control.

## BFGS in a Slide [1]: CASTEP's Default

- Energy surface around minimum is “quadratic”:
  - Thus Hessian matrix H is quantity of interest.
  - Hessian Matrix not known a-priori & an initial guess needs to be supplied.
- Build it up as ions move according to Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm (also known as a *quasi-Newton* method).
- Ionic positions given by:
$$R_{i+1} = R_i + \lambda \Delta R_i$$
$$\Delta R_i = H_i^{-1} F_i$$

where  $\lambda=1$  is optimal step in a quadratic surface.  
Optimal  $\lambda$  found via linear interpolation such that  $F\Delta x \rightarrow 0$ .
- What you get:
  - Similar convergence to Conjugate gradients.
  - Information on Hessian, particularly of ions.
  - Complex to code.

# BFGS in CASTEP

In *param* file:

- *Task* : *GeometryOptimization*
- *geom\_method* : *BFGS*
  - Can vary ionic positions or cell (this is the only way to do *both* at present).
  - Basic variables: fractional ionic coordinates & strains.
- Initialization parameters (first guess at Hessian):
  - *geom\_frequency\_est* (default = 50 THz).
  - *geom\_modulus\_est* (default = 500 GPa).
  - Improved ESTIMATES of these numbers will also be computed in the calculation (in case you need them to run things again later on).

## Other Methods in Brief (Fixed-cell)

In *param* file:

- *geom\_method* : *delocalized*
  - Uses “delocalized” internal coordinates with BFGS.
  - Possible to implement non-linear constraints (fixed bond lengths/angles, etc).
- *geom\_method* : *dampedMD* [1]

[1] For a fair amount of detail see: M.I.J.Probert, *J. Computational Phys.*, 191, 130-146 (2003).

# Geometry Optimization: Convergence

Calculation will execute a maximum of *geom\_max\_iter* steps and will converge if within a tolerance of

- Energy: *geom\_energy\_tol* for at least *geom\_convergence\_win* steps.
- Ions: *geom\_force\_tol* (force) and *geom\_disp\_tol* (displacement).
- Cell: *geom\_stress\_cell*.

Fortunately, CASTEP provides sensible defaults.

Quick exercise: find these. Do they make sense?

## Geometry Optimization: Important Points

- Force convergence: slower than energy convergence (e.g., higher PW cutoffs).
- Stress convergence: slower than forces.
- Finite Basis-set Corrections:
  - If unit cell changes at constant PW cutoff: number of PWs changes, total energies change.
  - Use in param file: "*finite\_basis\_corr : automatic*"
  - CASTEP will attempt to correct for this (typically works quite well).
- Can also implement constraints (more later).



# Geometry Optimization: Output in Some Detail

k-point coordinates for BZ sampling

```

k-Points For BZ Sampling
MP grid size for SCF calculation is 4 4 4
Number of kpoints used = 4
*****
+ Number      Fractional coordinates      Weight +
+-----+-----+-----+-----+-----+
+ 1  0.375000  0.375000  0.375000  0.1250000 +
+ 2  0.375000  0.375000  0.125000  0.3750000 +
+ 3  0.375000  0.125000  0.125000  0.3750000 +
+ 4  0.125000  0.125000  0.125000  0.1250000 +
*****

Symmetry and Constraints

Number of symmetry operations = 192
There are no ionic constraints specified or generated for this cell
Set iprint > 1 for details on symmetry rotations/translations

Centre of mass is NOT constrained

Number of cell constraints= 5
Cell constraints are: 1 1 1 0 0 0

External pressure/stress (GPa)
0.00000  0.00000  0.00000
0.00000  0.00000  0.00000
0.00000  0.00000  0.00000
    
```

Electronic Minimization of input structure at 3 cutoff-energies

finite\_basis\_corr : 2  
finite\_basis\_npoints : 3

```

Calculating finite basis set correction with 3 cut-off energies.
Calculating total energy with cut-off of 310.000eU.
SCF loop      Energy      Fermi energy      Energy gain      Timer
              per atom
Initial      3.7936765E+002  5.45678864E+001  2.19
1 -7.81028767E+002  9.15143036E+000  1.45049553E+002  4.31
2 -8.65374355E+002  6.24557607E+000  1.05431985E+001  6.06
3 -8.66729071E+002  6.18394160E+000  1.69339425E-001  7.92
4 -8.66155704E+002  6.24532924E+000  -7.16708585E-002  10.19
5 -8.65881773E+002  6.33710190E+000  -3.42413112E-002  12.19
6 -8.65886804E+002  6.34873999E+000  6.28813456E-004  14.88
7 -8.65886821E+002  6.35040244E+000  2.11659477E-006  16.83
8 -8.65886826E+002  6.35124580E+000  6.63918565E-007  18.25
9 -8.65886827E+002  6.35119532E+000  1.20543241E-007  19.62

Final energy, E = -865.8868269164 eU
Final free energy (E-TS) = -865.8868269164 eU
(energies not corrected for finite basis set)

NB est. 0K energy (E-0.5TS) = -865.8868269164 eU

Calculating total energy with cut-off of 315.000eU.
SCF loop      Energy      Fermi energy      Energy gain      Timer
              per atom
Initial      -8.65886825E+002  6.35121604E+000  21.02
1 -8.65888694E+002  6.35099799E+000  2.33695419E-004  22.41
2 -8.65888695E+002  6.35000702E+000  2.00421095E-007  22.94
    
```

# Geometry Optimization: Output in Some Detail

BFGS Algorithm Starts

```

***** Stress Tensor *****
* Cartesian components (GPa) *
*-----*-----*-----*
* x      y      z      *
* x  2.781621  0.000000  0.000000 *
* y  0.000000  2.781621  0.000000 *
* z  0.000000  0.000000  2.781621 *
* Pressure: -2.7816 *
*****
BFGS: Finished iteration 0 with enthalpy= -8.65890128E+002 eU
-----
| Parameter | value | tolerance | units | OK? |
|-----|-----|-----|-----|-----|
| dE/ion | 0.000000E+000 | 1.000000E-005 | eV | No |
| Smax | 2.781621E+000 | 5.000000E-002 | GPa | No |
-----
Starting BFGS iteration 1 ...
-----
| Step | lambda | F.delta | enthalpy |
|-----|-----|-----|-----|
| previous | 0.000000 | 0.000569 | -865.890128 |
    
```

Status of convergence criteria

BFGS Algorithm: First Iteration, including calculation of electronic energy

```

-----
| Step | lambda | F.delta | enthalpy |
|-----|-----|-----|-----|
| previous | 0.000000 | 0.000569 | -865.890128 |
| trial step | 1.000000 | 0.000468 | -865.904352 |
-----
BFGS: improving iteration 1 with line minimization (lambda= 5.641208)
-----
Unit Cell
-----
Real Lattice(A)      Reciprocal Lattice(1/A)
5.373887  0.000000  0.000000  1.1692064  0.0000000  0.0000000
0.000000  5.373887  0.000000  0.000000  1.1692064  0.0000000
0.000000  0.000000  5.373887  0.000000  0.000000  1.1692064

Lattice parameters(A)      Cell Angles
a = 5.373889      alpha = 90.000000
b = 5.373889      beta = 90.000000
c = 5.373889      gamma = 90.000000

Current cell volume = 155.190812 A**3
-----
SCF loop      Energy      Fermi energy      Energy gain      Timer
              per atom
Initial      -8.65879097E+002  6.67754922E+000  52.02
1 -8.65886826E+002  6.35124580E+000  2.00421095E-007  22.94
    
```

F.delta is search direction (constant during iteration).  
Ideally, step length lambda should make F.delta = 0  
(lambda = 1 at beginning but improved during iteration).

# Geometry Optimization: Output in Some Detail

BFGS: Next Iteration

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_1st_try_GEOMOPT_v1 Files\Document...
File Edit Options Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_1st_try_GEOMOPT_v1 Files\Document...

Starting BFGS iteration      2 ...

-----
| Step | lambda | F.delta | enthalpy | <-- min BFGS
|-----|-----|-----|-----| <-- min BFGS
| previous | 0.000000 | 0.000004 | -865.933336 | <-- min BFGS
|-----|-----|-----|-----| <-- min BFGS

BFGS: starting iteration      2 with trial guess (lambda= 1.000000)

-----
Unit Cell
-----
Real Lattice(A)      Reciprocal Lattice(1/A)
5.3757662  0.0000000  0.0000000  1.1687981  0.0000000  0.0000000
0.0000000  5.3757662  0.0000000  0.0000000  1.1687981  0.0000000
0.0000000  0.0000000  5.3757662  0.0000000  0.0000000  1.1687981

Lattice parameters(A)      Cell Angles
a = 5.375766                alpha = 90.000000
b = 5.375766                beta  = 90.000000
c = 5.375766                gamma = 90.000000

Current cell volume = 155.353526 A**3

-----
|<-- SCF
|<-- SCF
Ln 532 Col 1      683      |WR|      Rec Off |No Wrap |DOS |INS |NUM
    
```

BFGS: Convergence Criteria Satisfied

```

Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_1st_try_GEOMOPT_v1 Files\Document...
File Edit Options Programmer's File Editor - [C:\calculations\DFTcourse_UCL\silicon_1st_try_GEOMOPT_v1 Files\Document...

| Step | lambda | F.delta | enthalpy | <-- min BFGS
|-----|-----|-----|-----| <-- min BFGS
| previous | 0.000000 | 0.000004 | -865.933336 | <-- min BFGS
| trial step | 1.000000 | 0.000000 | -865.933388 | <-- min BFGS
|-----|-----|-----|-----| <-- min BFGS

BFGS: finished iteration      2 with enthalpy= -8.65933380E+002 eV

| Parameter | value | tolerance | units | OK? | <-- BFGS
|-----|-----|-----|-----|-----| <-- BFGS
| dE/ion | 5.523670E-006 | 1.000000E-005 | eV | Yes | <-- BFGS
| Smax | 6.798946E-003 | 5.000000E-002 | GPa | Yes | <-- BFGS
|-----|-----|-----|-----|-----| <-- BFGS

BFGS: Geometry optimization completed successfully.

