DENSITY FUNCTIONAL THEORY AND THE TOTAL ENERGY METHOD

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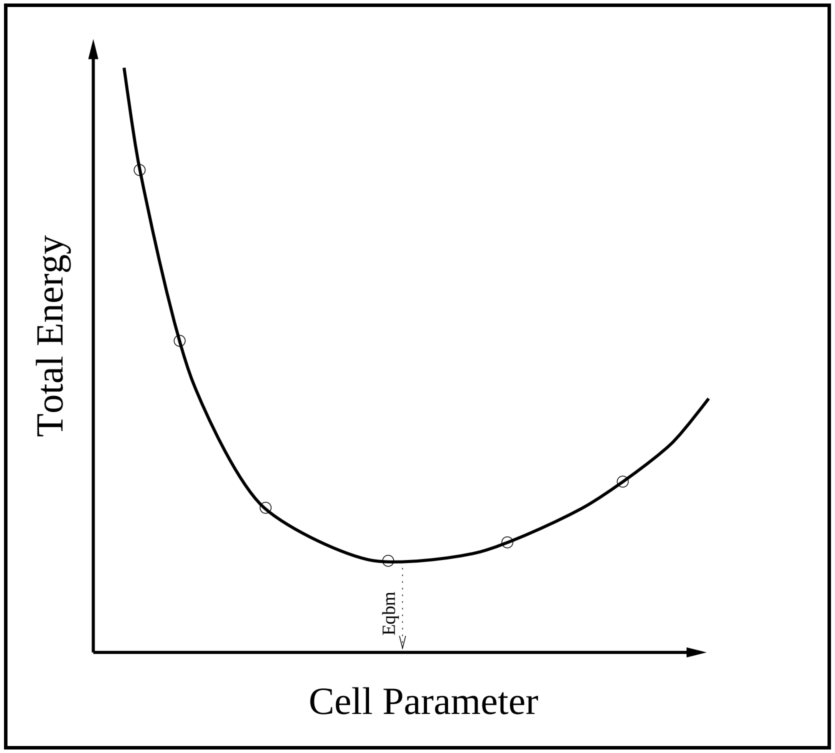
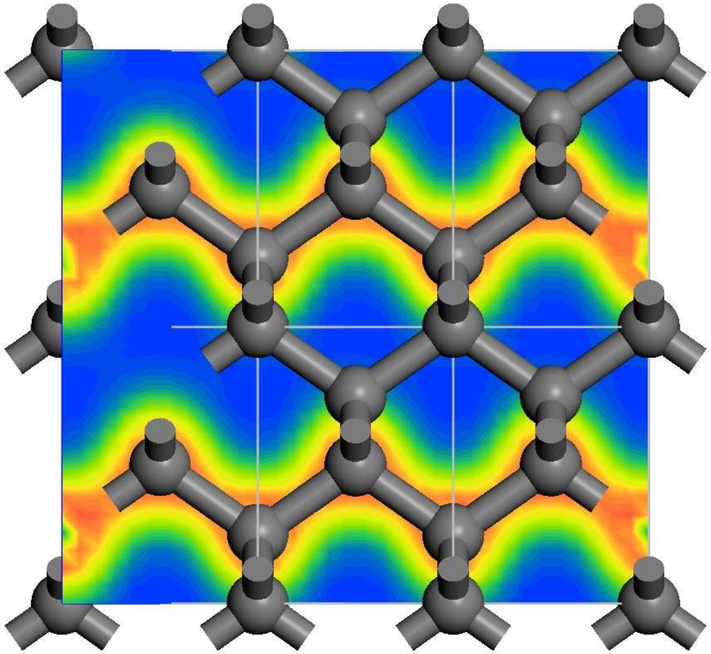
Lecture One

TOTAL ENERGY CALCULATIONS



- Many properties depend on the total energy of a system
  - equilibrium lattice constants (density)
  - bulk moduli
  - phonons
  - elastic constants
  - phase transitions
  - chemistry, bonding etc.

THE QUANTUM WORLD



Diamond

- Most low energy physics, chemistry and biology can be explained by the Quantum Mechanics of electrons and ions.

- In nearly all cases, treating the electrons as quantum mechanical alone is enough.

THE QUANTUM NIGHTMARE

$$\boxed{\begin{aligned} H\Psi &= E\Psi = \sum_{i=1}^{N}\Big(\frac{-\hbar^2}{2m}\nabla_i^2\Psi \\ &- Ze^2\sum_{\mathbf{R}}\frac{1}{|\mathbf{r_i}-\mathbf{R}|}\Psi\Big) \\ &+ \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r_i}-\mathbf{r_j}|}\Psi \end{aligned}}$$

- The red term describes correlation and is very difficult to account for
- The Hamiltonian can be generalised:

$$\boxed{H = T + V + U}$$

where U is the mutual interaction energy of the electrons and $V = \sum_{i=1}^{N} v(\mathbf{r}_i)$, the interaction with an arbitary external field.

