

TOTAL ENERGIES OF ELECTRONIC SYSTEMS

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OUTLINE :

1. MANY ELECTRON THEORY
2. DFT theorems
3. LDA results
4. LDA inherent difficulties
5. GRADIENTS GEA
6. GRADIENTS GGA
7. LIMITATIONS band gaps, symmetry...
8. REAL SPACE orbital dep. func.s

TOPICS NOT COVERD :

SPIN DEPENDENCE

CURRENT DFT

RELATIVISTIC DFT

EXCITED STATES

TIMEDEPENDENT DFT

TEMPERATUREDEPENDENT DFT

MUTICOMPONENT DFT

DFT FOR SUPERCONDUCTORS

FRACTIONAL OCCUPATION NUMBERS

A DIFFERENT APPROACH:

- Let us do without Density Functional Theory (DFT) as long as possible
- How far do we get?

THE HAMILTONIAN

$$H = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N w(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^N v(\vec{r}_i - \vec{r}_j)$$

$$v(\vec{r}) = 1/r$$

- units a.u.
- non-relativistic
- no spin-orbit
- no magnetic fields
- no time dependence

TYPICALLY $w(\vec{r}) = -\sum_{\mu}^M z_{\mu} \cdot v(\vec{r} - \vec{R}_{\mu})$

$$E = \langle \Psi | H | \Psi \rangle \quad \langle \Psi | \Psi \rangle = 1$$

The simplest term in the energy

$$\begin{aligned} W &= \langle \Psi | \hat{W} | \Psi \rangle = \langle \Psi | \sum_i^N w(\vec{r}_i) | \Psi \rangle = \\ &= \int d^3r w(\vec{r}) \langle \Psi | \sum_i^N \delta(\vec{r} - \vec{r}_i) | \Psi \rangle = \\ &= \int d^3r w(\vec{r}) \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = \\ &= \int d^3r w(\vec{r}) \cdot n(\vec{r}) \end{aligned}$$

a very intuitive and classical result!

We have above defined the density operator $\hat{n}(\vec{r})$

$$\hat{n}(\vec{r}) = \sum_i^N \delta(\vec{r} - \vec{r}_i)$$

and the density $n(\vec{r})$

$$\begin{aligned} n(\vec{r}) &= \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = \\ &= \langle \Psi | \sum_i^N \delta(\vec{r} - \vec{r}_i) | \Psi \rangle = \\ &= N \int \delta(\vec{r} - \vec{r}_1) |\Psi(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \dots \\ &\quad \dots, \vec{r}_N \sigma_N)|^2 d^3r_1 \dots d^3r_N \cdot \\ &\quad \cdot d\sigma_1 \dots d\sigma_N \end{aligned}$$

$$n(\vec{r}) = N \int d\sigma_1 dx_2 \dots dx_N |\Psi(\vec{r}\sigma_1, x_2, \dots, x_N)|^2$$

$$(\vec{r}, \sigma) = x$$

We move to the next simplest term - the kinetic energy

$$T = \langle \Psi | \hat{T} | \Psi \rangle = \langle \Psi | -\frac{1}{2} \sum_i^N \nabla_i^2 | \Psi \rangle =$$

$$= -\frac{N}{2} \int d\sigma_1 d^3r_1 \Psi^*(\vec{r}_1, \sigma_1, x_2, \dots, x_N) \nabla_1^2 \Psi(\vec{r}_1, \sigma_1, x_2, \dots, x_N) dx_2 \dots dx_N$$

Define: $\Gamma_{\sigma\sigma'}^{(1)}(\vec{r}, \vec{r}')$

$$\Gamma_{\sigma\sigma'}^{(1)}(\vec{r}, \vec{r}') = N \int \Psi^*(\vec{r}\sigma, x_2, \dots, x_N) \Psi(\vec{r}'\sigma', x_2, \dots, x_N) dx_2 \dots dx_N$$

Then

$$T = -\frac{1}{2} \sum_{\sigma} \int [\nabla^2 \Gamma_{\sigma\sigma}^{(1)}(\vec{r}, \vec{r}')]_{\vec{r}=\vec{r}'} d^3r$$

$$T = -\frac{1}{2} \mathcal{R} [\nabla^2 \Gamma^{(1)}] \quad \text{abstract}$$

Lesson: Very little of the total information in the wave function is needed in order to calculate the energies.