-----
BFGS: Final Configuration:
-----
Unit Cell
-----
Real Lattice(A)      Reciprocal Lattice(1/A)
5.3757662  0.0000000  0.0000000  1.1687981  0.0000000  0.0000000
0.0000000  5.3757662  0.0000000  0.0000000  1.1687981  0.0000000
0.0000000  0.0000000  5.3757662  0.0000000  0.0000000  1.1687981

Lattice parameters(A)      Cell Angles
a = 5.375766                alpha = 90.000000
b = 5.375766                beta  = 90.000000
c = 5.375766                gamma = 90.000000

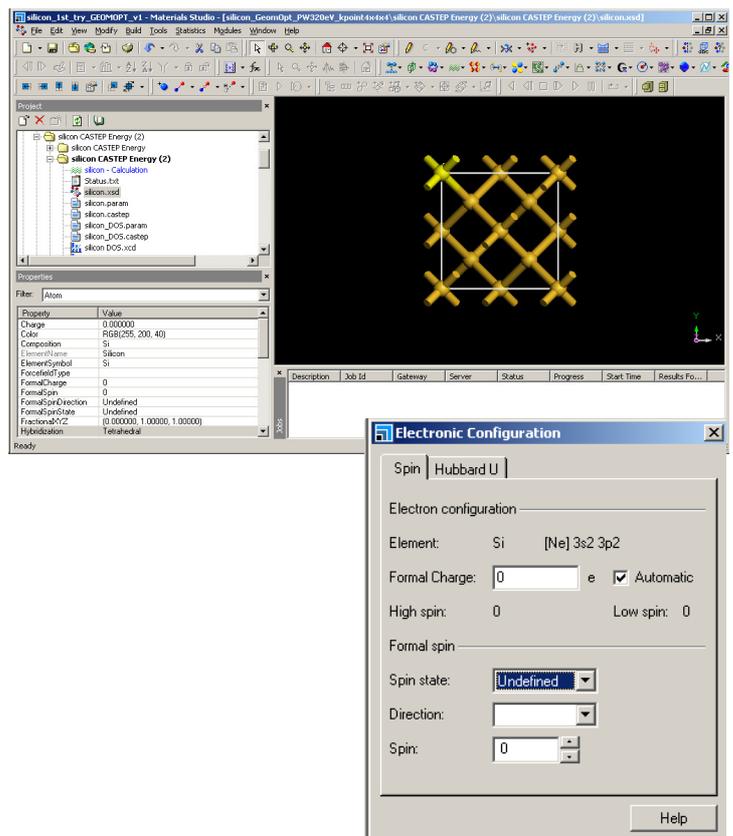
-----
|<-- SCF
|<-- SCF
Ln 531 Col 2      683      |WR|      Rec Off |No Wrap |DOS |INS |NUM
    
```

Far more detail given with *iprint : 2 or 3*

## Interlude: Dealing with Spins

In MS:

- Can be modified in Properties Toolbar.
- Or in *Modify* → *Electronic Configuration* (where Hubbard U parameter can also be set).



# Interlude: Dealing with Spins

## In CASTEP:

- Param file:
  - Set initial magnetic state *spin: 2* (in  $\hbar$  units)
  - Constrain spin *spin\_fix : 2*
- In cell file: initialize individual spin states

```
%BLOCK POSITIONS_FRAC
O 0.0 0.0 0.0 SPIN=+0.5
O 0.5 0.5 0.5 SPIN=-0.5
%ENDBLOCK POSITIONS_FRAC
```
- More with: *castep -help search spin*

## Geometry Optimization: Suggestion for Further Work

- Take Graphite from MS library.
- Perform geometry optimizations with both LDA and GGA.
- What is going on?

# Properties, at Last

With a properly converged structure we can now access ground-state properties such as:

- Electronic band structure (and density of states).
- Optical properties (refractive index, dielectric constants).
- Phonons (dispersion & density of states).
- IR spectra.
- NMR spectra.
- Thermodynamic properties.
- Even STM profiles (which I have not tried myself in detail but looks interesting).

For the remainder of this session and next we will be exploring some of these (these are all CASTEP *tasks*).

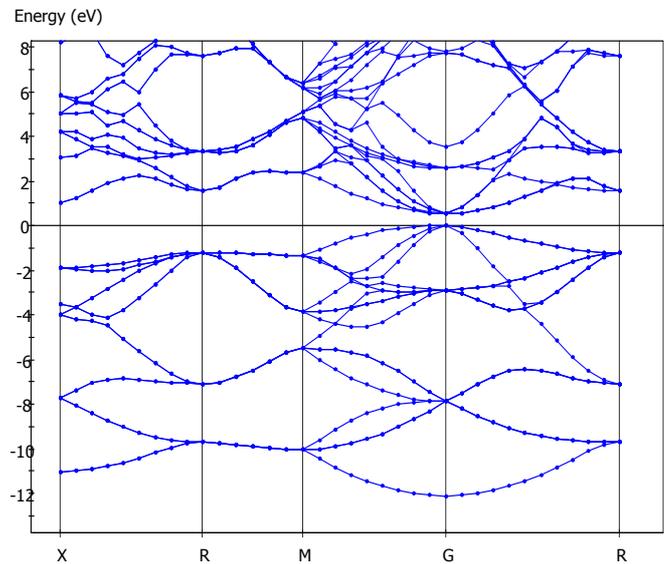
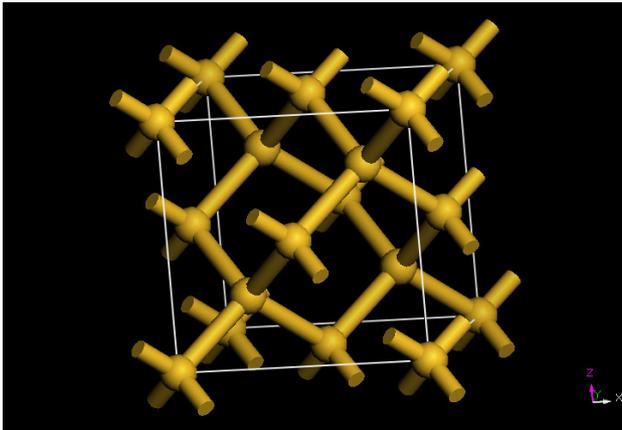
## Properties: Electronic Band Structure

Exercise:

- Perform a Band Structure Calculation on Silicon using your geometry-optimized structure.
- Hint: this is easiest if done from MS first.
- Have a look at the .cell, .param, and .castep files: can you make sense of what is there?
- Ask MS to analyze calculation as well.

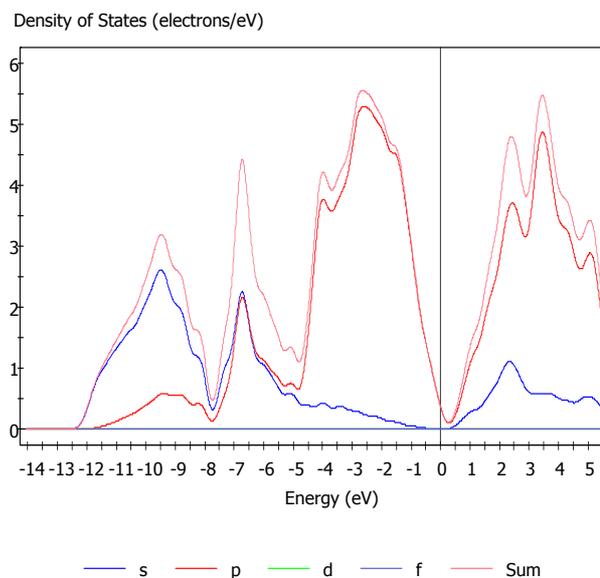


# Silicon: Non-Primitive Cell, LDA Approximation



## Silicon: Electronic Density of States

- Use a regular k-grid (*bs\_kpoints\_mp\_grid*)
- Can also calculate partial DOS (s, p, d, f bands).

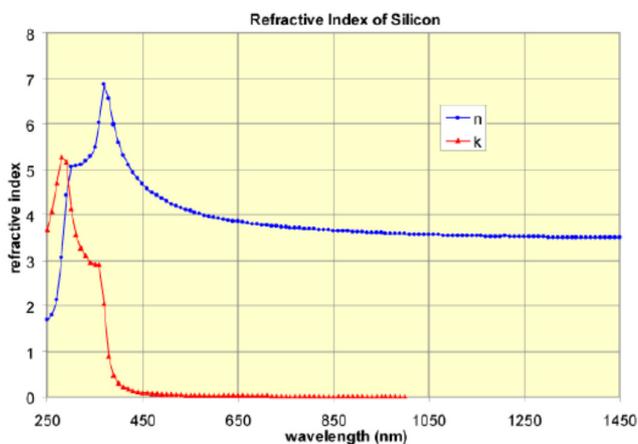


# Optical Properties

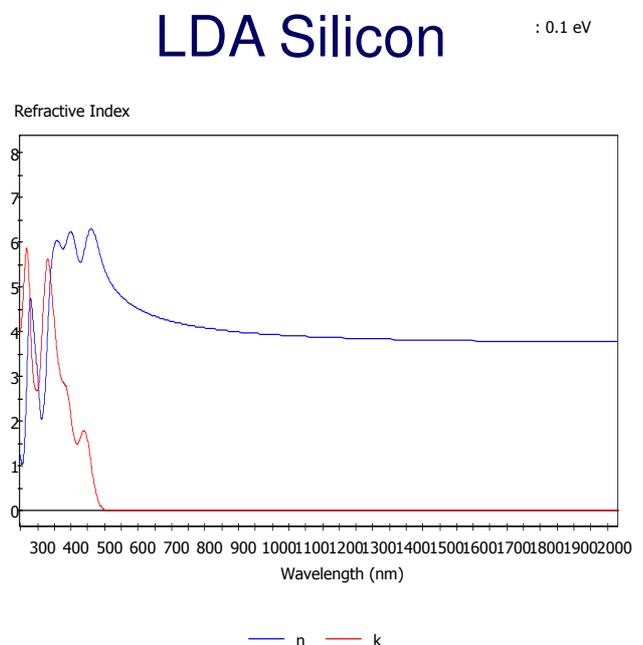
- Similar in spirit to Band Structure calculation
  - Param file: *task: Optics*
  - Cell file: three choices
    - optics\_kpoints\_mp\_grid*
    - optics\_kpoints\_path*
    - optics\_kpoints\_grid*
- Access to: reflectivity, absorption, refractive index, dielectric properties, conductivity for polarized, unpolarized and polycrystalline systems.

## LDA Silicon: Optical Properties

### Literature



From: MA Green & MJ Keevers, "Optical Properties of Intrinsic Silicon at 300K", *Progress in Photovoltaics Research and Applications*, Vol. 3, pp. 189-192, 1995.



# A Glimpse at Next Lecture

## More Properties & a Few Advanced Features

- Today we focused on
  - Running CASTEP from within MS and also stand-alone.
  - Learned something about what goes on under the hood.
  - Dealt with Geometry Optimization.
  - Calculated a few properties (band structure, optics).
- But ... there is much more!
- Next (and last) lecture:
  - Will continue calculating other properties which are important (e.g., phonons).
  - Will explore a few advanced features of CASTEP & MS.
  - **Best if you bring your problem with you ... we may have the chance to have a go at it!**

## Outline of Course

1. Fundamentals: Materials Modelling, Electronic Structure & DFT.
2. The Practice of DFT calculations using the CASTEP code & Materials Studio.
3. A Closer Look under the Hood: from Structure to Properties.
4. **More Properties & Advanced Features.**

# Lecture IV

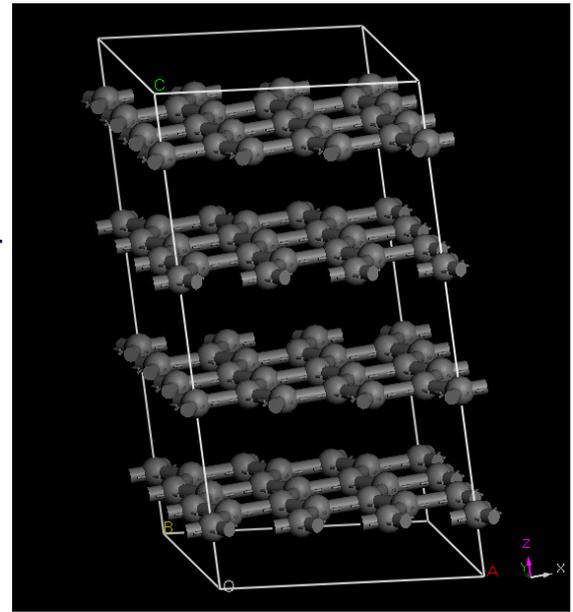
## More Properties & Advanced Features

### Outline of Today's Lecture

- Properties: vibrations.
- A Few Advanced Features:
  - Pseudopotentials.
  - Constraints in MS & CASTEP.
  - Brief Notes on Scripting
- Where to Go From Here: Recap & Outlook.

# From Last Lecture: Graphite & the LDA/GGA

- The exercise: optimize bulk graphite structure.
- Compare LDA and GGA exchange-correlation functionals.
- What did you find?



# From Last Lecture: Graphite & the LDA/GGA

Carbon 44 (2006) 231–242

Density functional study of graphite bulk and surface properties

Newton Ooi \*, Asit Rairkar, James B. Adams

Department of Chemical and Materials Engineering, P.O. Box 870006, Ira A. Fulton School of Engineering and Applied Sciences, Arizona State University, Tempe, AZ 85287-6006, USA

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### Abstract

The structural and electronic properties of bulk graphite were compared using density functional theory calculations with the local density (LDA) and generalized gradient (GGA) approximations to determine the relative ability of each to model this material. The GGA fails to generate interplanar bonding, but the LDA does, even though the band structures obtained from both approximations were essentially identical. The atomic geometry, electronic structure, and enthalpy of the graphite (0001) surface were then obtained using the LDA. The calculated surface energy was  $\sim 0.075 \text{ J/m}^2$  and the calculated work function was in 4.4–5.2 eV range, both of which correspond well to published, measured and calculated values. The surface is semi-metallic, just like in the bulk, with the conduction band minimum and valence band maximum just touching with minimal overlap in the H-K region in the Brillouin Zone, so the electron affinity was identical to the work function. The (0001) surface undergoes no noticeable relaxation and no reconstruction, as the strong covalent bonding prevents any corrugation of the basal planes.  
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Keywords: Graphite; Computational chemistry; Electrical (electronic) properties; Electronic structure; Surface properties

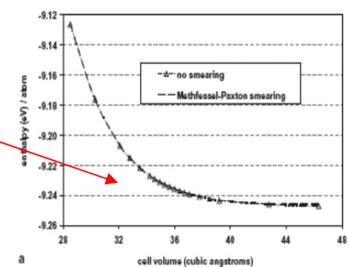
Table 1  
Graphite bulk properties

Source	$a_0$ (Å)	$c_0$ (Å)	$V_0$ (Å <sup>3</sup> )	$E_C$ (eV)	$B_0$ (GPa)
LDA PAW	2.448	6.582	34.16	8.89	30.30
LDA US	2.443	6.575	33.98	8.79	28.98
Experiment $\sim 300 \text{ K}$ [38]	2.46	6.71	35.28	X	X
Experiment $\sim 300 \text{ K}$ [39]	2.603	6.706	35.12	X	33.8
Experiment $\sim 300 \text{ K}$ [40]	2.462	6.711	35.638	X	X
Experiment $\sim 300 \text{ K}$ [41]	X	X	X	7.37	X
Calculation at 0 K [Boettger]	2.448	6.784	35.208	8.87	38.3
Calculation at 0 K [42]	2.443	6.679	34.508	9.00	288

Some details:

PW-DFT  
Ultrasoft PS  
300–400 eV energy cutoff  
8x8x8 k grid

GGA fails!



LDA overbinds  
by  $\sim 20\%$

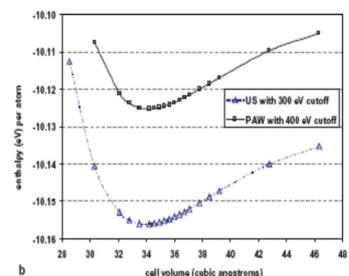
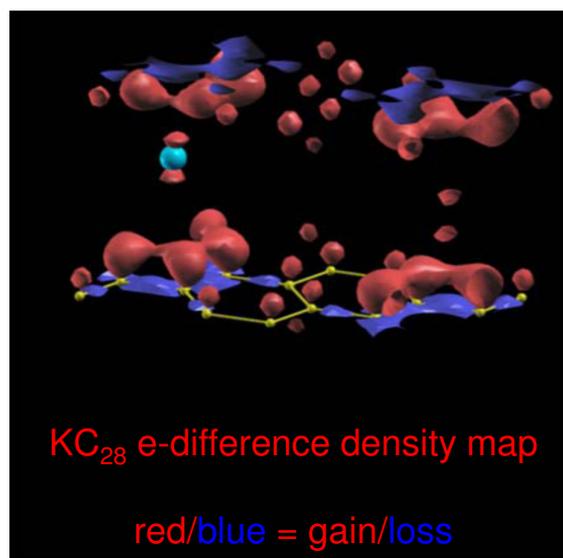
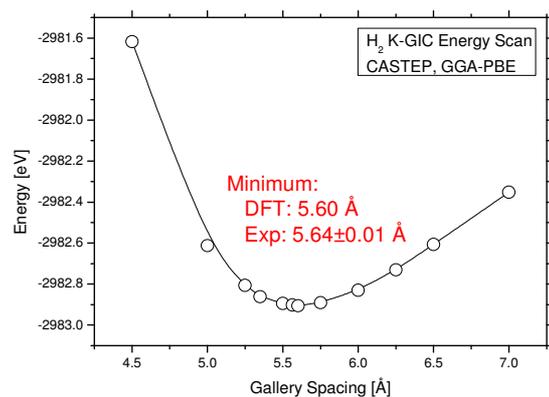
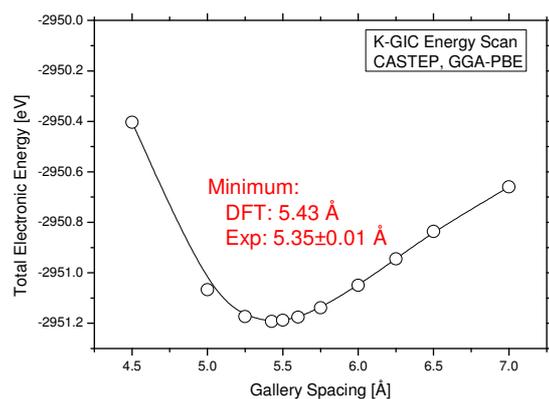


Fig. 2. Enthalpy versus volume test for graphite: (a) GGA PAW enthalpy versus volume and (b) LDA enthalpy versus volume.

# Graphitic Materials: The Need for Benchmarks



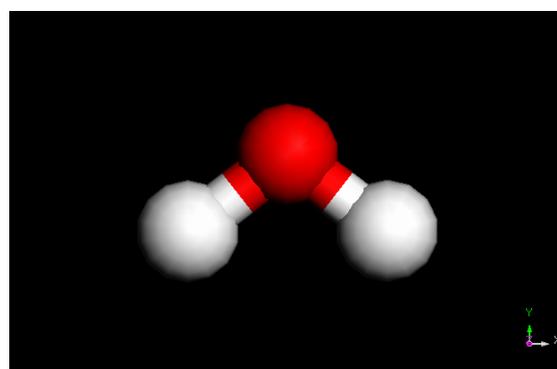
- Model validation: DFT can reproduce experimental data *quantitatively*.
- Expansion of graphite c-axis is significant: H<sub>2</sub> is too big to fit.

## Molecular Vibrations: Water

Goal: use MS to calculate the vibrational density of states of an isolated water molecule

Two tasks for all of you:

- Outline/discuss the step(s) of the calculation (say 5 minute discussion).
- Perform the steps you know ...

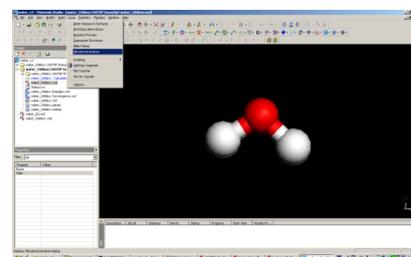


# A Suggested Course of Action

- Create a periodic model, e.g., water in a box.
- Choose a level of theory.
- Perform a single-point energy calculation to ensure everything is OK.
- The critical step: optimize GEOMETRY – why?.
- Perform the actual “phonon calculation.”

## Materials Studio Tips

- Remember: the system is not periodic!
- Properties: phonons.
- The level of theory chosen will probably limit which type of calculation you will be able to carry out.
- Have a look at CASTEP output first.
- For further analysis, also have a look at
  - Analysis → IR Spectrum
  - Tools → Vibrational Analysis
  - Properties → Polarizability & IR Spectrum



# A Closer Look at the Output

.castep output

.phonon output

