

# Density Functional Theory

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# Density Functional Theory

Over 90% of modern Quantum Chemistry calculations use some form of density functional methodology.

Over 95% of band theory calculations in Solid State Physics are based upon some form of density functional approach.

# Density Functional Theory

Two theorems by Pierre Hohenberg and Walter Kohn (Nobel Prize 1998):

P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864 (1964)

# Density Functional Theory

$N$ -electron time-independent Schrödinger equation:

$$H\Psi = E\Psi$$

The  $N$ -electron Hamiltonian

$$H = T + V + W$$

Kinetic energy

Interaction

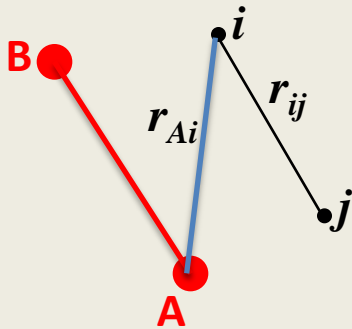
External potential

# Density Functional Theory

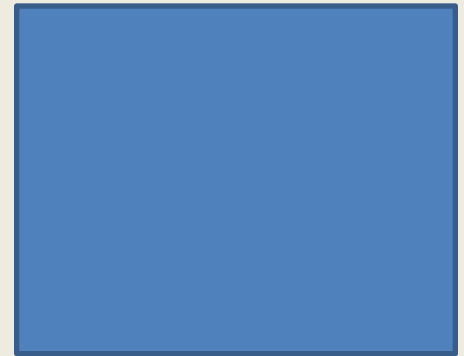
The kinetic energy operator:  $T = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2$

The two-electron interaction operator:  $W = \frac{1}{2} \sum_{i < j=1}^N \frac{1}{r_{ij}}$

The 'external' confining potential:

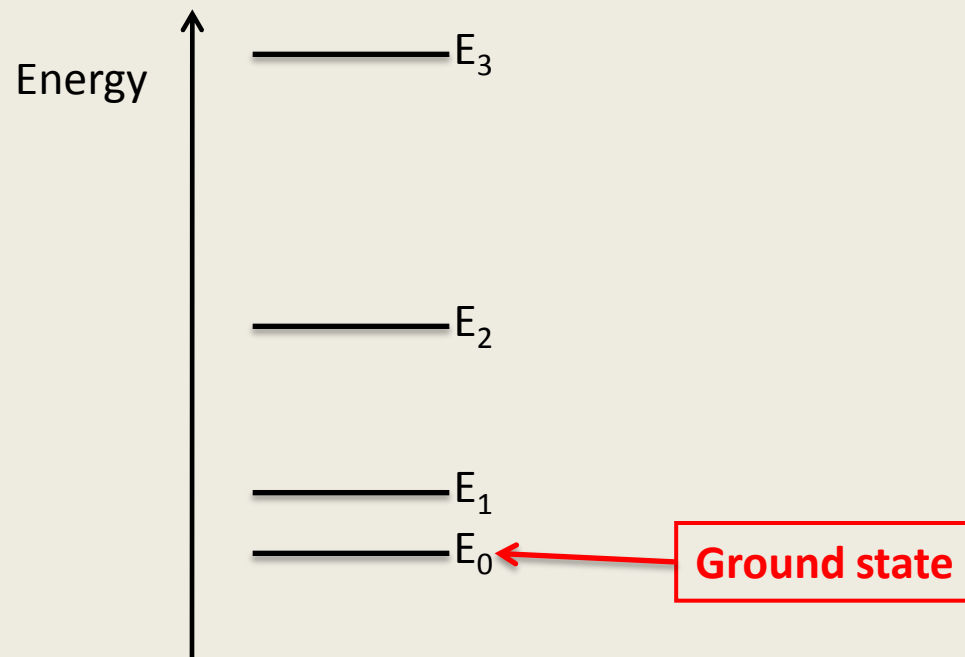


$$V = \sum_{i=1}^N V_i$$



# Density Functional Theory

A 'confining' potential implies a spectrum of 'bound' states:



# Density Functional Theory

The N-electron wave function is a function of N space-spin co-ordinates

$$\Psi = \Psi(1, 2, \dots, i, \dots, N)$$

$$i \equiv (x_i, y_i, z_i, \sigma_i) = (\vec{r}_i, \sigma_i)$$

The Born Probability interpretation of the wave function

$$P(1, 2, \dots, N) = |\Psi(1, 2, \dots, N)|^2$$

# Density Functional Theory

The electron density:

$$\rho(\vec{r}_1) = N \int |\Psi(1, 2, \dots, N)|^2 d\sigma_1 d2 d3 \dots dN$$

The electron density is the probability of finding any electron at spatial position  $\vec{r}_1$ .



# Density Functional Theory

## The Hohenberg-Kohn theorem

### Theorem I

For any system of interacting particles in an external potential  $V$ , the density  $\rho$ , is uniquely determined, i.e. the external potential is a unique functional of the density.

# Density Functional Theory


## Proof of Theorem I

Assume two different external potentials  $V^{(1)}$  and  $V^{(2)}$  give rise to the same density,  $\rho$ .

Define two distinct Hamiltonians,

$$H^{(i)} = T + V^{(i)} + W, \quad i = 1, 2$$

Using the variation principle for case 1:

$$E_0^{(1)} = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle$$


Inequality strict if ground state is non-degenerate.