TOTAL ENERGY AS A FUNCTIONAL OF THE DENSITY

A **Functional** is a function of a function, e.g.:

$A[f(\mathbf{r})] = \int f(\mathbf{r})^2 d\mathbf{r}$

- For a given external potential $v(\mathbf{r})$ the many-body wavefunction is Ψ, the ground-state energy is:

  $E_g = \langle \Psi | H_0 + V | \Psi \rangle$

- The electron density is:

  $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$

  with the *density operator* defined as:

  $\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$

DENSITY FUNCTIONAL THEORY: THE TWO THEOREMS

Theorem 1: Two different potentials cannot give rise to the same ground-state density $n(\mathbf{r})$.

Corollary: $n(\mathbf{r})$ uniquely determines the external potential $v(\mathbf{r})$ and therefore the many-body wavefunction Ψ.

Theorem 2: The ground-state energy for a fixed $v(\mathbf{r})$ is given by minimising $E_g[n(\mathbf{r})]$ with respect to $n(\mathbf{r})$. The $n(\mathbf{r})$ that gives the minimum energy is the ground-state density.

PERTURBATION THEORY

- If we know the wavefunctions and energies for a given Hamiltonian $H_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$ we can say something about similar Hamiltonians $H = H_0 + \alpha H_1$

- The wavefunctions of this new Hamiltonian H can be expanded:

$$|\psi_n\rangle = |\psi_n^0\rangle + \sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \sum_{k\neq n} \alpha^2 C_{nk}^2 |\psi_k^0\rangle + \ldots$$

- Also expanding the energy E_n in powers of α we obtain:

$$\begin{aligned}(H_0 + \alpha H_1)[|\psi_n^0\rangle + \textstyle\sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \ldots] \\ = (E_n^0 + \alpha E_n^1 + \ldots)[|\psi_n^0\rangle + \textstyle\sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \ldots]\end{aligned}$$

THE FIRST ORDER ENERGY SHIFT

$$\begin{aligned}(H_0 + \alpha H_1)[|\psi_n^0\rangle + \textstyle\sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \ldots] \\ = (E_n^0 + \alpha E_n^1 + \ldots)[|\psi_n^0\rangle + \textstyle\sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \ldots]\end{aligned}$$

- Comparing terms in α we arrive at the expression:

$$H_1|\psi_n^0\rangle + \textstyle\sum_{k\neq n} E_k^0 C_{nk}^1 |\psi_k^0\rangle = \textstyle\sum_{k\neq n} E_n^0 C_{nk}^1 |\psi_k^0\rangle + E_n^1 |\psi_n^0\rangle$$

- If we take the scalar product with $\langle\psi_n^0|$, and use the orthonormality relation $\langle\psi_n^0|\psi_k^0\rangle = \delta_{nk}$ we get an expression for the first order shift in the energy:

$$\boxed{\alpha E_n^1 = \langle\psi_n^0|\alpha H_1|\psi_n^0\rangle}$$

THE SECOND ORDER ENERGY SHIFT

$$
\begin{aligned}
&(H_0 + \alpha H_1)[|\psi_n^0\rangle + \textstyle\sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \ldots] \\
&\qquad = (E_n^0 + \alpha E_n^1 + \ldots)[|\psi_n^0\rangle + \textstyle\sum_{k\neq n} \alpha C_{nk}^1 |\psi_k^0\rangle + \ldots]
\end{aligned}
$$

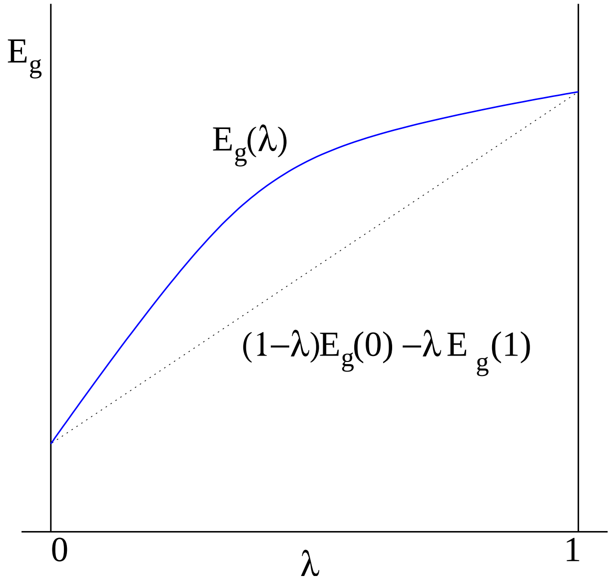
- Comparing terms in α^2 we arrive at the expression:

$$\boxed{E_n^2 = \sum_{k\neq n} \frac{\langle\psi_n^0|H_1|\psi_k^0\rangle\langle\psi_k^0|H_1|\psi_n^0\rangle}{E_n^0 - E_k^0} = \sum_{k\neq n} \frac{|\langle\psi_n^0|H_1|\psi_k^0\rangle|^2}{E_n^0 - E_k^0}}$$

- Expressions can also be found for the first, second etc, order changes to the wavefunctions