```

-----
Vibrational Frequencies
-----
* Performing frequency calculation at 1 wavevector (q-pt)
-----
* q-pt= 1 ( 0.000000 0.000000 0.000000 ) 1.000000
-----
* Acoustic sum rule correction < 121.486912 cm-1 applied
-----
* N      Frequency
*      (cm-1)
-----
* 1      -0.040076
* 2      -0.039415
* 3      -0.036409
* 4      204.592550
* 5      217.858004
* 6      457.851592
* 7      1578.771037
* 8      3793.679957
* 9      3913.135364
-----
D D D D   F F F F   P P P P   T T T T
D         D F F F   P P P P   T
D         D F F F   P P P P   T
D         D F F F   P P P P   T
D D D D   F         P         T

Welcome to Castep Linear Response (DFPT)
Copyright (c) 2006 - 2008

Please cite the following publications in all
work arising from your use of CASTEP LR.

K. Refson, S. J. Clark and P. R. Tulip
Variational density functional perturbation
theory for dielectrics and lattice dynamics
Phys. Rev. B 73(15), 155114 (2006)
    
```

which ones make sense?

```

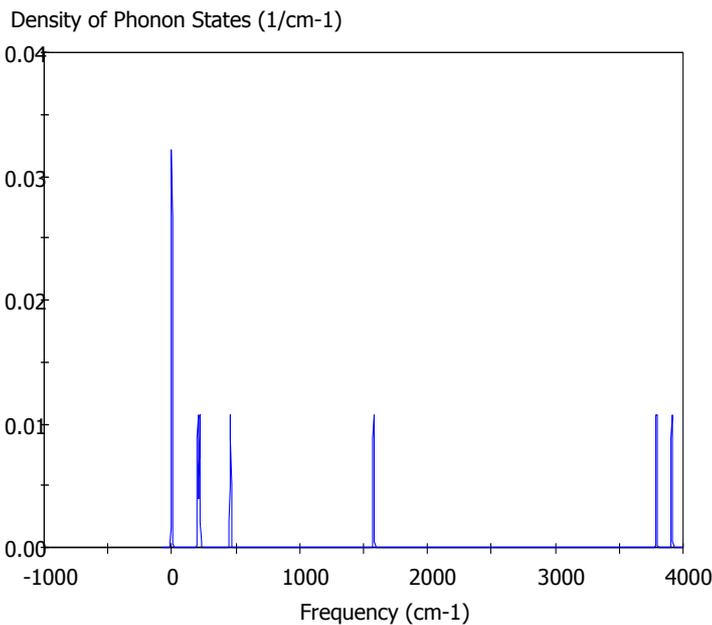
BEGIN header
Number of ions      3
Number of branches  9
Number of wavevectors 1
Frequencies in      cm-1
IR intensities in   (D/A)**2/amu
Unit cell vectors (A)
10.000000  0.000000  0.000000
0.000000  10.000000  0.000000
0.000000  0.000000  10.000000
Fractional Co-ordinates
1  0.010903  0.995110  0.000000  H  1.008000
2  0.165352  0.995537  0.000000  H  1.008000
3  0.087974  0.055082  1.000000  O  15.999000
END header
q-pt= 1  0.000000  0.000000  0.000000  1.000000
1  -0.040076
2  -0.039415
3  -0.036409
4  204.592550
5  217.858004
6  457.851592
7  1578.771037
8  3793.679957
9  3913.135364

