Further Applications

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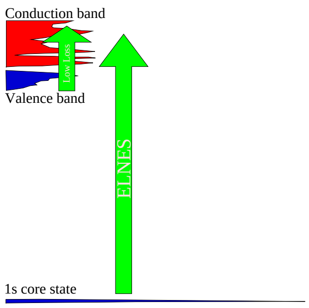
Overview

- Lecture IV: Further Applications
  - Core level and optical spectroscopies
  - Systematic prediction of new materials

Spectral Properties

- Many techniques for extracting information about occupied and unoccupied electronic states
- Can be classified by:
  - between which states the transitions take place
  - how the transitions are induced
  - how the effect is measured
- For example, an Electron Energy Loss experiment

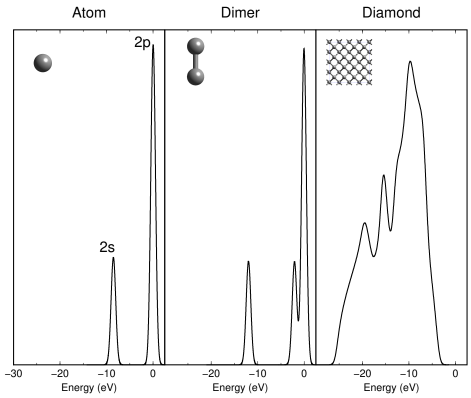


Pictorial representation of possible spectral processes for diamond.

A simple example

- In an isolated atom (e.g. C), the potential is spherically symmetric
- The energy levels are those of 1s, 2s, 2p ...
- As another atom approaches, the potential is disturbed and the levels split
- As more and more atoms arrive, the potential becomes further complicated, the levels become multiply split, and a better description is that of a continuum

A SIMPLE EXAMPLE *cont.*



Total densities of states for a carbon atom, dimer and diamond. These are the results of actual DFT pseudopotential calculations.

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THE TRANSITION PICTURE

- Transitions caused by disturbances of the system
- A restriction to "perturbations" allows an interpretation through Fermi's Golden Rule

$$R_{i\to f} \propto |\langle\phi_i|\Delta\hat{V}|\phi_f\rangle|^2\rho(E_f)$$

- Matrix element term $|\langle\phi_i|\Delta\hat{V}|\phi_f\rangle|^2$, probability that any transition will take place
- DOS term indicates how many such transitions are possible to a given energy
- $\Delta\hat{V}$ describes the perturbation

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THEORY

What is the rôle of theory?

- To enable interpretation of highly nonintuitive experimental results
- In the building of a specialist intuition
- Use the theoretical understanding to suggests new routes to more information

How is this done?

- Model experimental results at increasing levels of sophistication

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BAND-STRUCTURE CALCULATIONS

- Kohn-Sham eigenstates do not formally correspond to single particle state required in spectral calculations
- However, it is nearly universal to interpret them in this way
- Very good agreement between theory and experiment has been found
- More accurate calculation of "quasiparticle" energies show a relation to Kohn-Sham energies

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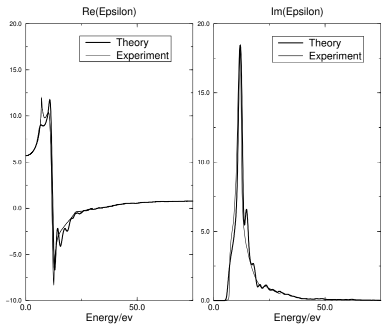
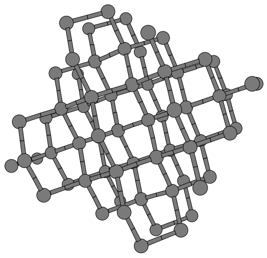
Optical Properties of Insulators

$$\varepsilon_2(\mathbf{q}\to \mathbf{0}_{\hat{\mathbf{u}}}, \hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{\mathbf{k},v,c} |\langle\psi_{\mathbf{k}}^c|\hat{\mathbf{u}}.\mathbf{r}|\psi_{\mathbf{k}}^v\rangle|^2\delta(E_{\mathbf{k}}^c - E_{\mathbf{k}}^v - E),$$

- Similar to Fermi's Golden rule — ε_2 is related to real transitions
- ε_1 is obtained through a Kramers-Kronig transform — the response is causal
- There are many complications
  - Local field effects — the local electric field at any given site is not the external electric field
  - Excitonic effects are ignored
  - Kohn-Sham eigenvalues are used for quasiparticle energies
- Despite this — the dielectric properties of diamond are well reproduced

Dielectric Properties of Diamond





The complex dielectric function for diamond was calculated with a 0.5ev Gaussian smearing and a 0.7ev Scissor operator applied to the conduction bands.

