Spin density functional theory

Within spin DFT we can describe systems in their ground state that can interact with a static magnetic field $\vec{B}(\vec{r})$

For one particle this changes the Hamiltonian into

$$\hat{h}_{\sigma\sigma'}(\vec{r}) = -\frac{\delta_{\sigma\sigma'}}{2}\nabla^2 + u_{\sigma\sigma'}(\vec{r})$$

$$u_{\sigma\sigma'}(\vec{r}) = v(\vec{r})\,\delta_{\sigma\sigma'} - \mu\,\vec{B}\cdot\vec{\sigma}_{\sigma\sigma'}$$

where we defined the Pauli spin matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

The one-particle Schrödinger equation then attains the form

$$\sum_{\sigma'=\pm 1} h_{\sigma\sigma'}(\vec{r})\,\psi(\vec{r}\sigma') = \epsilon\,\psi(\vec{r}\sigma)$$

or in matrix notation

$$\left[-\frac{\nabla^2}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \begin{pmatrix} u_{\uparrow\uparrow}(\vec{r}) & u_{\uparrow\downarrow}(\vec{r}) \\ u_{\downarrow\uparrow}(\vec{r}) & u_{\downarrow\downarrow}(\vec{r}) \end{pmatrix}\right]\begin{pmatrix} \psi(\vec{r}\uparrow) \\ \psi(\vec{r}\downarrow) \end{pmatrix} = \epsilon\begin{pmatrix} \psi(\vec{r}\uparrow) \\ \psi(\vec{r}\downarrow) \end{pmatrix}$$

The wave function can now in general not be chosen to be of the form

$$\psi = \begin{pmatrix} \psi(\vec{r}\uparrow) \\ 0 \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} 0 \\ \psi(\vec{r}\downarrow) \end{pmatrix}$$

as was the case in the absence of field $\vec{B}(\vec{r})$

The matrix $u_{\sigma\sigma'}$ can be written out more explicitly as

$$\begin{pmatrix} u_{\uparrow\uparrow}(\vec{r}) & u_{\uparrow\downarrow}(\vec{r}) \\ u_{\downarrow\uparrow}(\vec{r}) & u_{\downarrow\downarrow}(\vec{r}) \end{pmatrix} = \begin{pmatrix} v(\vec{r}) - \mu B_z(\vec{r}) & -\mu\left(B_x(\vec{r}) - iB_y(\vec{r})\right) \\ -\mu\left(B_x(\vec{r}) + iB_y(\vec{r})\right) & v(\vec{r}) + \mu B_z(\vec{r}) \end{pmatrix}$$

If the magnetic field has only a z-component $(0,0,B_z)$ then we can write

$$u_{\sigma\sigma'}(\vec{r}) = \begin{pmatrix} v_\uparrow(\vec{r}) & 0 \\ 0 & v_\downarrow(\vec{r}) \end{pmatrix}$$

$$\begin{cases} v_\uparrow(\vec{r}) = v(\vec{r}) - \mu B_z(\vec{r}) \\ v_\downarrow(\vec{r}) = v(\vec{r}) + \mu B_z(\vec{r}) \end{cases}$$

and the Schrödinger equation becomes

$$\begin{pmatrix} h_\uparrow(\vec{r}) & 0 \\ 0 & h_\downarrow(\vec{r}) \end{pmatrix} \begin{pmatrix} \psi(\vec{r}\uparrow) \\ \psi(\vec{r}\downarrow) \end{pmatrix} = \epsilon \begin{pmatrix} \psi(\vec{r}\uparrow) \\ \psi(\vec{r}\downarrow) \end{pmatrix}$$

where

$$\begin{cases} h_\uparrow(\vec{r}) = -\frac{1}{2}\nabla^2 + v_\uparrow(\vec{r}) \\ h_\downarrow(\vec{r}) = -\frac{1}{2}\nabla^2 + v_\downarrow(\vec{r}) \end{cases}$$

In this case the eigenfunctions have the general form

$$\Phi_i(\vec{r}) = \begin{pmatrix} \varphi_\uparrow(\vec{r}) \\ 0 \end{pmatrix} \qquad h_\uparrow(\vec{r})\,\varphi_\uparrow(\vec{r}) = \epsilon_{i\uparrow}\,\varphi_\uparrow(\vec{r})$$

and

$$\Phi_i(\vec{r}) = \begin{pmatrix} 0 \\ \varphi_\downarrow(\vec{r}) \end{pmatrix} \qquad h_\downarrow(\vec{r})\,\varphi_\downarrow(\vec{r}) = \epsilon_{i\downarrow}\,\varphi_\downarrow(\vec{r})$$

