

21- the results for real systems.

idea of generalized gradient approximation

Instead of a strict expansion in orders of δs
choose $f(n, \nabla n, \nabla^2 n \dots)$ such that exact properties
are fulfilled, or choose a functional form for
 f using some parameters that are fitted to
reproduce the xc energies of some systems.

Ideally an approximation to E_{xc} should have the
following features:

- i) non-empirical derivation, i.e. no parameters that
are fitted to results from specific systems
- ii) universality, i.e. work for any system and any
type of bonds
- iii) simplicity, i.e. can be implemented on a computer
- iv) accuracy, i.e. good enough to be useful for real
systems

There is a lot of freedom in constructing a GGA
which makes the process highly non-trivial and
results in many different functionals

A.D. Becke J. Chem. Phys. 84, 4524 (1986) B86

A.D. Becke Phys. Rev. A 38, 3098 (1988) B88

J.P. Perdew, Y. Wang Phys. Rev. B 33, 8800 (1986) PW86

J.P. Perdew, K. Burke, M. Ernzerhof Phys. Rev. Lett. 77,
3865 (1996) PBE

...

DFT codes usually have a large number of GGAs
implemented.

6. Spin density functional theory

In addition to an external scalar field $v(\vec{r})$ we now have an external magnetic field $\vec{B}(\vec{r})$ which couples to the spin degrees of freedom of our system.

$$H = \sum_{j=1}^N \left(-\frac{\nabla_j^2}{2} \right) + \sum_{j=1}^N v(\vec{r}_j) + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|} + \underbrace{\mu_0 \sum_{j=1}^N \vec{\sigma}(j) \cdot \vec{B}(\vec{r}_j)}_U$$

with $\mu_0 = \frac{e\hbar}{2mc} = \frac{1}{2c}$ $\vec{\sigma}$: vector of Pauli matrices

$$\vec{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \vec{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \vec{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\mu_0 \vec{\sigma}(j) \cdot \vec{B}(\vec{r}_j) = \mu_0 \begin{pmatrix} B_z(\vec{r}_j) & \\ & B_x(\vec{r}_j) - i B_y(\vec{r}_j) \\ B_x(\vec{r}_j) + i B_y(\vec{r}_j) & \\ & -B_z(\vec{r}_j) \end{pmatrix}$$

for one particle

$$H\psi = E\psi$$

$$\begin{pmatrix} -\frac{\nabla^2}{2} + v + B_z & B_x - i B_y \\ B_x + i B_y & -\frac{\nabla^2}{2} + v - B_z \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

$$\psi = \psi_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\vec{\sigma}_z \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \vec{\sigma}_z \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

→ one can expand every wave function in eigenfunctions of $\vec{\sigma}_z$

→ spin-dependent wave function $\Psi(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N)$

For calculating the energy we need to evaluate

$$\langle \Psi | H | \Psi \rangle.$$

$$\langle \Psi | \mu_0 \sum_{j=1}^N \vec{\sigma}(j) \cdot \vec{B}(\vec{r}_j) | \Psi \rangle$$

$$= \mu_0 \sum_{j=1}^N \int d^3r_1 \dots d^3r_N \sum_{\sigma_1, \dots, \sigma_N} \Psi^*(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N) \vec{\sigma}(j) \cdot \vec{B}(\vec{r}_j) \Psi(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N)$$

23- look at $j=1$ term

$$\mu_0 \int d^3r_1 \sum_{\sigma_1=1,2} \vec{B}(\vec{r}_1) \int d^3r_2 \dots d^3r_N \sum_{\sigma_2 \dots \sigma_N} \Psi^*(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N) \vec{\sigma}(1) \Psi(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N)$$

all other terms contribute exactly the same

$$\Rightarrow \langle \Psi | \mu_0 \sum_{j=1}^N \vec{\sigma}(j) \vec{B}(\vec{r}_j) | \Psi \rangle = - \int d^3r_1 \vec{B}(\vec{r}_1) \vec{m}(\vec{r}_1)$$

with

$$\vec{m}(\vec{r}_1) = -\mu_0 N \sum_{\sigma_1} \int d^3r_2 \dots d^3r_N \sum_{\sigma_2 \dots \sigma_N} \Psi^*(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N) \vec{\sigma}(1) \Psi(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N)$$

the magnetization density of the system.