Prediction of new materials

- Prediction of new materials a central area of condensed matter science
- Aim to predict all possible crystal structures of a given composition
- Then screen for interesting/useful properties
- Synthesis may then be directed towards most promising candidates (properties and likely success)

Possible Strategies

- "Brute force" methods, e.g. simulated annealing
  - either too time consuming for moderately complex structures if reliable models for the total energy are used
  - or, the models are not reliable (e.g. difficulties handling variety of bonding)
- Random approaches cannot prove all structures have been found
- A more elegant approach is presented ...

Systematic prediction of new materials

1. Graph theory used to enumerate all possible, topologically distinct trial structures
2. First principles quantum mechanics used to establish ...
   - stability
   - structural parameters
   - properties
     - density
     - bulk moduli
     - electronic structure

An illustration — sp^2 carbon framework structures

- sp^2-bonding $\rightarrow$ each carbon atom bonded to 3 neighbours
- Framework $\rightarrow$ the structure is 3-dimensionally connected
- Graphite, fullerenes will not emerge
- Framework structures may be expected to have unusual properties — short strong bonds
- Considerable experimental effort in the synthesis of carbon based structures
- Maybe the predicted materials have been synthesised, but not recognised
- Or will inspire further work ...

Step One - Graph Theory

- Can be proved, Graph Theoretically, there are no sp^2 framework structures with 1,2,3, or 5 atoms per primitive cell
- Here, all with 4 and 6 are investigated
- A set of topologically distinct "trial structures" are passed on to the next stage – fourteen in this case

Step Two - First Principles QM

- Full geometry optimisation performed, with and without symmetry imposed
- Density Functional based total energy code, CASTEP
- Planewaves, Vanderbilt Ultrasoft pseudopotentials
- Generalised Gradient Approximation for exchange-correlation

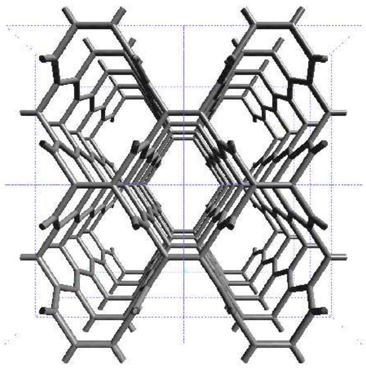
Results of Relaxation

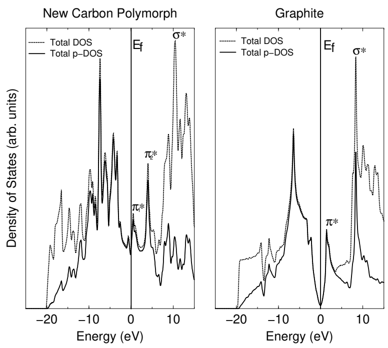
- All 14 structures could be relaxed
- Bond lengths between 1.34 and 1.48Å in all but one case — 1.55Å in a structure 4-fold co-ordinated
- Four membered rings — 6(3)3-26 — *not* unfavourable
- All structures less dense than diamond
- Around 0.4eV/atom less stable than diamond
- 6(3)1-10 the most stable, 6(3)4-25 and 6(3)2-22 close (within 0.03eV/atom)
- Bulk moduli — close to that of diamond, but 6(3)6-09 does not exceed it

Electronic Structure

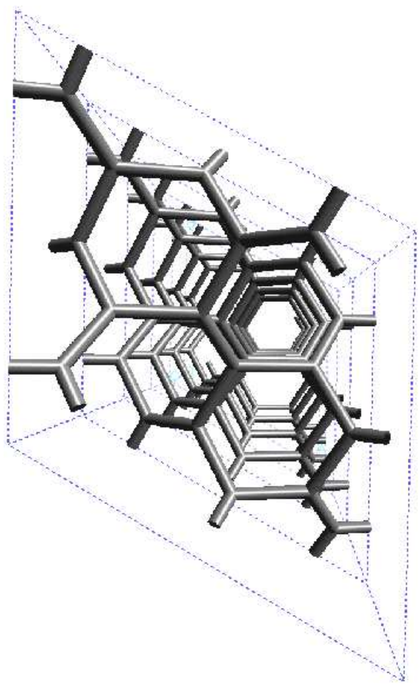
- Electronically, the proposed polymorphs are found to have a wide variety of electronic properties
  - 6(3)2-22 is a 1.9eV semiconductor (GGA)
  - 6(3)1-10 is a semimetal, like graphite
  - 6(3)4-25 is metallic
- Further analysis of the DOS can lead to possible spectral signatures for these structures
- p-projected DOS are related to ELNES as could be measured in a transmission electron microscope — only small samples needed