The Hamiltonian for a many-particle system in a magnetic field has the form

$$\hat{H} = \hat{T} + \hat{U} + \hat{W}$$

$$\hat{U} = \sum_{i=1}^{N} \hat{u}(\vec{r}_i)$$

where

$$\left(\hat{u}(r_i)\,\Psi\right)(\vec{r}_1\sigma_1,\ldots,\vec{r}_N\sigma_N) = \sum_{\sigma_i'=\pm 1} u_{\sigma_i\sigma_i'}(\vec{r}_i)\,\Psi(r_1\sigma_1,\ldots r_i\sigma_i'\ldots\vec{r}_N\sigma_N)$$

Further important operators are the spin operators

$$\hat{S}_i = \frac{1}{2}\sum_{j=1}^{N} \hat{\sigma}_i^{(j)} \qquad (i = x,y,z)$$

where

$$\left(\hat{\sigma}_i^{(j)}\Psi\right)(\vec{r}_1\sigma_1,\ldots,\vec{r}_N\sigma_N) = \sum_{\sigma_j'=\pm 1} \sigma_{i,\sigma_j\sigma_j'}\,\Psi(\vec{r}_1\sigma_1,\ldots\vec{r}_j\sigma_j'\ldots\vec{r}_N\sigma_N)$$

If $u_{\sigma\sigma'}(\vec{r})$ is diagonal $u_{\sigma\sigma'}(r) = \begin{pmatrix} v_\uparrow(r) & 0 \\ 0 & v_\downarrow(r) \end{pmatrix}$

Then the Hamiltonian commutes with $\hat{S}_z$

$[\hat{H}, \hat{S}_z] = 0$, and the eigenstates can be labeled with the eigenvalues of $\hat{S}_z$. , $\hat{S}_z\Psi = m_z\Psi$

However, for general magnetic fields $\vec{B}(\vec{r})$ the Hamiltonian no longer commutes with $\hat{S}_z$.

The spin density matrix

Let us now look at the expectation value of $\hat{U}$

$$\langle \Psi | \hat{U} | \Psi \rangle = \sum_{\sigma_1 \cdots \sigma_N} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \; \Psi^*(\vec{r}_1\sigma_1, \cdots, \vec{r}_N\sigma_N)\,(U\Psi)(\vec{r}_1\sigma_1, \cdots, \vec{r}_N\sigma_N)$$

$$= \sum_{\sigma_1 \cdots \sigma_N} \sum_{j=1}^{N} \sum_{\sigma_j' = \pm 1} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \; \Psi^*(\vec{r}_1\sigma_1, \cdots, \vec{r}_N\sigma_N)\, U_{\sigma_j\sigma_j'}(\vec{r}_j)\, \Psi(\vec{r}_1\sigma_1 \cdots \vec{r}_j\sigma_j' \cdots \vec{r}_N\sigma_N)$$

$$= N \sum_{\sigma_1 \cdots \sigma_N} \sum_{\sigma_1' = \pm 1} \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \; U_{\sigma_1\sigma_1'}(\vec{r}_1)\, \Psi^*(\vec{r}_1\sigma_1 \cdots \vec{r}_N\sigma_N)\, \Psi(\vec{r}_1\sigma_1', \vec{r}_2\sigma_2 \cdots \vec{r}_N\sigma_N)$$

$$= \sum_{\sigma_1, \sigma_1'} \int d^3\vec{r} \; n_{\sigma_1\sigma_1'}(\vec{r})\, U_{\sigma_1\sigma_1'}(\vec{r}) \qquad (*)$$

Where we defined the spin density matrix $\left(n_{\sigma\sigma'}(\vec{r}) = n^*_{\sigma'\sigma}(\vec{r}) \right)$

$$n_{\sigma\sigma'}(\vec{r}) = N \sum_{\sigma_2 \cdots \sigma_N} \int d^3\vec{r}_2 \cdots d^3\vec{r}_N \; \Psi^*(\vec{r}\sigma, \vec{r}_2\sigma_2 \cdots \vec{r}_N\sigma_N)\, \Psi(\vec{r}\sigma', \vec{r}_2\sigma_2 \cdots \vec{r}_N\sigma_N)$$

So the natural variables to be used in the Hohenberg-Kohn theorem are $U_{\sigma\sigma'}(\vec{r})$ and $n_{\sigma\sigma'}(\vec{r})$.