Phonon Eigenvectors
Node Ion      X      Y
1  1  -0.006497010436  0.000000000000  -0.229257103156  0.000000000000
1  2  -0.006093001769  0.000000000000  -0.244300635199  0.000000000000
1  3  -0.002993837983  0.000000000000  -0.942047393033  0.000000000000
2  1  0.004181934320  0.000000000000  0.000507970498  0.000000000000
2  2  0.004411339689  0.000000000000  0.00237205428  0.000000000000
2  3  0.014504361222  0.000000000000  0.004840706619  0.000000000000
3  1  0.176330223162  0.000000000000  0.000058779595  0.000000000000
3  2  0.175123919813  0.000000000000  -0.00456304873  0.000000000000
3  3  0.961459276487  0.000000000000  -0.004152031466  0.000000000000
    
```

Note: eigenvector information (can simulate motion)

# Vibrational Density of States

CASTEP Density of Phonon States



Intramolecular modes (cm<sup>-1</sup>)

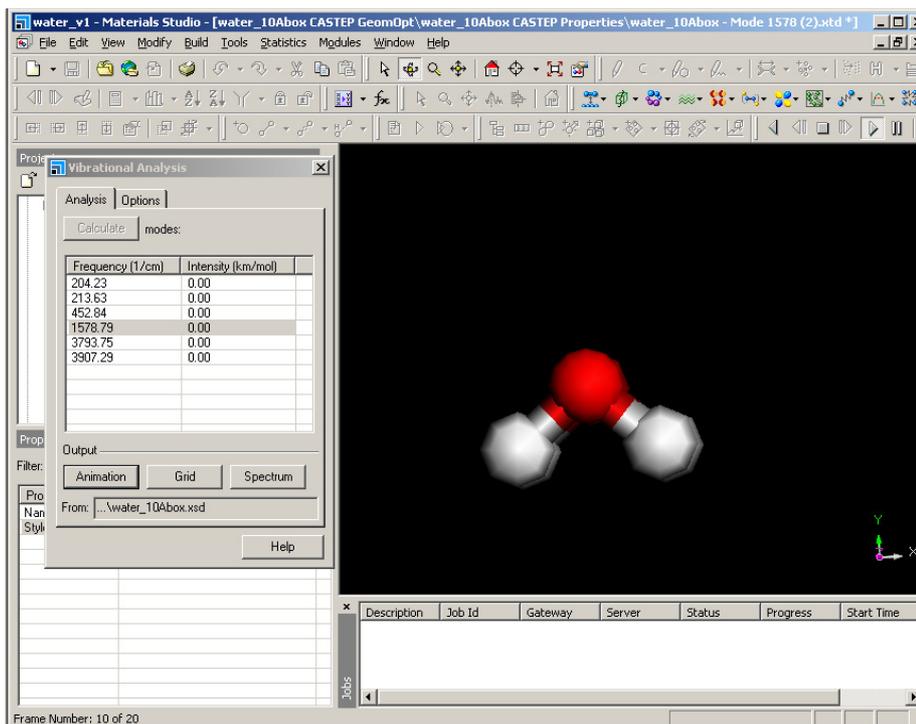
Mode	GGA-PBE	Literature
Bend	1579	1594
Symm OH stretch	3794	3657
Asymm OH stretch	3913	3755

Suggest ways to improve these calculations.

Hint: what does GEOM\_FORCE\_TOL do?

[1] P. F. Bernath, *The spectroscopy of water vapour: Experiment, theory and applications*, *Phys. Chem. Chem. Phys.* 4, 1501 (2002). Also see <http://www.lsbu.ac.uk/water/vibrat.html> (very comprehensive!)

# Visualizing Vibrational Modes



## Why It Makes Sense to Be Systematic

For the water molecule (GGA-PBE), computational effort on a single processor server is

- Single-point energy calculation: 80 sec
- Geometry optimization (from exp values): 400 sec
- Vibrational density of states (single k point!): 1000 sec

Cost clearly increases and the quality of the final result critically depends on previous steps.

# Useful Rules of Thumb

Convergence is a must as a function of

- Plane-wave cutoff.
- Periodic systems: k-point sampling in electronic problem.
- Box size: appearance of “ghost” states in isolated molecules or slabs.
- Geometry: should have small residual forces, otherwise you are not at the actual minimum and you will get imaginary frequencies (geom\_force\_tol : 0.005 eV/Å or better).

Performance:

- Accuracies down to ~10's of  $\text{cm}^{-1}$  are realistic and within reach.
- GGA functional is a good starting point.
- PBE, PW91 recommended for H-containing and H-bonded materials.
- All calculations are harmonic, thus anharmonicity effects can always be the cause of disagreement with experiment (for OH stretches, there is a fortunate cancellation of errors for GGA-PBE).

## Phonon Calculations in a Bit More Detail

- Total energy (electronic + nuclear) is central quantity
  - And it is a function of nuclear positions about the equilibrium geometry.
  - At equilibrium first derivatives (forces) are zero.
  - In the harmonic approximation, only second derivatives exist.
  - Knowledge of 2<sup>nd</sup> derivative matrix (Hessian) provides us with
    - » Normal-mode frequencies (directly accessible from experiment).
    - » Eigenvectors (experiment can only provide partial projections).
- Three common methods:
  - “Frozen-phonon.”
  - Finite displacement.
  - Supercell method.

# “Frozen” Phonons

- **What is done:**
  - Given a structure, choose an eigenvector (e.g. with the help of symmetry).
  - Compute energy as a function of displacement amplitude.
  - Derive force constants / frequencies from this energy scan.
- **Remarks:**
  - Not general, typically useful for small systems (cells) of high symmetry.
  - Need to identify eigenvectors first.
  - Supercell must be commensurate with  $q$ .

## Finite Displacement

- **What is done:**
  - Execute small displacements, one ion at a time.
  - Use single-point energy calculations to evaluate forces on every ion.
  - Compute derivative of force wrt displacement to get second derivatives and associated frequencies.
- **Remarks:**
  - Only need 6 energy calculations per ion – why?
  - General method (but can take advantage of symmetry as well).

# Supercell Method

- What is done:
  - Force-constant matrix is short-ranged (decays at least as  $1/R^3$ ).
  - Can define a cutoff radius over which 2<sup>nd</sup> derivatives are negligible and can be set to zero.
  - Procedure:
    - » Pick a large supercell to compute force constants in real space and at  $q=0$  using finite-difference methods.
    - » Fourier transform to get dynamical matrix at any desired  $q$ .
    - » Diagonalise to obtain eigenfrequencies and eigenvectors.
- Remarks:
  - It is an extension of finite-displacement method.

## Linear Response (Density Functional Perturbation Theory – DFPT)

- What is done:
  - Compute first-order (linear response) of Kohn-Sham orbitals to a displacement with wave-vector  $q$ .
  - CASTEP uses the so-called Variational DFPT [1].
- Remarks:
  - This method is quite general & transcends phonon calculations: it can be applied to other types of perturbation (can you think which ones?)
  - At present, CASTEP-DFPT only implemented for insulators & norm-conserving pseudopotentials (but hopefully extensions will come soon).

# Summary of What is Available on CASTEP [1]

- **Finite displacement**
  - Primitive cell at  $q=0$
  - Supercell at any  $q$ .
  - No restrictions on what can be done.
  
- **DFPT**
  - At arbitrary  $q$ .
  - On MP  $q$  grid + Fourier interpolation to primitive cell to get fine grid of  $q$  points.
  - Currently restricted to norm-conserving pseudopotentials & insulators.

[1] K Refson et al., *Phys. Rev. B* 73, 155114 (2006)

What Have We Done Then with Water?

Have a look at CASTEP files to find out.

# Water: The Cell File

phonon\_kpoint\_list

```
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\water_v1 Files\Documents\water_10Abox CASTEP Ge...
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\water_v1 Files\Documents\water_10Abo...

%BLOCK LATTICE_CART
  10.000000009313519      0.0000000000000000      0.0000000000000000
  0.0000000000000000      10.000000009313519      0.0000000000000000
  0.0000000000000000      0.0000000000000000      10.000000009313519
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
  H  0.0109033003414910  -0.0048896284400374  0.0000000111364981
  H  0.1653522712164767  -0.0044626464856123  0.0000000116619568
  O  0.0879744234543153  0.0550822756599789  -0.0000000227984549
%ENDBLOCK POSITIONS_FRAC

%BLOCK PHONON_KPOINT_LIST
  0.0000000000000000  0.0000000000000000  0.0000000000000000  1.0000000000000000
%ENDBLOCK PHONON_KPOINT_LIST

