Tricks of the Trade

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OVERVIEW

- Lecture II: Tricks of the trade
  - Finding the groundstate
  - Forces and stresses
  - Geometry optimisation
  - Molecular dynamics
  - Application: Structural properties of lanthanides and actinides
  - The CASTEP code

WE MADE LOTS OF PROGRESS BUT ...

... these approximations are not enough to allow calculations for large systems.

- Conventional matrix diagonalisation
  - too slow for large basis set
  - calculates too many (unoccupied) states

CALCULATING THE TOTAL ENERGY

- Eigenvalue term
- Potential term
- Ion-ion term

To get eigenvalues we use:

$$H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$$
$$H = -\frac{1}{2}\nabla^2 + V(\mathbf{r})$$

- Most stable computational approach is to directly minimise E
- Do not solve $H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$ directly
- Use iterative diagonalisation for just the states that we need

- We still need to operate on $|\psi_i\rangle$ with H

OPERATING WITH H ON $|\psi_i\rangle$

- H divides into two parts
  - The potential — diagonal in real space
  - The kinetic energy — diagonal in reciprocal space
- Use FFTs — $N \ln N$ — and evaluate each term in appropriate space
- $V(\mathbf{r})$ in real space
- Kinetic energy in reciprocal space — $\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2$

EVALUATING THE ENERGY

- The eigenvalue sum — $\epsilon_i = \langle\psi_i|H|\psi_i\rangle$
- Potential energy — product of potential with density
- $E_{ion-ion}$ — slow convergence in real and reciprocal space so use Ewald identity (splits sum between two spaces)

ITERATIVE DIAGONALISATION

- Need energy gradient for each band i and iteration m

$$\begin{aligned} |\eta_i^m\rangle &= -(H - \epsilon_i^m)|\psi_i^m\rangle \\ \epsilon_i^m &= \langle\psi_i^m|H|\psi_i^m\rangle \end{aligned}$$

- Antisymmetry of wavefunctions → orthogonality of bands at each k-point
- Enforce orthogonality via the gradient …

$$|\eta'^m_i\rangle = |\eta_i^m\rangle - \sum_j \langle\psi_j|\eta_i^m\rangle|\psi_j\rangle$$

- Orthogonalisation is costly — dominates in the limit of a very large system

MINIMISATION

- Conjugate gradients — use history to ensure independence (exact for quadratic functions)
- Preconditioning — to encourage all components of the wavefunction to converge at comparable rates

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IONIC DEGREES OF FREEDOM

- Often want the gradient of the total energy wrt some parameter
  — e.g. $\mathbf{F}_i = -\frac{\partial E}{\partial \mathbf{R}_i}$

The Hellmann-Feynman theorem

The total energy is:

$$E = \langle \Psi | H | \Psi \rangle$$

Differentiate wrt α

$$\frac{\partial E}{\partial \alpha} = \langle \frac{\partial \Psi}{\partial \alpha} | H | \Psi \rangle + \langle \Psi | \frac{\partial H}{\partial \alpha} | \Psi \rangle + \langle \Psi | H | \frac{\partial \Psi}{\partial \alpha} \rangle$$

While, $H|\Psi\rangle = E|\Psi\rangle$ so

$$\frac{\partial E}{\partial \alpha} = \langle \Psi | \frac{\partial H}{\partial \alpha} | \Psi \rangle + E \frac{\partial}{\partial \alpha} \langle \Psi | \Psi \rangle = \langle \Psi | \frac{\partial H}{\partial \alpha} | \Psi \rangle$$

EXPLORING THE BORN-OPPENHIEMER SURFACE

- Born-Oppenheimer approx. → ionic positions are parameters
- Generally want to explore $3M$ parameter space
- Molecular dynamics
  - integrate Newtonian equations of motion
- Geometry optimisation
  - Local or global energy minima
  - Parameter space too big (can't use e.g. simulated annealing)
  - Place in basin of attraction and use steepest descents, conjugate gradients or BFGS

EXAMPLE: STRUCTURAL PROPERTIES OF LANTHANIDE AND ACTINIDE COMPOUNDS

ALL-ELECTRON APPROACHES TO f-ELECTRONS

- Numerous all-electron, first principles studies
  - (FP)-LMTO
  - (F)(L)APW
- many accurate and relevant results
  - e.g low pressure phases of elemental lanthanides
- in general — restricted to small size and high symmetry
- calculations of stresses not routine
- claim: electronic/magnetic properties require more than LDA/GGA
  - SIC etc.

RESULTS

- To build confidence, we have performed calculations on a spectrum of compounds
  - UO, UO_2, UO_3, U_3O_8, UC_2, α-CeC_2, CeB_6, CeO_2, NdB_6, TmOI, LaBi, $LaTiO_3$, YbO, and elemental Lu.
- Example: Uranium oxides
  - UO_2: $a_{\mathrm{exp}} \approx 5.458$ Å (depends on degree of reduction of U^{4+} to U^{6+}), $a_{\mathrm{theo}} = 5.474$ Å
  - UO: $a_{\mathrm{exp}} = 4.92(2)$ Å, $a_{\mathrm{theo}} = 4.961$ Å
  - Three polymorphs of UO_3: agreement, apart from O(z) internal co-ordinate in one of them. We suggest theory is more reliable.
  - Mixed valence U_3O_8 $P\bar{6}m2$: good agreement (within 0.01 Å) for lattice parameters, and fractional co-ordinates within 0.002)
- LDA vs. GGA : Lu metal $V_0 = 59.80$ Å^3 (exp.), 59.014 Å^3(GGA), and 53.373 Å^3(LDA)

ELASTIC PROPERTIES

- Not just equilibrium constants are reproduced
- Elastic constants are calculated using the method of imposed strains
- Results consistent with accuracy expected from DFT — and specifically previous all-electron studies (Trygg *et al* (1995) and Dudarev *et al*(1998))

Table 1: The elastic constants (in GPa) of UO_2 where $C' = \frac{1}{2}(C_{11} - C_{12})$, $B = \frac{2}{3}(C_{11} + 2C_{12})$.

	C_{11}	C_{12}	C_{44}	C'	B
exp	389.3	118.7	59.7	135.3	208.9
calc	318.2	96.0	43.1	111.1	170.1

THE CASTEP CODE

The CASTEP planewave pseudopotential code allows the calculation of the total energy of a system (and various derivatives) using:

- Periodic BCs
- Supercells
- Planewaves
- Pseudopotentials (NC and USPs)
- Parallel code
- User interface (CERIUS^2 by MSI)