If we use the explicit form of $U_{\sigma\sigma'}$:

$$U_{\sigma\sigma'}(\vec{r}) = \delta_{\sigma\sigma'}\, v(\vec{r}) - \mu\, \vec{B}(\vec{r}) \cdot \vec{\sigma}_{\sigma\sigma'}$$

then we can write $(*)$ also as

$$\langle \Psi | \hat{U} | \Psi \rangle = \int d^3\vec{r} \; n(\vec{r})\, v(\vec{r}) - \int d^3\vec{r} \; \vec{B}(\vec{r}) \cdot \vec{m}(\vec{r})$$

where $n(\vec{r}) = n_{\uparrow\uparrow}(\vec{r}) + n_{\downarrow\downarrow}(\vec{r})$

$$m_j(\vec{r}) = \mu \sum_{\sigma\sigma'} \sigma_{j,\sigma\sigma'}\, n_{\sigma\sigma'}(\vec{r})$$

More explicitly we have

$$m_x(\vec{r}) = \mu \left(n_{\uparrow\downarrow}(\vec{r}) + n_{\downarrow\uparrow}(\vec{r}) \right)$$

$$m_y(\vec{r}) = -i\mu \left(n_{\uparrow\downarrow}(\vec{r}) - n_{\downarrow\uparrow}(\vec{r}) \right)$$

$$m_z(\vec{r}) = \mu \left(n_{\uparrow\uparrow}(\vec{r}) - n_{\downarrow\downarrow}(\vec{r}) \right)$$

In this representation we see that the natural objects to be used in the HK theorem are

$(v(\vec{r}), \vec{B}(\vec{r}))$ and $(n(\vec{r}), \vec{m}(\vec{r}))$

We will see that in spin DFT there is no 1-1 correspondence anymore. However, the following statement is still true.

A nondegenerate ground state Ψ is a unique functional of the ground state density matrix $n_{\sigma\sigma'}$.

Proof. Let us consider Ψ_1 and Ψ_2

$$\hat{H}_1 \Psi_1 = (\hat{T} + \hat{U}_1 + \hat{W}) \Psi_1 = E_1 \Psi_1$$
$$\hat{H}_2 \Psi_2 = (\hat{T} + \hat{U}_2 + \hat{W}) \Psi_2 = E_2 \Psi_2$$

and assume $\Psi_1 \neq \Psi_2$ that they both yield the same ground state spin density matrix $n_{\sigma\sigma'}(\vec{r})$.

Then $E_1 = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle = \langle \Psi_1 | \hat{H}_2 + (\hat{U}_1 - \hat{U}_2) | \Psi_1 \rangle$

$$= \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle + \sum_{\sigma\sigma'} \int d^3\vec{r}\; n_{\sigma\sigma'}(\vec{r}) \left(u_{1,\sigma\sigma'}(\vec{r}) - u_{2,\sigma\sigma'}(\vec{r}) \right)$$

$$> E_2 + \sum_{\sigma\sigma'} \int d^3\vec{r}\; n_{\sigma\sigma'}(\vec{r}) \left(u_{1,\sigma\sigma'}(\vec{r}) - u_{2,\sigma\sigma'}(\vec{r}) \right)$$

Interchanging the indices $1 \leftrightarrow 2$ and adding the equations leads to the contradiction

$$E_1 + E_2 < E_1 + E_2$$

$\Rightarrow$ Our assumption was wrong!

$$\Psi_1 \neq \Psi_2 \Rightarrow n^{(1)}_{\sigma\sigma'} \neq n^{(2)}_{\sigma\sigma'}$$

So we can write $\Psi[n_{\sigma\sigma'}]$.