%BLOCK CELL_CONSTRAINTS
  1 2 3
  4 5 6
%ENDBLOCK CELL_CONSTRAINTS

FIX_COM : false
%BLOCK IONIC_CONSTRAINTS
%ENDBLOCK IONIC_CONSTRAINTS

%BLOCK SPECIES_MASS
  H  1.0080000162
  O  15.9989995956
%ENDBLOCK SPECIES_MASS

Ln1 Col1      40      WR      Rec Off NoWrap DOS INS
```

But also we could have chosen:

*phonon\_kpoint\_path* with spacing *phonon\_kpoint\_path\_spacing*  
*phonon\_kpoint\_mp\_grid a b c*  
*phonon\_kpoint\_mp\_spacing d*

## A Technical Note on k-point Grids

- Always include  $q=0$  point in your grid.
- For even  $a,b,c$  MP grid, this can be ensured with  
*phonon\_fine\_kpoint\_mp\_offset 0.125 0.125 0.125*
- Important for phonon DOS calculations (to perform accurate k integrals)

## Water: The Param File

- *task: phonon*
- *secondd\_method / phonon\_method : finitedisplacement*  
*phonon\_finite\_disp*: default is 0.05 Å (a good starting point).

Note: default for *secondd\_method* is *linearresponse*, which we could not use here; *phonon\_method* is an old keyword.

- **Convergence issues**
  - *elec\_energy\_tolerance*: needs to be quite tight to get good ground-state properties, particularly for linear-response calculations.
  - *phonon\_energy\_tolerance*
  - *phonon\_max\_cycles*

## Other Useful Keywords

- *phonon\_fine\_method* :
  - *supercell*, to use finite-displacement method (need also extra *CELL* block).
  - *interpolate*, to use linear response DFPT.

Note: in both cases, can explicitly define *phonon\_force\_constant\_cutoff*

- **Convergence issues**
  - *elec\_energy\_tolerance*: needs to be quite tight to get good ground-state properties, particularly for linear-response calculations.
  - *phonon\_energy\_tolerance*
  - *phonon\_max\_cycles*

# The Power of DFPT: Electric Fields

- To calculate, for example, LO-TO splittings in ionic systems.
- But also to calculate perturbations due to electric fields
  - To compute polarizability (Raman response) or total dielectric permittivities.
  - *task : efield*, convergence controlled with *efield\_energy\_tol*
  - *task : efield+phonon*, DFPT phonon + electric-field calculation to determine permittivity & polarizability.

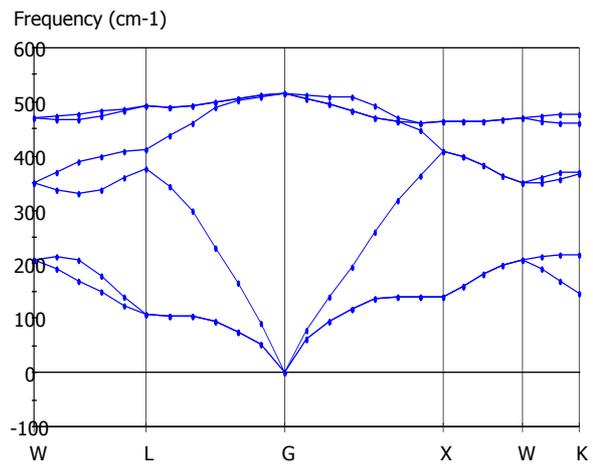
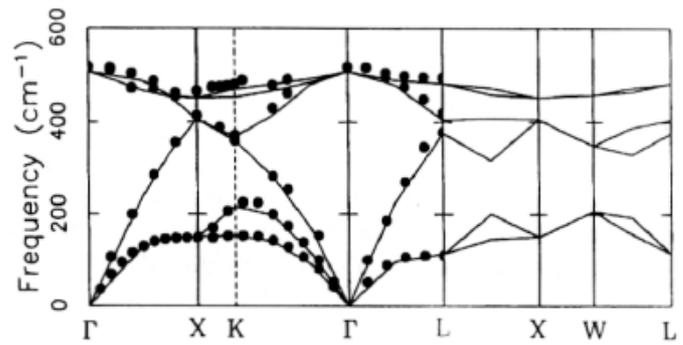
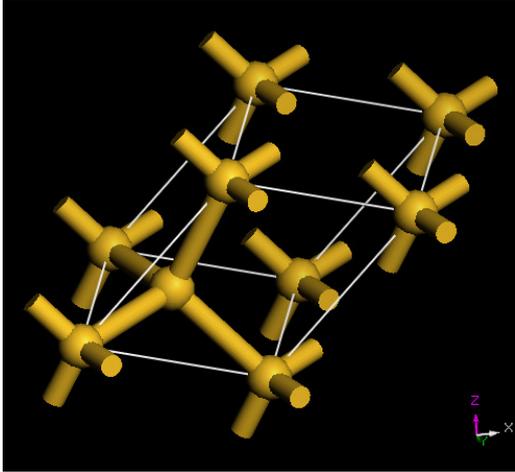
## From Phonons to Thermodynamic Properties

- Once phonon dispersion relations are known (supercell or interpolation methods), Free Energy can be calculated as an integral over  $k$

$$A(T) = E + k_B T \sum_k \log \left[ 2 \sinh \frac{\hbar \omega(k)}{2k_B T} \right]$$

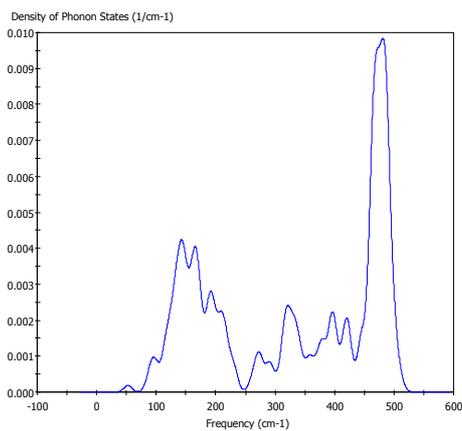
- *task: thermodynamics* computes Free Energy at a range of temperatures set by:
  - *thermo\_t\_start*
  - *thermo\_t\_stop*
  - *thermo\_t\_spacing*
- *Beware: electronic part is not calculated as function of T.*

# Periodic Solids and Phonon Dispersion: Silicon



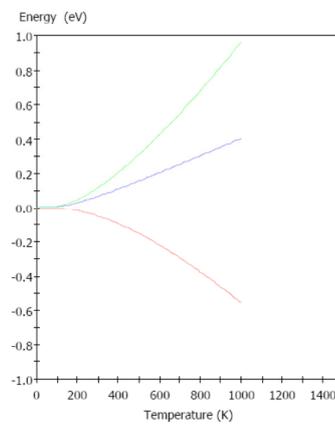
# Silicon: Phonon DOS and Thermodynamics

CASTEP Density of Phonon States



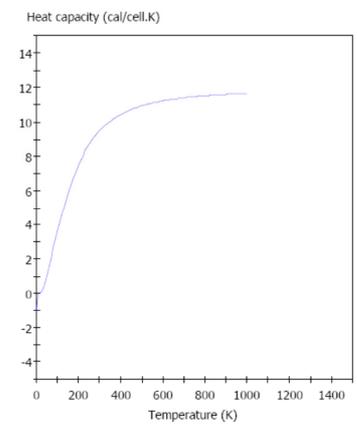
CASTEP Thermodynamic Properties

Zero point energy=0.1239576143 eV



— Enthalpy — T\*Entropy — Free Energy

CASTEP Thermodynamic Properties



# Phonons: What is Currently Missing in CASTEP

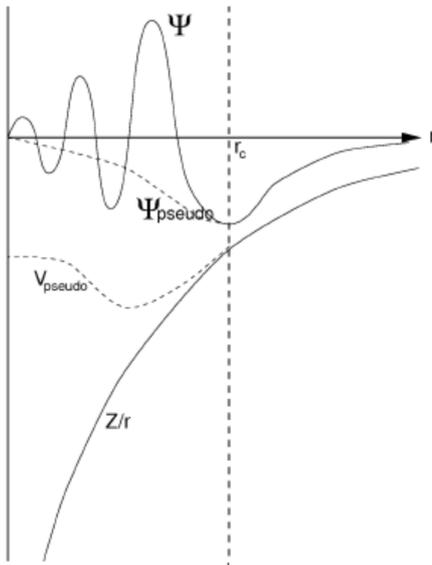
- Beyond the harmonic approximation: anharmonic effects and rotational motions.
- But the above could be (in principle) calculated via MD (even quantum MD); but these calculations are very costly.
- Magnetic phonons: magnons (as well as spin-orbit coupling).

## Other Properties (see MS and [www.castep.org](http://www.castep.org))

- Molecular Dynamics (*task: Molecular Dynamics*):
  - Same machinery as “classic” MD but without force fields.
  - Can also do path-integral MD (*md\_use\_pathint = true*)
- NMR (*task: magres*):
  - Calculates chemical shifts & electric field gradients.
  - Requires on-the-fly pseudopotentials & highly converged calculations.
- Transition-state Search: chemical reactions.
- EELS/ELNES:
  - Recent addition (v4.3).
  - Requires additional input file (for the time being).

# Pseudopotentials: Rationale

From Ref. [1] below



- Operational definition of core electrons: they are not modified by surrounding environment (e.g., presence of other atoms).
- Valence electrons: need to be orthogonal to core, thus strong oscillations of valence wavefunctions close to nucleus.
- These oscillations are too costly if plane waves are used as basis set, but they do not play a role in binding (thus an approximation may be in order)
- Pseudopotential approach:
  - Only valence electrons are considered: orthogonality conditions relaxed; valence wavefunctions can be smooth..
  - But need to construct a new ionic potential which accounts for presence of core states.
  - Huge computational savings follow.
- Historical note: this concept is not new; the definition of neutron scattering lengths is based on the same concept, but applied to nuclear scattering (Fermi 1930s).

[1] CJ Pickard, PhD Thesis (Univ. Cambridge, 1997), Ch. 2. See also: [www.tcm.phy.cam.ac.uk/~cjp20](http://www.tcm.phy.cam.ac.uk/~cjp20)

# Pseudopotentials: Construction

- An ALL-ELECTRON DFT calculation is performed on the ISOLATED ATOM.
- A core radius ( $r_c$ ) is chosen so that core regions of different atoms do not overlap significantly:  $r_c$  dictates how transferable (and expensive) the pseudopotential will be.
- All-electron valence wavefunctions are modified for  $r < r_c$  to remove the expensive bits (nodes): these new wavefunctions are the “pseudowavefunctions.”
- Schrodinger equation is then inverted to find potential that produces these pseudowavefunctions: this potential is the pseudopotential.
- Important technicalities:
  - Norm conservation: charge in the region  $r < r_c$  remains the same.
  - Pseudopotential depends on angular momentum of wavefunction (s,p,d partial waves).

# Pseudopotentials: Properties

- The pseudo wavefunctions should be identical to all-electron wavefunctions beyond cut-off radius.
- Energy eigenvalues should also be the same.
- Norm-conservation: physically, the total charge should also be the same
- Schrodinger equation is then inverted to find potential that produces these pseudowavefunctions: this potential is the pseudopotential.
- Scattering properties (logarithmic derivatives or “phase shifts”) should also be preserved after “pseudization.”

## Norm-conserving Pseudopotentials

### The Theory

Charge is strictly preserved

Pseudopotential split into local and non-local components.

$$\hat{V}_{pseudo} = \hat{V}_{local}(r) + \sum_l |\chi_l\rangle V_l \langle \chi_l|$$

Non-local components depend on angular momentum (l quantum number).

This non-local component represents deviation from all-electron potential inside core region.

### The practice:

- Larger basis-set & cutoff energies than necessary.
- Less flexible.
- Transferability can still be an issue.

# Ultrasoft Pseudopotentials

## The Theory

Normalization condition relaxed [1].

Pseudowavefunctions split into two parts.

- Ultrasoft wavefunction (not norm-conserving).
- A core augmentation charge (missing core charge).

“Beta projectors” define non-local part (inside cut-off region). The more you use per angular momentum channel, the better the answer.

Local potential: important to account for  $l$  values not included in Beta projectors.

$$\hat{V}_{ultrasoft} = \hat{V}_{local}(r) + \sum_{n,m} D_{nm}^0 |\beta_n\rangle\langle\beta_m|$$

$$|\beta_n\rangle = \sum_m \frac{|\chi_m\rangle}{\langle\chi_m|\phi_n\rangle}$$

$$D_{nm}^0 = \langle\phi_n|\chi_m\rangle + \epsilon_m q_{nm}$$

## The practice

- Less “hard” and more efficient: smaller PW basis set required.
- Practice shows that they can be highly transferable if properly constructed

[1] D. Vanderbilt, *Phys. Rev. B* 41, 7892 (1990); CY Lee et al., *Phys. Rev. B* 47, 4863 (1993).

## A Minimalist Example in CASTEP

Try CASTEP'ing the following cell file.

To note:

- Why don't we worry about the .param file?

- What have we told CASTEP to do?

- Which files are generated (remember Lecture 3)?