6.1. Hohenberg Kohn theorem

1. $\Psi(\vec{r}_1 \sigma_1, \dots, \vec{r}_N \sigma_N)$ is uniquely determined by $s(\vec{r})$ and $\vec{m}(\vec{r})$

proof (along the same lines as before)

assume Ψ and Ψ' yield the same set $\{s(\vec{r}), \vec{m}(\vec{r})\}$

$$H\Psi = (T+V+W+U)\Psi = E\Psi$$

$$H'\Psi' = (T+V'+W+U')\Psi' = E'\Psi'$$

$$E = \langle \Psi | H | \Psi \rangle = \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | V - V' | \Psi' \rangle + \langle \Psi' | U - U' | \Psi' \rangle$$

$$= E' + \int d^3r (v(\vec{r}) - v'(\vec{r})) s(\vec{r}) - \int d^3r (\vec{B}'(\vec{r}) - \vec{B}(\vec{r})) \vec{m}(\vec{r})$$

same for E'

$$E' < E + \int d^3r (v'(\vec{r}) - v(\vec{r})) s(\vec{r}) - \int d^3r (\vec{B}'(\vec{r}) - \vec{B}(\vec{r})) \vec{m}(\vec{r})$$

$$E + E' < E + E' \quad \{$$

\Rightarrow if $\Psi \neq \Psi' \Rightarrow \{s(\vec{r}), \vec{m}(\vec{r})\} \neq \{s'(\vec{r}), \vec{m}'(\vec{r})\}$

$$\Rightarrow \Psi[s, \vec{m}]$$

2. variational principle

$$E[s, \vec{m}] > E_0 \quad \text{for } s \neq s_0 \text{ or } \vec{m} \neq \vec{m}_0$$

$$E[s, \vec{m}] = E_0 \quad \text{for } s = s_0 \text{ and } \vec{m} = \vec{m}_0$$

3. universality

$$F[s, \vec{m}] = \langle \Psi[s, \vec{m}] | T + W | \Psi[s, \vec{m}] \rangle$$

6.2. Kohn-Sham system

non-interacting system with the same $s(\vec{r})$ and $\vec{m}(\vec{r})$ as the interacting system

$$\left(-\frac{\nabla^2}{2} + v_s(\vec{r}) + \mu_0 \vec{\sigma} \cdot \vec{B}_s(\vec{r}) \right) \Psi_j(\vec{r}) = \epsilon_j \Psi_j(\vec{r})$$

$$\Psi_j(\vec{r}) = \begin{pmatrix} \psi_{j1}(\vec{r}) \\ \psi_{j2}(\vec{r}) \end{pmatrix}$$

$$s(\vec{r}) = \sum_{j=1}^N |\Psi_j(\vec{r})|^2 \quad \vec{m}(\vec{r}) = -\mu_0 \sum_{j=1}^N \Psi_j^*(\vec{r}) \vec{\sigma} \Psi_j(\vec{r})$$

Minimize the energy $E[s, \vec{m}]$ with respect to $s(\vec{r})$ and $\vec{m}(\vec{r})$

$$\Rightarrow v_s(\vec{r}) = v_0(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r})$$

$$\vec{B}_s(\vec{r}) = \vec{B}_0(\vec{r}) + \vec{B}_{xc}(\vec{r})$$

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[s, \vec{m}]}{\delta s(\vec{r})} \quad \vec{B}_{xc}(\vec{r}) = - \frac{\delta E_{xc}[s, \vec{m}]}{\delta \vec{m}(\vec{r})}$$

6.3. Collinear magnetism

special case: $\vec{B}(\vec{r}) = (0, 0, B(\vec{r}))$, i.e. the magnetic field always points in z-direction

$\Rightarrow \vec{\sigma} \cdot \vec{B} = \sigma_z \cdot B(\vec{r})$, i.e. only σ_z and m_z play a role in the calculation of the energy

This does not mean that m_x and m_y have to be zero!