We can then also define an energy functional

$$E_u[n_{\sigma\sigma'}] = \langle \Psi[n_{\sigma\sigma'}] | \hat{T} + \hat{U} + \hat{W} | \Psi[n_{\sigma\sigma'}] \rangle$$

$$= \underbrace{F_{HK}[n_{\sigma\sigma'}]}_{\text{universal functional}} + \sum_{\sigma\sigma'} \int d^3\vec{r}\; n_{\sigma\sigma'}(\vec{r})\, u_{\sigma\sigma'}(\vec{r})$$

$$F_{HK}[n_{\sigma\sigma'}] = \langle \Psi[n_{\sigma\sigma'}] | \hat{T} + \hat{W} | \Psi[n_{\sigma\sigma'}] \rangle$$

The ground state spin density matrix is obtained by minimization of the energy

$$\frac{\delta E_u}{\delta n_{\sigma\sigma'}(\vec{r})} = 0$$

or equivalently

$$\frac{\delta F_{HK}[n_{\sigma\sigma'}]}{\delta n_{\sigma\sigma'}(\vec{r})} = -u_{\sigma\sigma'}(\vec{r})$$

There is, however, no 1-1 correspondence between potentials $u_{\sigma\sigma'}$ and spin-density matrices $n_{\sigma\sigma'}(\vec{r})$. If we look at the first part of the HK proof

$$\hat{H}_1 \Psi_1 = (\hat{T} + \hat{U}_1 + \hat{W})\Psi_1 = E_1 \Psi_1$$
$$\hat{H}_2 \Psi_1 = (\hat{T} + \hat{U}_2 + \hat{W})\Psi_1 = E_2 \Psi_1$$

$$\Rightarrow \quad (\hat{U}_1 - \hat{U}_2)\Psi_1 = (E_1 - E_2)\Psi_1$$

We cannot conclude from this equation that

$\Delta\hat{U} = \hat{U}_1 - \hat{U}_2$ must be a constant, since $\Delta\hat{U}$ is a nonlocal operator in spin space.

The von Barth - Hedin example

(U. von Barth, L. Hedin, J. Phys. C5, 1629 (1972))

Consider the one-particle system

$$\sum_{\tau=\pm 1} h_{\sigma\sigma'}(\vec{r})\,\psi(\vec{r}\sigma') = \varepsilon\,\psi(\vec{r}\sigma)$$

and construct the vector

$$\hat{u}_i(\vec{r}) = \frac{\sum_{\sigma\beta=\pm 1} \psi^*(\vec{r}\sigma)\,\sigma_{i,\sigma\beta}\,\psi(\vec{r}\beta)}{\sum_{\sigma=\pm 1} |\psi(\vec{r}\sigma)|^2}$$

Then $$\sum_{\beta} (\hat{u}\cdot\vec{\sigma})_{\sigma\beta}\,\psi(\vec{r}\beta) = \psi(\vec{r}\sigma)$$

Check: We use the following property of the Pauli matrices

$$\sum_{i}^{3} \sigma_{i,\sigma\beta}\,\sigma_{i,\gamma\delta} = 2\,\delta_{\sigma\delta}\,\delta_{\gamma\beta} - \delta_{\sigma\beta}\,\delta_{\gamma\delta}$$

Then:

$$\sum_{\beta} (\hat{u}\cdot\vec{\sigma})_{\sigma\beta}\,\psi(\vec{r}\beta) = \sum_{\beta}\sum_{i}^{3} \hat{u}_i(\vec{r})\,\sigma_{i,\sigma\beta}\,\psi(\vec{r}\beta)$$

$$= \frac{\sum_{\gamma\delta\beta} \psi^*(\vec{r}\gamma)\,\psi(\vec{r}\delta)\,\psi(\vec{r}\beta)\,\sum_{i}^{3}\sigma_{i,\sigma\beta}\sigma_{i,\gamma\delta}}{\sum_{\beta}|\psi(\vec{r}\beta)|^2}$$

$$= \frac{\sum_{\gamma\delta\beta} \psi^*(\vec{r}\gamma)\,\psi(\vec{r}\delta)\,\psi(\vec{r}\beta)\,(2\,\delta_{\sigma\delta}\,\delta_{\gamma\beta} - \delta_{\sigma\beta}\,\delta_{\gamma\delta})}{\sum_{\beta}|\psi(\vec{r}\beta)|^2}$$

$$= \frac{\sum_{\beta} 2\,\psi^*(\vec{r}\beta)\,\psi(\vec{r}\beta)\,\psi(\vec{r}\sigma) - \sum_{\gamma}\psi^*(\vec{r}\gamma)\,\psi(\vec{r}\gamma)\,\psi(\vec{r}\sigma)}{\sum_{\beta}|\psi(\vec{r}\beta)|^2}$$

$$= \frac{\sum_{\beta}|\psi(\vec{r}\beta)|^2}{\sum_{\beta}|\psi(\vec{r}\beta)|^2}\,\psi(\vec{r}\sigma) = \psi(\vec{r}\sigma)$$

q.e.d.