```
%BLOCK LATTICE_CART
0.00 1.77 1.77
1.77 0.00 1.77
1.77 1.77 0.0
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
C 0.00 0.00 0.00
C 0.25 0.25 0.25
%ENDBLOCK POSITIONS_FRAC
symmetry_generate
```

# CASTEP Output (v4.3)

PARAM defaults used  
(but cell file always needed)

A quick way to know defaults!

The all-electron  
calculation  
(six electrons in C)

The pseudopotential  
calculation

The pseudopotential  
(n=2 only)

Actual data in C\_OTF.usp

This complex-looking string  
defines what has been done.

Note: on-the-fly pseudopotential in file: C\_OTF.usp

## On-the-fly Pseudopotential File: C\_OTF.usp

Recommended  
plane-wave cutoff  
energies

Same as CASTEP file

The actual  
pseudopotential data  
note: default is *ultrasoft*

# Full Testing of Pseudopotential

## Cell Input

## Castep Output

```
%BLOCK LATTICE_CART
0.00 1.77 1.77
1.77 0.00 1.77
1.77 1.77 0.0
%ENDBLOCK LATTICE_CART

%BLOCK POSITIONS_FRAC
C 0.00 0.00 0.00
C 0.25 0.25 0.25
%ENDBLOCK POSITIONS_FRAC
symmetry_generate

%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)|
%ENDBLOCK SPECIES_POT
```

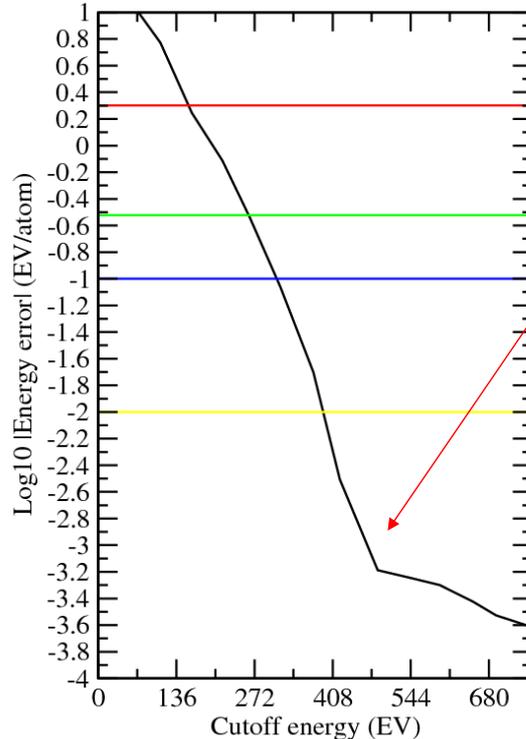
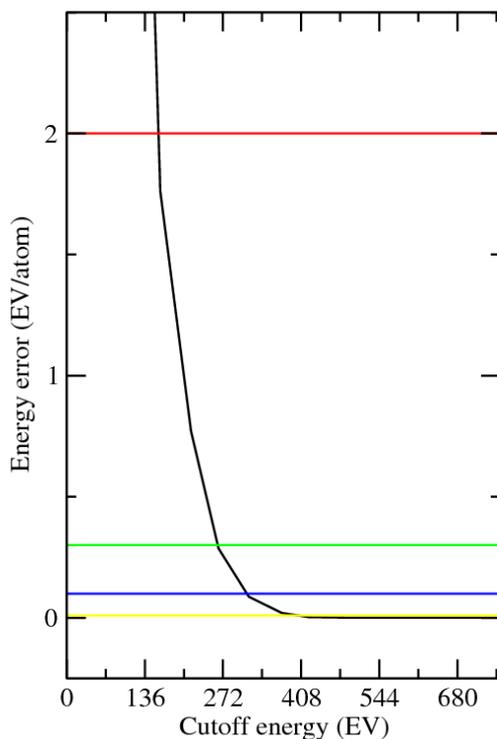
```
Programmer's File Editor - [diamond_fulltest.castep]
Pseudopotential Report - Date of generation 17-05-2008
Element: C Ionic charge: 4.00 Level of theory: LDA
Reference Electronic Structure
Orbital Occupation Energy
2s 2.000 -0.501
2p 2.000 -0.199
Pseudopotential Definition
Beta l e Rc scheme norm
1 0 -0.501 1.395 qc 0
2 0 0.250 1.395 qc 0
3 1 -0.199 1.395 qc 0
4 1 0.250 1.395 qc 0
loc 2 0.000 1.395 pn 0
Augmentation charge Rinner = 1.395
Partial-core correction Rc = 1.305
"2|1.4|1.4|1.3|6|10|12|20:21(qc=6)|"
Author: Chris J. Pickard, Cambridge University
Doing a self consistent calculation for the test configuration
Atomic calculation performed for C: 1s2 2s2 2p2
Converged in 56 iterations to an ae energy of -1018.807 eV
AE eigenvalue n1 10 = -9.95226116
AE eigenvalue n1 20 = -0.50140334
AE eigenvalue n1 21 = -0.19918477
PS eigenvalue n1 20 = -0.50139111
PS eigenvalue n1 21 = -0.19916613
Pseudo atomic calculation performed for C 2s2 2p2
Converged in 15 iterations to a total energy of -145.8653 eV
```

Note the extra '|'

All-electron  
"Pseudized"

# Full Testing of Pseudopotential: Other Data

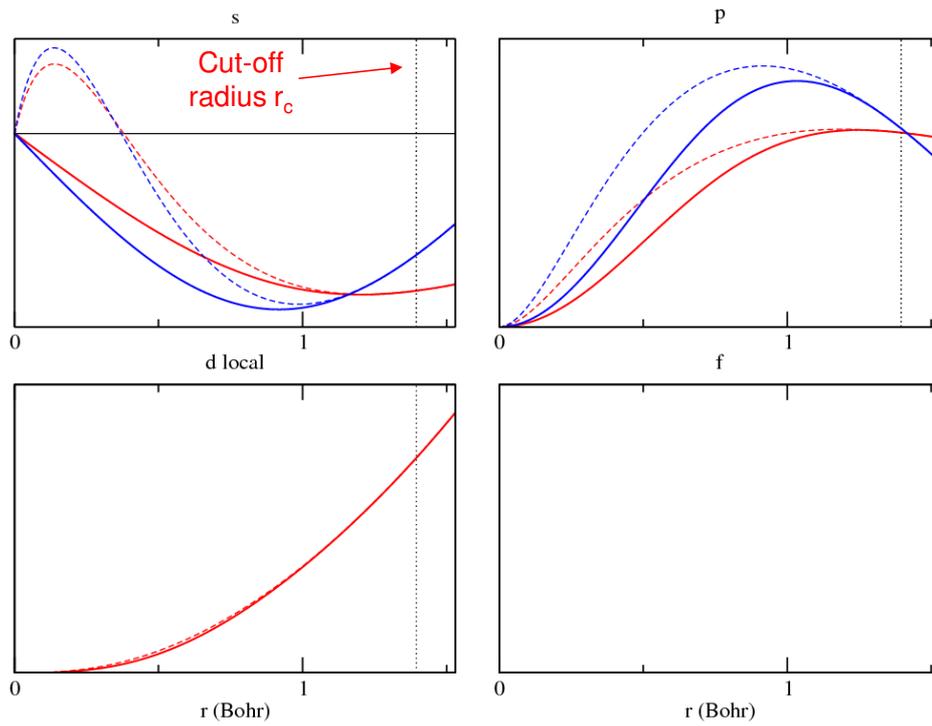
## Atomic Energy Convergence with Cut-off: C\_OTF.econv



Fast convergence to 500 eV (related to  $q_c$  parameter in PS string)

# Full Testing of Pseudopotential: Other Data

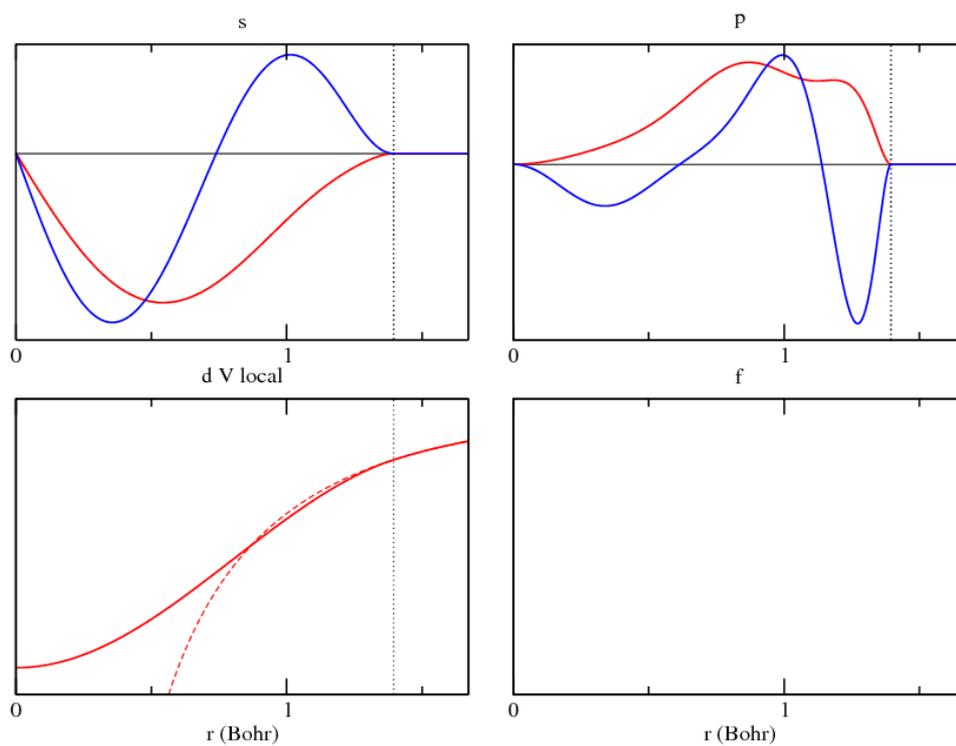
All-electron vs Pseudo PARTIAL WAVES: C\_OTF.pwave



Trivia question: which one is which?  
Hint: look at s partial waves ...

# Full Testing of Pseudopotential: Other Data

Non-local Projectors & Local Potential: C\_OTF.beta



# Testing Your Own Electronic Configuration

## Cell Input

```
%BLOCK SPECIES_POT  
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)|  
%ENDBLOCK SPECIES_POT
```

This defines Carbon as  $2s^2 2p^2$  (default).

Only outermost electron shell  $n=2$  will be considered for testing purposes.

That is, written in full:

```
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)[2s2,2p2]
```

# Testing Your Own Electronic Configuration

Promote a 2s electron to 2p as follows

```
%BLOCK SPECIES_POT  
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)[2s1,2p3]  
%ENDBLOCK SPECIES_POT
```

Pseudopotential calculation will be TESTED on the electronic configuration you have supplied.

BUT it still uses the default  $2s^2 2p^2$  to generate the pseudopotential.

Useful to test transferability.

```
Programmer's File Editor - [diamond_2s_2p3.castep]  
File Edit Options Template Execute Macro Window Help  
-----  
Atomic calculation performed for C: 1s2 2s2 2p2  
Converged in 56 iterations to an ae energy of -1018.807 eV  
Identity difference: 4.300931527184486E-004  
-----  
| Pseudopotential Report - Date of generation 17-05-2008 |  
-----  
Element: C Ionic charge: 4.00 Level of theory: LDA  
-----  
Reference Electronic Structure  
Orbital Occupation Energy  
2s 2.000 -0.501  
2p 2.000 -0.199  
-----  
Pseudopotential Definition  
Beta l e Rc scheme norm  
1 0 -0.501 1.395 qc 0  
2 0 0.250 1.395 qc 0  
3 1 -0.199 1.395 qc 0  
4 1 0.250 1.395 qc 0  
loc 2 0.000 1.395 pn 0  
-----  
Augmentation charge Rinner = 1.305  
Partial core correction Rc = 1.305  
-----  
| "2|1.4|1.4|1.3|6|10|12|20:21(qc=6)[2s1,2p3]" |  
-----  
Author: Chris J. Pickard, Cambridge University  
-----  
Doing a self consistent calculation for the test configuration  
Atomic calculation performed for C: 1s2 2s1 2p3  
Converged in 44 iterations to an ae energy of -1010.565 eV  
-----  
AE eigenvalue n1 10 = -9.98304759  
AE eigenvalue n1 20 = -0.51758214  
AE eigenvalue n1 21 = -0.21406938  
-----  
PS eigenvalue n1 20 = -0.51701246  
PS eigenvalue n1 21 = -0.21405887  
-----  
Pseudo atomic calculation performed for C 2s2 2p2  
Converged in 15 iterations to a total energy of -145.8653 eV  
-----  
Ln 1 Col 1 323 W/R Rec Off No Wrap DDS INS
```

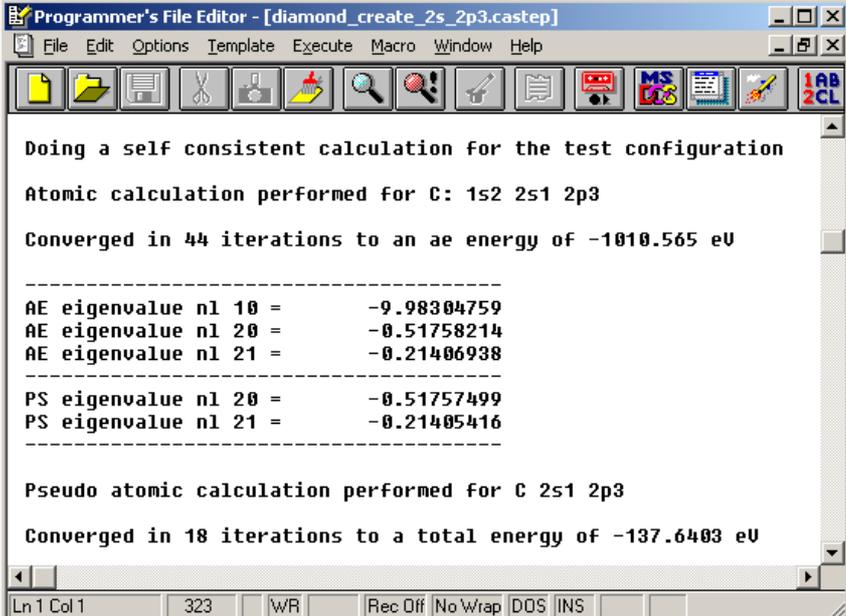
# Creating Your Own Electronic Configuration

Use of curly braces { }