Polymorph 6(3)4-25

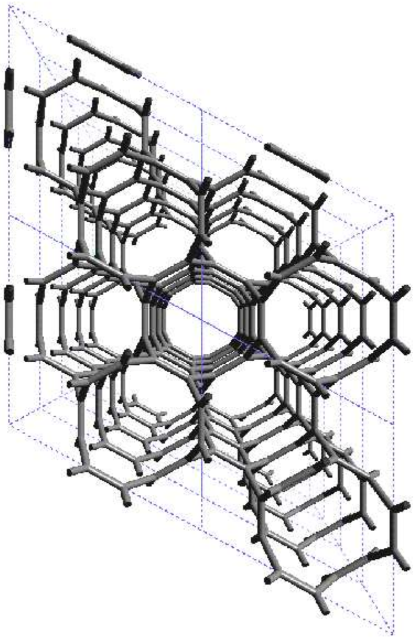




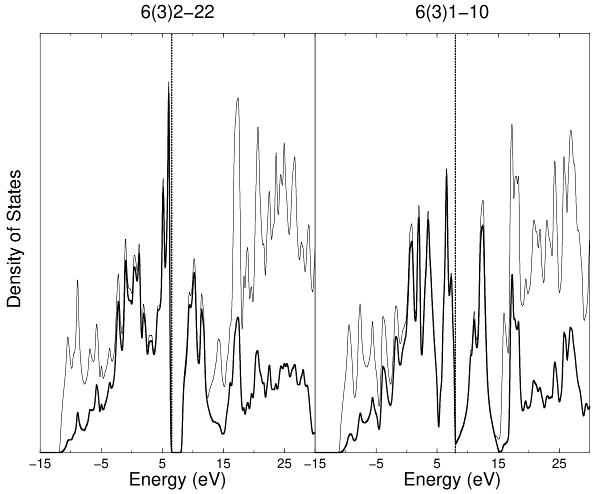
Polymorph 6(3)1-10



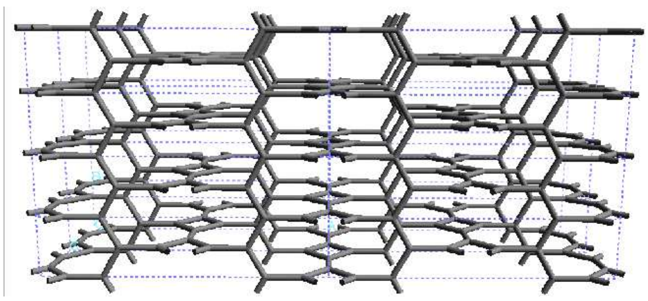
Polymorph 6(3)2-22



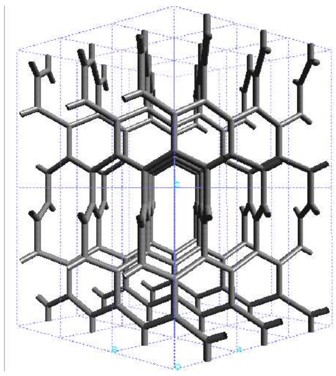
6(3)2-22 vs. 6(3)1-10

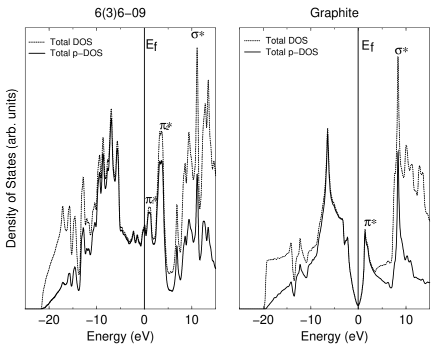


Polymorph 6(3)3-26



Polymorph 6(3)6-09





Summary

- The fertility of combining graph theory and quantum mechanics is demonstrated

- While some of the 14 structures have been previously known, the whole set was generated without prior knowledge, and leaves no gaps

- The method is open to extension — mixed co-ordination, species etc.

- New developments in QM total energy techniques can readily be applied

- We hope the structures themselves will be of interest — mechanical and electronic properties

B. Winkler, C.J. Pickard, V. Milman, W.E. Klee, and G.Thimm.
Prediction of a nanoporous sp2-carbon framework structure by combining graph theory with quantum mechanics.
Chemical Physics Letters, 312:536-541, 1999.