PROOF OF THEOREM 1

Theorem 1 is an expression of the *convexity* of the ground-state energy as a function of external potential, $v(\lambda;\mathbf{r})$



- Convexity follows from 2^{nd} order perturbation theory:

  $$\frac{d^2E_g}{d\lambda^2} = 2\sum_{n\neq 0}\frac{|\langle\Psi_0(\lambda)|\Delta V|\Psi_n(\lambda)\rangle|^2}{E_0(\lambda)-E_n(\lambda)} < 0$$

  $\Psi_0(\lambda)$ and $\Psi_n(\lambda)$ are the ground and n^{th} excited states, and $\Delta V = v(1;\mathbf{r}) - v(0;\mathbf{r})$

Proof of Theorem 1 continued

Theorem 1 is equivalent to stating that a change of external potential $\Delta v(\mathbf{r})$ must lead to a change of density $\Delta n(\mathbf{r})$

- First order perturbation theory implies:

  $\frac{dE_g}{d\lambda} = \langle\Psi_0|\Delta V|\Psi_0\rangle$

- Convexity demands that $\frac{dE_g}{d\lambda}$ at $\lambda = 0$ is greater than at $\lambda = 1$.

- This implies that:

  $\int d\mathbf{r}\Delta v(\mathbf{r})n(1;\mathbf{r}) < \int d\mathbf{r}\Delta v(\mathbf{r})n(0;\mathbf{r})$

- Hence:

  $\int d\mathbf{r}\Delta v(\mathbf{r})\Delta n(\mathbf{r}) < 0$ and so $\Delta n(\mathbf{r})$ cannot be zero, proving Theorem 1.

Theorem 2: The Variational Principle

- As the ground-state energy E_g is uniquely specified by $n(\mathbf{r})$ it can be written as a functional $E_g[n(\mathbf{r})]$
- We can explicitly separate out the term due to the external potential:

$$E_g[n(\mathbf{r})] = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + F[n(\mathbf{r})]$$

- $F[n(\mathbf{r})]$ is the ground-state expectation value of H_0 when the density is $n(\mathbf{r})$

Theorem 2 (or the *variational theorem*) The ground-state energy for a fixed $v(\mathbf{r})$ is given by minimising $E_g[n(\mathbf{r})]$ with respect to $n(\mathbf{r})$. The $n(\mathbf{r})$ that gives the minimum energy is the ground-state density.

THEOREM 2: THE PROOF

Proof: The potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ are two different external potentials. The corresponding ground-state energies are E_g and E_g', and the ground-state many-body wavefunctions are Ψ and Ψ'.

By the Rayleigh-Ritz variational principle:

$$\boxed{E_g < \langle \Psi' | H_0 + V | \Psi' \rangle = \int d\mathbf{r} v(\mathbf{r}) n'(\mathbf{r}) + F[n'(\mathbf{r})]}$$

The density due to Ψ' is $n'(\mathbf{r})$

If we assume that the ground-state is non-degenerate, this proves Theorem 2.

THE EXCHANGE AND CORRELATION ENERGY

- The total energy can be split into three parts:

  $$E_{\text{tot}} = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + F[n]$$

  $$F[n] = T[n] + G[n]$$

  $T[n]$ is the kinetic energy of non-interacting electrons with a density distribution of $n(\mathbf{r})$

- We can also separate out the Hartree energy:

  $$E_{\text{H}}[n(\mathbf{r})] = \frac{1}{2} e^2 \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- The exchange-correlation energy $E_{\text{xc}}[n]$ is defined as what is left:

  $$E_{\text{tot}} = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + T[n] + E_{\text{H}}[n] + E_{\text{xc}}[n]$$

This is all exact. If we knew what $E_{\text{xc}}[n]$ was we could calculate the exact ground-state energy for any system! But, sadly, we don't ...

THE LOCAL DENSITY APPROXIMATION

- If we are to make any progress we must *guess* a form for E_{xc}

- We do know the E_{xc} very accurately (via Quantum Monte Carlo calculations) for jellium (the uniform electron gas).

- We know the exchange-correlation energy per electron $\varepsilon_{\mathrm{xc}}(n)$ for a range of n

- The Local Density Approximation (LDA) is the follows:

  Approximate the xc energy of an electron at point $\mathbf{r}$ to be $\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))$, the value for jellium using the density $n(\mathbf{r})$ for point $\mathbf{r}$.

  $$E_{\mathrm{xc}}^{\mathrm{LDA}} = \int d\mathbf{r} n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))$$

This works very well for the structural properties of many solids.

OTHER DENSITY FUNCTIONALS

- Why does the LDA work so well? There are some justifications (based on the known properties of the electron gas), but mainly it just works.
- LDA is not that good for total energy differences, barrier heights etc. Can we do better?
- The LDA only considers the value of the density at a point — we could consider its gradients. This leads to the Generalised Gradient Approximations (GGAs)
- GGAs are better for energy differences (so more useful to chemists), and for the structural properties of heavy elements
- There are *ab initio* GGAs such as: PW91, PBE, rPBE and hybrid functionals: B3LYP and many others