Density Functional Theory and the Total Energy Method

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Lecture One
Many properties depend on the total energy of a system

- equilibrium lattice constants (density)
- bulk moduli
- phonons
- elastic constants
- phase transitions
- chemistry, bonding etc.
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

\[ H \Psi = E \Psi = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 \Psi \right) - Ze^2 \sum_{R} \frac{1}{|r_i - R|} \Psi ) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \Psi \]

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

\[
H = T + V + U
\]

where \( U \) is the mutual interaction energy of the electrons and \( V = \sum_{i=1}^{N} v(r_i) \), the interaction with an arbitrary external field.
**Total Energy as a Functional of the Density**

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

\[ A[f(r)] = \int f(r)^2 dr \]

- For a given external potential \( v(r) \) • The electron density is: the many-body wavefunction is \( \Psi \), the ground-state energy is:

  \[ n(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle \]

  \[ E_g = \langle \Psi | H_0 + V | \Psi \rangle \]

  with the **density operator** defined as:

  \[ \hat{n}(r) = \sum_{i=1}^{N} \delta(r - r_i) \]
Density Functional Theory: The Two Theorems

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

**Corollary:** \( n(r) \) uniquely determines the external potential \( v(r) \) and therefore the many-body wavefunction \( \Psi \).

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

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

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

$$|\psi_n\rangle = |\psi^0_n\rangle + \sum_{k\neq n} \alpha C^1_{nk}|\psi^0_k\rangle + \sum_{k\neq n} \alpha^2 C^2_{nk}|\psi^0_k\rangle + \ldots$$

- Also expanding the energy $E_n$ in powers of $\alpha$ we obtain:

$$\begin{align*}
(H_0 + \alpha H_1)[|\psi^0_n\rangle + \sum_{k\neq n} \alpha C^1_{nk}|\psi^0_k\rangle + \ldots] \\
= (E^0_n + \alpha E^1_n + \ldots)[|\psi^0_n\rangle + \sum_{k\neq n} \alpha C^1_{nk}|\psi^0_k\rangle + \ldots]
\end{align*}$$
The First Order Energy Shift

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

- Comparing terms in \(\alpha\) we arrive at the expression:

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

- 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:

\[\alpha E_n^1 = \langle \psi_n^0 |\alpha H_1 |\psi_n^0\rangle\]
The Second Order Energy Shift

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

- Comparing terms in \(\alpha^2\) we arrive at the expression:

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

- Expressions can also be found for the first, second etc, order changes to the wavefunctions
Theorem 1 is an expression of the convexity of the ground-state energy as a function of external potential, $v(\lambda; r)$

- Convexity follows from 2nd order perturbation theory:

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

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

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

- First order perturbation theory

implies:

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

This implies that:

$$\int dr \Delta v(r) n(1; r) < \int dr \Delta v(r) n(0; r)$$

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

Hence:

$$\int dr \Delta v(r) \Delta n(r) < 0$$ and so $\Delta n(r)$ cannot be zero, proving Theorem 1.
Theorem 2: The Variational Principle

- As the ground-state energy $E_g$ is uniquely specified by $n(r)$ it can be written as a functional $E_g[n(r)]$
- We can explicitly separate out the term due to the external potential:
  $$E_g[n(r)] = \int d\mathbf{r} \psi(\mathbf{r})^2 + F[n(r)]$$
  - $F[n(r)]$ is the ground-state expectation value of $H_0$ when the density is $n(r)$

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

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

By the Rayleigh-Ritz variational principle:

$$E_g < \langle \Psi' | H_0 + V | \Psi' \rangle = \int dr v(r) n'(r) + F[n'(r)]$$

The density due to $\Psi'$ is $n'(r)$

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:

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


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

- We can also separate out the Hartree energy:

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

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

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

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 …
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 $\varepsilon_{xc}(n)$ 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 $\varepsilon_{xc}(n(\mathbf{r}))$, the value for jellium using the density $n(\mathbf{r})$ for point $\mathbf{r}$.

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

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