Assume $\vec{m} = (0, 0, m_z(\vec{r}))$, i.e. $\vec{m} \parallel \vec{B}$ which is true

for many systems

$$m_z(\vec{r}) = -\mu_0 N \int d^3r_2 \dots d^3r_N \sum_{\sigma_2 \dots \sigma_N} \left[\Psi^*(\vec{r}_1 \uparrow, \vec{r}_2 \sigma_2 \dots \vec{r}_N \sigma_N) \sigma_z(1) \Psi(\vec{r}_1 \uparrow, \dots, \vec{r}_N \sigma_N) + \Psi^*(\vec{r}_1 \downarrow, \vec{r}_2 \sigma_2 \dots \vec{r}_N \sigma_N) \sigma_z(1) \Psi(\vec{r}_1 \downarrow, \dots, \vec{r}_N \sigma_N) \right]$$

$$= -\mu_0 N \int d^3r_2 \dots d^3r_N \sum_{\sigma_2 \dots \sigma_N} \left[|\Psi(\vec{r}_1 \uparrow, \vec{r}_2 \sigma_2 \dots \vec{r}_N \sigma_N)|^2 - |\Psi(\vec{r}_1 \downarrow, \vec{r}_2 \sigma_2 \dots \vec{r}_N \sigma_N)|^2 \right]$$

$$= -\mu_0 (s_{\uparrow}(\vec{r}_1) - s_{\downarrow}(\vec{r}_1))$$

$$\text{total density } s(\vec{r}) = s_{\uparrow}(\vec{r}) + s_{\downarrow}(\vec{r})$$

instead of using s and m_z one uses s_{\uparrow} and s_{\downarrow} in the Hamiltonian

$$\mu_0 \vec{s} \cdot \vec{B} = \mu_0 s_z B = \mu_0 \begin{pmatrix} B & 0 \\ 0 & -B \end{pmatrix}$$

$$\Rightarrow H = \begin{pmatrix} -\frac{\nabla^2}{2} + v(\vec{r}) + \mu_0 B(\vec{r}) & 0 \\ 0 & -\frac{\nabla^2}{2} + v(\vec{r}) - \mu_0 B(\vec{r}) \end{pmatrix}$$

$$= \begin{pmatrix} -\frac{\nabla^2}{2} + v_{\uparrow}(\vec{r}) & 0 \\ 0 & -\frac{\nabla^2}{2} + v_{\downarrow}(\vec{r}) \end{pmatrix}$$

$$\text{with } v_{\uparrow}(\vec{r}) = v(\vec{r}) + \mu_0 B(\vec{r}), \quad v_{\downarrow}(\vec{r}) = v(\vec{r}) - \mu_0 B(\vec{r})$$

\Rightarrow the two spin directions completely decouple in the Hamiltonian

Kohn-Sham system

$$H = T + V_s \quad V_s = \begin{pmatrix} v_{s\uparrow} & 0 \\ 0 & v_{s\downarrow} \end{pmatrix}$$

one obtains 2 sets of KS equations

$$\left(-\frac{\nabla^2}{2} + v_{s\uparrow}(\vec{r}) \right) \varphi_{j\uparrow}(\vec{r}) = \epsilon_{j\uparrow} \varphi_{j\uparrow}(\vec{r})$$

$$\left(-\frac{\nabla^2}{2} + v_{s\downarrow}(\vec{r}) \right) \varphi_{j\downarrow}(\vec{r}) = \epsilon_{j\downarrow} \varphi_{j\downarrow}(\vec{r})$$

$$s_{\uparrow}(\vec{r}) = \sum_{j=1}^{N_{\uparrow}} |\varphi_{j\uparrow}(\vec{r})|^2 \quad s_{\downarrow}(\vec{r}) = \sum_{j=1}^{N_{\downarrow}} |\varphi_{j\downarrow}(\vec{r})|^2$$