Ground state wave functions

# Density Functional Theory

## Proof of Theorem I

Inequality strict if ground state is non-degenerate.

$$E_0^1 = \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle$$

We can write the r.h.s as

$$\begin{aligned} \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle &= \langle \Psi^{(2)} | H^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle - \langle \Psi^{(2)} | H^{(2)} | \Psi^{(2)} \rangle \\ &= E_0^{(2)} + \int d\vec{r} [V^{(1)}(\vec{r}) - V^{(2)}(\vec{r})] \rho(\vec{r}) \end{aligned}$$

So that, finally

$$E_0^1 < E_0^{(2)} + \int d\vec{r} [V^{(1)}(\vec{r}) - V^{(2)}(\vec{r})] \rho(\vec{r})$$

# Density Functional Theory

## Proof of Theorem I

So that, finally

$$E_0^{(1)} < E_0^{(2)} + \int d\vec{r} [V^{(1)}(\vec{r}) - V^{(2)}(\vec{r})] \rho(\vec{r})$$

Repeating this process for case 2, leads to

$$E_0^{(2)} < E_0^{(1)} + \int d\vec{r} [V^{(2)}(\vec{r}) - V^{(1)}(\vec{r})] \rho(\vec{r})$$

Reductio ad absurdum

$$E_0^{(1)} < E_0^{(2)} + \int d\vec{r} [V^{(1)}(\vec{r}) - V^{(2)}(\vec{r})] \rho(\vec{r}) < E_0^{(1)}$$

# Density Functional Theory

## The Hohenberg-Kohn theorem

### Theorem II

A *universal* functional of the density  $E(\rho)$ , can be defined. The *exact* ground state is the *global* minimum value of this functional.

# Density Functional Theory

## The Hohenberg-Kohn theorem

1. The ground state density,  $\rho$ , uniquely determines the ground state wave-function  $\Psi_d(\rho)$ , as well as the external potential  $V(\rho)$ .
2. As a consequence, any observable of a static many-particle system is a functional of the ground-state density.

# Density Functional Theory

## The Hohenberg-Kohn theorem

### 3. The total energy functional

$$E_V[\rho] = \langle \Psi[\rho] | T + W + V | \Psi[\rho] \rangle$$

of a system characterised by external potential,  $V$ , is equal to the exact ground state energy if and only if the exact ground state density,  $\rho_0$ , is inserted.

# Density Functional Theory

## The Hohenberg-Kohn theorem

4. For all other densities,  $\rho \neq \rho_0$ ,

$$E_0 < E_V[\rho]$$

Consequently, the exact density,  $\rho_0$ , and the exact ground state energy can be obtained by solving the Euler-Lagrange equation

$$\frac{\delta}{\delta\rho(r)} E_V[\rho] = 0$$



# Density Functional Theory

## The Hohenberg-Kohn theorem

### 5. The functional

$$F[\rho] = \langle \Psi[\rho] | T + W | \Psi[\rho] \rangle$$

is universal, i.e. it is independent of the external potential,  $V$ , of the particular many-particle system.

It has the same form for **ALL** systems with a fixed inter-particle interaction,  $W$  (including  $W = 0$ ).

# Density Functional Theory

## The Kohn-Sham Equations (Kohn & Sham 1966)

Kohn and Sham introduced a fictitious non-interacting system with a Slater determinant as the exact ground state wave-function. This Slater determinant possesses the same density,  $\rho$ , and energy  $E$ , as the exact interacting system, and must necessarily have a different potential,  $V_{KS}$ .

# Density Functional Theory

## The Kohn-Sham Equations

The Kohn-Sham satisfies a set of orbital equations analogous to the HF equations

$$\left[ -\frac{1}{2}\nabla^2 + V_{KS}[\rho] \right] \phi_i[\rho](\vec{r}, \sigma) = \varepsilon_i[\rho] \phi_i[\rho](\vec{r}, \sigma), \quad i = 1, \dots, N$$

where the density

$$\rho(\vec{r}) = \sum_{\sigma} \sum_{i=1}^N |\phi_i[\rho](\vec{r}, \sigma)|^2$$

# Density Functional Theory

## The Kohn-Sham Equations

The Kohn-Sham potential is defined as

$$V_{KS}[\rho](\vec{r}) = V(\vec{r}) + \int d^3r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}[\rho](\vec{r})$$

where the exchange-correlation potential is

$$V_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$$

# Density Functional Theory

## Implementations

### B3LYP (Becke, Lee, Yang and Perdew)

$$E_{xc}^{\text{B3LYP}} = E_{xc}^{\text{LDA}} + a_0(E_x^{\text{HF}} - E_x^{\text{LDA}}) + a_x(E_x^{\text{GGA}} - E_x^{\text{LDA}}) + a_c(E_c^{\text{GGA}} - E_c^{\text{LDA}}),$$

where ,  $a_0 = 0.2$ ,  $a_x = 0.72$ , and  $a_c = 0.81$ , are three empirical parameters determined by fitting the calculated quantities to a set of experimental atomization energies, ionization potentials, proton affinities, and total atomic energies.

# Density Functional Theory

Current implementations of density functional theory are semi-empirical. They are very accurate in most situations, but tend to break down for weak interactions.

There is an overriding need for advances in understanding of the nature of the exact energy functional.

# Density Functional Theory

The exact formula is:

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