```
%BLOCK SPECIES_POT  
C 2|1.4|1.4|1.3|6|10|12|20:21{2s1,2p3}(qc=6)[2s1,2p3]  
%ENDBLOCK SPECIES_POT
```

In this case, we have indeed changed the electronic configuration that generates the pseudopotential to  $1s^1 2p^3$

AND tested it on the same configuration.



```
Programmer's File Editor - [diamond_create_2s_2p3.castep]  
File Edit Options Template Execute Macro Window Help  
Doing a self consistent calculation for the test configuration  
Atomic calculation performed for C: 1s2 2s1 2p3  
Converged in 44 iterations to an ae energy of -1010.565 eV  
-----  
AE eigenvalue n1 10 = -9.98304759  
AE eigenvalue n1 20 = -0.51758214  
AE eigenvalue n1 21 = -0.21406938  
-----  
PS eigenvalue n1 20 = -0.51757499  
PS eigenvalue n1 21 = -0.21405416  
-----  
Pseudo atomic calculation performed for C 2s1 2p3  
Converged in 18 iterations to a total energy of -137.6403 eV  
Ln 1 Col 1 323 |WR |Rec Off No Wrap DOS INS
```

## Pseudopotential String

```
%BLOCK SPECIES_POT  
C 2|1.4|1.4|1.3|6|10|12|20:21{2s1,2p3}(qc=6)[2s1,2p3]  
%ENDBLOCK SPECIES_POT
```

List of *nl* channels to be used in pseudization (*2s* and *2p* in this case) ..

as well as number of *non-local projectors* to be used for each, e.g.,

20U:20U	will use one ultrasoft per channel.
20UU:20UU $\equiv$ 20:21	will use two ultrasoft projectors per channel (default).
20N:20N	will use norm-conserving projectors for both channels.

For example, if 20:21 (two ultrasoft projectors per channel) is replaced by 20U:20U one will get less accurate results, e.g., see what happens to the “identity difference” in .castep file.

Identity difference: a measure of pseudopotential transferability (the smaller, the better).

# Pseudopotential String: The Other Bits

local channel / (d state)  
Choice can be arbitrary but typically  
set to first / not present in core.

Recommended COARSE,  
MEDIUM & FINE energies.  
Not used in calculation but  
determined from .econv file  
(unit: Hartree)



Radii for local & non-local  
channels ( $r_c$ ) and for  
augmentation charge ( $r_{inner}$ ).  
units: Angstrom

Placeholder for other  
settings (qc is an  
optimization parameter  
controlling "hardness"  
of pseudopotential)

## Including Core Electrons

Quick exercise:

Write & CASTEP a cell file that will treat all electrons in Carbon.

Hint: core channel needs to be specified EXPLICITLY

# Including Core Electrons

A first try:

```
%BLOCK SPECIES_POT  
C 2|1.4|1.4|1.3|6|10|12|10:20:21(qc=6)|  
%ENDBLOCK SPECIES_POT
```

Check output, what happens?

Can you tell what is and what is NOT OK?

# Including Core Electrons

A second try:

```
%BLOCK SPECIES_POT  
C 2|1.4|1.4|1.3|6|10|12|10U:20:21(qc=6)|  
%ENDBLOCK SPECIES_POT
```

Judging from the “identity difference,”  
this one seems to be OK.

Next step would be to try it out to see  
how it performs

```
Programmer's File Editor - [C:\calculations\DFTcourse_UCL\pseudopot_v1 Files\...]  
File Edit Programmer's File Editor - [C:\calculations\DFTcourse_UCL\pseudopot_v1 Files\Documents\di  
Atomic calculation performed for C: 1s2 2s2 2p2  
Converged in 56 iterations to an ae energy of -1018.807 eV  
Identity difference: 1.814088881531733E-003  
-----  
| Pseudopotential Report Date of generation 19-05-2008 |  
-----  
| Element: C Ionic charge: 6.00 Level of theory: LDA |  
-----  
| Reference Electronic Structure |  
| Orbital Occupation Energy |  
| 1s 2.000 -9.952 |  
| 2s 2.000 -0.501 |  
| 2p 2.000 -0.199 |  
-----  
| Pseudopotential Definition |  
| Beta l e Rc scheme norm |  
| 1 0 -9.952 1.395 qc 0 |  
| 2 0 -0.501 1.395 qc 0 |  
| 3 0 0.250 1.395 qc 0 |  
| 4 1 -0.199 1.395 qc 0 |  
| 5 1 0.250 1.395 qc 0 |  
| loc 2 0.000 1.395 pn 0 |  
-----  
| Augmentation charge Rinner = 1.305 |  
| No partial core correction |  
-----  
| "[2|1.4|1.4|1.3|6|10|12|10U:20:21(qc=6)|]" |  
-----  
| Author: Chris J. Pickard, Cambridge University |  
-----  
Doing a self consistent calculation for the test configuration  
Atomic calculation performed for C: 1s2 2s2 2p2  
Converged in 56 iterations to an ae energy of -1018.807 eV  
-----  
AE eigenvalue n1 10 = -9.95226116  
AE eigenvalue n1 20 = -0.50140334  
AE eigenvalue n1 21 = -0.19918477  
-----  
PS eigenvalue n1 10 = -9.95168026  
PS eigenvalue n1 20 = -0.50140455  
PS eigenvalue n1 21 = -0.19915045  
-----  
Ln 76 Col 56 324 WR Rec Off No Wrap Unix INS
```

# Beyond "Valence" Electrons

Try now to generate on-the-fly pseudopotentials for Lithium or Beryllium.

What can you say something about what has been done by the Pseudopotential generator?

## Lithium

- OTF calculation treats all electrons as valence (e.g., to contemplate partial ionization in solid state, as it would happen in a salt).
- Thus, you will be performing an all-electron calculation with pseudized orbitals.

```
Programmer's File Editor - [D:\calculations\DFTcourse_UCL\pseudopot_v1 Files...
File Edit Options Template Execute Macro Window Help

Atomic calculation performed for Li: 1s2 2s1
Converged in 46 iterations to an ae energy of -199.592 eV
Identity difference: 1.303734231573781E-003

-----
| Pseudopotential Report - Date of generation 20-05-2008 |
-----
| Element: Li Ionic charge: 3.00 Level of theory: LDA |
-----
| Reference Electronic Structure |
| Orbital Occupation Energy |
| 1s 2.000 -1.878 |
| 2s 1.000 -0.106 |
-----
| Pseudopotential Definition |
| Beta l e Rc scheme norm |
| 1 0 -1.878 2.610 qc 0 |
| 2 0 -0.106 2.610 qc 0 |
| loc 1 0.000 1.901 pn 0 |
-----
| Augmentation charge Rinner = 1.296 |
| No partial core correction |
-----
| "1|1.9|2.6|1.3|5|7|8|100:200(qc=4.5)|" |
-----
| Author: Chris J. Pickard, Cambridge University |
-----
Doing a self consistent calculation for the test configuration
Atomic calculation performed for Li: 1s2 2s1
Converged in 46 iterations to an ae energy of -199.592 eV

-----
AE eigenvalue n1 10 = -1.87794290
AE eigenvalue n1 20 = -0.10572054
-----
PS eigenvalue n1 10 = -1.87742075
PS eigenvalue n1 20 = -0.10560206
-----

Pseudo atomic calculation performed for Li 1s2 2s1
Converged in 12 iterations to a total energy of -187.7837 eV

Ln 1 Col 1 328 |WR| Rec Off No Wrap Unix INS
```

# Beryllium

- Again, OTF calculation treats all electrons as valence (e.g., to contemplate ionization in solid state).
- Plus the addition of extra charge on unfilled p shell (to accommodate for polarization) [1].

```
Programmer's File Editor - [D:\calculations\DFTcourse_UCL\pseudopot_v1 Files\Documents...
File Edit Options Template Execute Macro Window Help

Atomic calculation performed for Be: 1s2 2s2 2p0.05
Converged in 45 iterations to an ae energy of -393.275 eU
Identity difference: 4.922327335497677E-004

-----
| Pseudopotential Report - Date of generation 17-05-2008 |
-----
| Element: Be Ionic charge: 4.00 Level of theory: LDA |
-----
| Reference Electronic Structure |
| Orbital Occupation Energy |
| 1s 2.000 -3.841 |
| 2s 2.000 -0.194 |
| 2p 0.050 -0.066 |
-----
| Pseudopotential Definition |
| Beta l e Rc scheme norm |
| 1 0 -3.841 1.403 qc 0 |
| 2 0 -0.194 1.403 qc 0 |
| 3 0 0.250 1.403 qc 0 |
| 4 1 -0.066 1.403 qc 0 |
| 5 1 0.250 1.403 qc 0 |
| loc 2 0.000 1.403 pn 0 |
-----
| Augmentation charge Rinner = 1.197 |
| No partial core correction |
-----
| "2]1.4]1.4]1.2]7]8]10]100:20:21(2p.05)[]" |
-----
| Author: Chris J. Pickard, Cambridge University |
-----

Doing a self consistent calculation for the test configuration
Atomic calculation performed for Be: 1s2 2s2 2p0.05
Converged in 45 iterations to an ae energy of -393.275 eU

-----
| AE eigenvalue n1 10 = -3.8415885 |
| AE eigenvalue n1 20 = -0.19388412 |
| AE eigenvalue n1 21 = -0.06629060 |
-----
| PS eigenvalue n1 10 = -3.84051985 |
| PS eigenvalue n1 20 = -0.19386225 |
| PS eigenvalue n1 21 = -0.06624966 |
-----