Let's go to the most complicated term - the interaction energy U

$$\begin{aligned} U &= \langle \Psi | \hat{U} | \Psi \rangle = \langle \Psi | \frac{1}{2} \sum_{i,j}^N v(\vec{r}_i - \vec{r}_j) | \Psi \rangle = \\ &= \frac{1}{2} N(N-1) \int v(\vec{r}_1 - \vec{r}_2) |\Psi(x_1, x_2, \dots, x_N)|^2 dx_1 \dots dx_N = \\ &= \frac{1}{2} \sum_{\sigma\sigma'} \int \Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') v(\vec{r} - \vec{r}') d^3r d^3r' \end{aligned}$$

Where we have defined the diagonal of the two-particle density matrix $\Gamma^{(2)}$

$$\Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') = N(N-1) \int |\Psi(\vec{r}\sigma, \vec{r}'\sigma', x_3, \dots, x_N)|^2 dx_3 \dots dx_N$$

$\Gamma^{(2)}$ has many important properties

$$\Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') \geq 0$$

$$\Gamma_{\sigma\sigma}^{(2)}(\vec{r}, \vec{r}) = 0 \quad \text{Pauli excl. princ.}$$

$$\Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') = \Gamma_{\sigma'\sigma}^{(2)}(\vec{r}', \vec{r}) \quad \text{symmetry}$$

$$\Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') \quad \text{is an observable}$$

Define the one-particle spin-density oper.

$$\hat{n}_{\sigma}(\vec{r}) = \sum_i^N \delta(\vec{r} - \vec{r}_i) \cdot \delta_{\sigma\sigma_i}$$

and the spin density

$$n_{\sigma}(\vec{r}) = \langle \Psi | \hat{n}_{\sigma}(\vec{r}) | \Psi \rangle$$

The two-particle spin-density operator is

$$\hat{n}_{\sigma\sigma'}(\vec{r}, \vec{r}') = \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i) \cdot \delta(\vec{r}' - \vec{r}_j) \delta_{\sigma\sigma_i} \delta_{\sigma'\sigma_j}$$

Notice! The same electron cannot be in two different places.

We have

$$\Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') = \langle \Psi | \hat{n}_{\sigma\sigma'}(\vec{r}, \vec{r}') | \Psi \rangle$$

$$\Gamma_{\sigma\sigma'}^{(2)}(\vec{r}, \vec{r}') \equiv n_{\sigma}(\vec{r}) n_{\sigma'}(\vec{r}') \cdot g_{\sigma\sigma'}(\vec{r}, \vec{r}')$$

the pair-correlation function

The sum rule becomes

$$\int n_{\sigma'}(\vec{r}') \{ g_{\sigma\sigma'}(\vec{r}, \vec{r}') - 1 \} = -\delta_{\sigma\sigma'}$$

and the interaction energy

$$U = \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r d^3r' n_{\sigma}(\vec{r}) n_{\sigma'}(\vec{r}') g_{\sigma\sigma'}(\vec{r}, \vec{r}') U(\vec{r} - \vec{r}')$$

It is customary to split off the classical Coulomb result

$$U_0 = \frac{1}{2} \int d^3r d^3r' n(\vec{r}) n(\vec{r}') U(\vec{r} - \vec{r}')$$

and write

$$U = U_0 + U_{xc}$$

where

$$U_{xc} = \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r d^3r' n_{\sigma}(\vec{r}) n_{\sigma'}(\vec{r}') \{ g_{\sigma\sigma'}(\vec{r}, \vec{r}') - 1 \} U(\vec{r} - \vec{r}')$$

In atomic and molecular systems $U_0 \gg U_{xc}$