$$v_{s\uparrow}(\vec{r}) = v_o(\vec{r}) + v_H(\vec{r}) + v_{xc\uparrow}(\vec{r})$$

$$= v_o(\vec{r}) + \mu_0 B_o(\vec{r}) + v_H(\vec{r}) + v_{xc\uparrow}(\vec{r})$$

$$v_{s\downarrow}(\vec{r}) = v_o(\vec{r}) - \mu_0 B_o(\vec{r}) + v_H(\vec{r}) + v_{xc\downarrow}(\vec{r})$$

$$\text{with } v_H(\vec{r}) = \int d^3r' \frac{s(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$v_{xc\sigma}(\vec{r}) = \frac{\delta E_{xc}[s_{\uparrow}, s_{\downarrow}]}{\delta s_{\sigma}(\vec{r})}$$

26-

The KS equations for up and down spin are coupled due to the Hartree potential which depends on $s(\vec{r}) = s_{\uparrow}(\vec{r}) + s_{\downarrow}(\vec{r})$. Also, depending on the approximation, $V_{xc\uparrow}$ generally depends on s_{\uparrow} and s_{\downarrow} .

Even without external magnetic field one might want to use spin DFT, for example for open-shell systems.

Two advantages: - up and down electrons are treated differently

- more freedom in constructing functionals

Note: without magnetic field everything is a functional of s , also s_{\uparrow} and s_{\downarrow} . Unfortunately, we have no idea what $s_{\uparrow}[s]$ looks like. Hence, it might be easier to construct functionals of s_{\uparrow} and s_{\downarrow} than functionals of s .

6.4. Local spin density approximation

spin scaling relations help in constructing spin DFT functionals from DFT functionals

$$T_s[s_{\uparrow}, s_{\downarrow}] = T_s[s_{\uparrow}, 0] + T_s[0, s_{\downarrow}]$$

$$T_s[s] = T_s[s/2, s/2] = 2 \cdot T_s[s/2, 0]$$

$$\Rightarrow T_s[s_{\uparrow}, s_{\downarrow}] = \frac{1}{2} T_s[2s_{\uparrow}] + \frac{1}{2} T_s[2s_{\downarrow}]$$

$$\text{relative spin polarization: } \xi = \frac{s_{\uparrow} - s_{\downarrow}}{s_{\uparrow} + s_{\downarrow}}$$

we need the spin scaling relations for t_s , e_x and e_c

$$t_s(s_{\uparrow}, s_{\downarrow}) = t_s(s) \frac{[(1+\xi)^{5/3} + (1-\xi)^{5/3}]}{2}$$

$$e_x(s_{\uparrow}, s_{\downarrow}) = e_x(s) \frac{[(1+\xi)^{4/3} + (1-\xi)^{4/3}]}{2}$$

27-

as always the correlation part is the hardest, and one has to use interpolation formulas

$$e_c(s_\uparrow, s_\downarrow) = e_c(s) + \alpha_c(s) \eta^2 + \mathcal{O}(\eta^4)$$

$$-\alpha_c(s) = -2c_0 (1 - \alpha_1 r_s) \ln \left[1 + \frac{1}{2c_0 (\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)} \right]$$

$$\begin{aligned} \text{with } c_0 &= 0.016887 & \beta_1 &= \frac{1}{2c_0} \exp\left(-\frac{c_1}{2c_0}\right) \\ c_1 &= 0.035475 & \beta_2 &= 2c_0 \beta_1^2 \\ \alpha_1 &= 0.11125 & \beta_3 &= 0.88026 \\ & & \beta_4 &= 0.49671 \end{aligned}$$

same formula for α_c as we had for $e_c(s)$ but with different parameters.

The parameters are determined by exact properties and Quantum Monte Carlo calculations for the unpolarized and for the fully polarized HEG. As in DFT, there exist different parametrizations.