Ln1 Col1 97 |wR| Rec Diff No Wrap Unix INS|
```

[1] See GB Bachelet et al, *Phys. Rev. B* 26, 4199 (1982); WE Pickett, *Comp. Phys. Rep.* 9, 115 (1989).

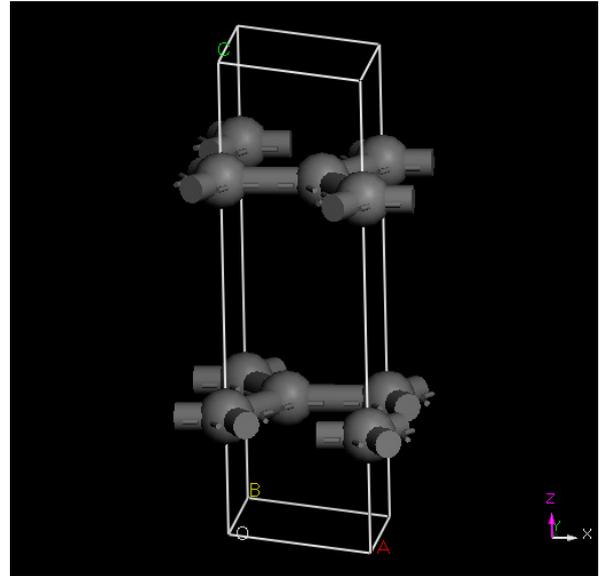
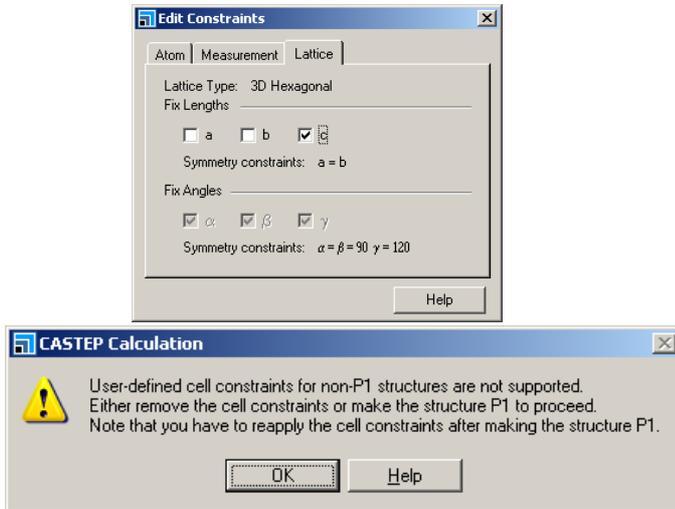
## Putting All This to Work: Diamond

- Take diamond and explore:
  - How changes in the pseudopotential core radius changes convergence as a function of plane-wave cutoff
  - Also check material properties such as lattice / cell spacings.
- We have just scratched the surface of an extensive subject; for more information on pseudopotentials see
  - Kohanoff or Martin (see References in 1<sup>st</sup> Lecture notes).
  - CASTEP Workshop lectures to be found in [www.castep.org](http://www.castep.org)

# “Cell” Constraints

Relatively easy to do on MS. For a given cell:

*Modify* → *Constraints*



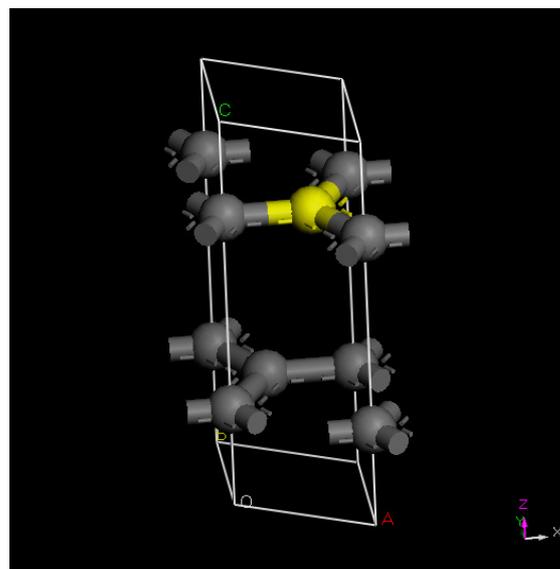
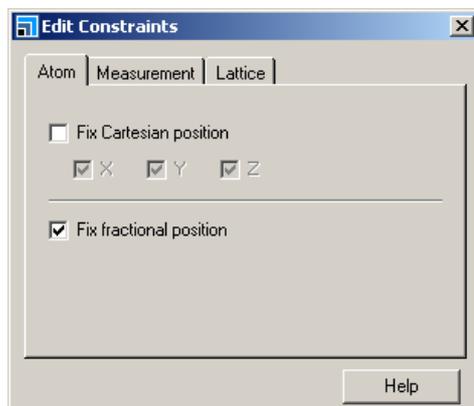
Note: cell constraints on non-P1 structures not supported.

Use *Build* → *Symmetry* → *Make P1*, then impose the cell constraint

# “Ionic” Constraints

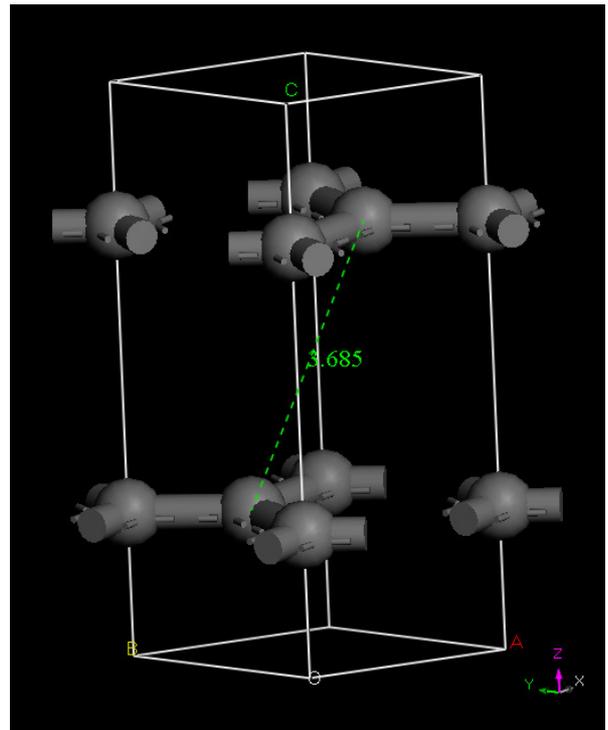
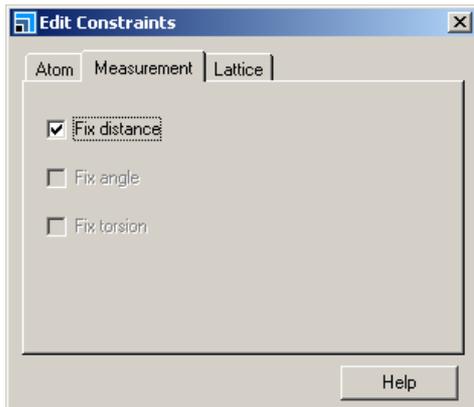
Relatively easy to do on MS. For a given atom:

*Modify* → *Constraints*



- Check .cell file generated by MS.
- By looking at cell file, can you make sense of how this is done for the cell and for the atom?

# Non-linear “Ionic” Constraints



Types of constraints: distance, bend, torsion.

## “Cell” Constraints In More Detail

Extra block specifying ABC lengths and angles.

```
%BLOCK CELL_CONSTRAINTS  
A      B      C  
alpha beta gamma  
%ENDBLOCK CELL_CONSTRAINTS
```

Example

```
%BLOCK CELL_CONSTRAINTS  
1      1      2  
0      0      0  
%ENDBLOCK CELL_CONSTRAINTS
```

- Lengths & angles:
  - Constant: set to ZERO.
  - Tied: SAME number.
- Can also fix:
  - Whole cell *fix\_all\_cell: true*
  - Cell volume *fix\_vol: true*

# Linear “Ionic” Constraints In More Detail

Linear constraints specified as a list

```
%BLOCK IONIC_CONSTRAINTS
const1 species1      atom1 Cx      Cy      Cz
const2 ....
%ENDBLOCK IONIC_CONSTRAINTS
```

- const: number of the constraint (1,2,...)
- species: atomic species (H, C, O, ...)
- C's and constraint coefficients.
- Also *fix\_all\_ions* & *fix\_com* to fix all positions or centre-of-mass.

Example:

```
%BLOCK IONIC_CONSTRAINTS
1      C      1      1      0      0
1      C      4     -1      0      0
%ENDBLOCK IONIC_CONSTRAINTS
```

# Non-linear “Ionic” Constraints In More Detail

Non-linear constraints for internal coordinates:

```
%BLOCK NONLINEAR_CONSTRAINTS
const_type      [species1, atom1, image1]      ... [species2, atom2, image2]
%ENDBLOCK NONLINEAR_CONSTRAINTS
```

- const\_type: type of constraint (fix, distance, bend, angle)
- species: C, H, O, ...
- atom: number in POSITIONS\_ cell block ( 0 0 0  $\equiv$  primary unit cell )
- image: periodic image
- Number of [species, atom, image]: fix (1), distance (2), bend (3), torsion (4).

Example:

```
%BLOCK NONLINEAR_CONSTRAINTS
fix      C 1 0 0 0
distance C 1 0 0 0  F 3 0 0 1
bend     C 1 0 0 0  C 2 0 0 0  C 3 0 0 0
%ENDBLOCK NONLINEAR_CONSTRAINTS
```

# Brief Notes on Scripting

- Very much platform-dependent.
- On Unix:
  - Bash (typical) or Perl scripts. The latter can be more sophisticated (can use real numbers).
  - Either of these two will be necessary to script your jobs on a computer cluster.
  - For those not familiar with these, see:
    - » Bash: <http://www.panix.com/~elflord/unix/bash-tute.html>  
[http://www.delorie.com/gnu/docs/bash/bashref\\_toc.html](http://www.delorie.com/gnu/docs/bash/bashref_toc.html)
    - » Perl: <http://www.perl.com/pub/a/2000/10/begperl1.html>  
<http://www.perl.com/pub/q/documentation>
- On Windows OS:
  - Command (BAT) files can be implemented.
  - MS has also introduced PERL scripting capabilities for Materials Studio. See Materials Studio documentation as well as Forum & Script Library at [www.accelrys.org](http://www.accelrys.org)
  - You can also emulate UNIX on Windows to save some work (cygwin: <http://www.cygwin.com/> )

## Where to Go From Here

- What this course was all about:
  - Introduce you to electronic-structure theory and DFT, necessary tools to engage with theorists / computational scientists (e.g., ask questions).
  - Walk you thru the use of
    - » CASTEP, a widely used DFT package.
    - » And a user-friendly graphical interface (MS).
  - Examine in some detail what goes under the hood (convergence issues, input parameters, pseudopotentials, etc).
  - Calculation of observables for comparison with experiment (e.g., lattice parameters, band structure, phonons).
  - QUITE A BIT OF GROUND, BUT THERE IS SO MUCH MORE.
- What next?
  - Do your best to apply what you've learnt !
  - Choose a problem you think might be amenable to first-principles computation:
    - » Talk to a theorist about it as well.
    - » Benchmark it as much as possible (other calculations or experiment).
    - » Use it as both descriptive & predictive tool (e.g., suggest new experiments).
    - » For computationally intensive work, parallelism is likely to be required (phonon dispersion with large cells, potential-energy maps).
  - Along the way, keep on learning more about the "art of ab initio computation." Hopefully, the references & pointers provided are a good starting point.

# Comments & Suggestions

**Always Welcome!**

Please let me know how it could be improved

*e-mail: [felix.fernandez-alonso@stfc.ac.uk](mailto:felix.fernandez-alonso@stfc.ac.uk)*