This means that for any potential $V_0(\vec{r})$ and

$$V_{\alpha\beta}(\vec{r}) = V_0(\vec{r})\left((\hat{u}\cdot\vec{\sigma})_{\alpha\beta} - \delta_{\alpha\beta}\right)$$

we have that

$$\sum_\beta V_{\alpha\beta}(\vec{r})\,\psi(\vec{r}\beta) = V_0(\vec{r})\left\{\sum_\beta (\hat{u}\cdot\vec{\sigma})_{\alpha\beta}\psi(\vec{r}\beta) - \psi(\vec{r}\alpha)\right\}$$

$$= V_0(\vec{r})\left(\psi(\vec{r}\alpha) - \psi(\vec{r}\alpha)\right) = 0$$

So if $\sum_\beta h_{\alpha\beta}(\vec{r})\,\psi(\vec{r}\beta) = \epsilon\,\psi(\vec{r}\alpha)$

then for $h'_{\alpha\beta}(\vec{r}) = h_{\alpha\beta}(\vec{r}) + V_{\alpha\beta}(\vec{r})$

we have that $\sum_\beta h'_{\alpha\beta}(\vec{r})\,\psi(\vec{r}\beta) = \epsilon\,\psi(\vec{r}\alpha)$

For small enough $V_0(\vec{r})$ then $\psi(\vec{r}\alpha)$ will also be ground state of $h'_{\alpha\beta}$.

So we have found a class of potentials that give the same ground state and therefore also the same spin density matrix $n_{\alpha\beta}(\vec{r})$, which for the one-particle system is given by

$$n_{\alpha\beta}(\vec{r}) = \psi^*(\vec{r}\alpha)\psi(\vec{r}\beta)$$

So there is no 1-1 correspondence between $n_{\alpha\beta}(\vec{r})$ and $v_{\alpha\beta}(\vec{r})$.

We further note that

$$\sum_i^3 \hat{u}_{i;i}^2(\vec{r}) = \sum_i^3 \sum_{\gamma\beta\delta} \frac{\psi^*(\vec{r}\alpha)\psi(\vec{r}\beta)\psi^*(\vec{r}\delta)\psi(\vec{r}\delta)\,\sigma_{i,\alpha\beta}\sigma_{i,\gamma\delta}}{\left(\sum_\gamma |\psi(\vec{r}\gamma)|^2\right)^2}$$

$$= \sum_{\gamma\beta\delta} \frac{\psi^*(\vec{r}\alpha)\psi(\vec{r}\beta)\psi^*(\vec{r}\delta)\psi(\vec{r}\delta)\,\left(2\delta_{\alpha\delta}\delta_{\gamma\beta} - \delta_{\alpha\beta}\delta_{\gamma\delta}\right)}{\left(\sum_\gamma |\psi(\vec{r}\gamma)|^2\right)^2}$$

$$= \sum_{\gamma\beta} \frac{2\,|\psi^*(\vec{r}\alpha)|^2\,|\psi(\vec{r}\beta)|^2}{\left(\sum_\gamma |\psi(\vec{r}\gamma)|^2\right)^2} - \sum_{\alpha\gamma} \frac{|\psi(\vec{r}\alpha)|^2\,|\psi(\vec{r}\gamma)|^2}{\left(\sum_\gamma |\psi(\vec{r}\gamma)|^2\right)^2}$$

$$= 1$$

So $\sum_i^3 \hat{u}_{i;i}(\vec{r})^2 = 1$

Some more insight into the von Barth-Hedin example can be obtained from the following case.

Consider the diagonal system for one particle

$$\underbrace{\left(-\frac{1}{2}\nabla^2 + \begin{pmatrix} v_\uparrow(\vec{r}) & 0 \\ 0 & v_\downarrow(\vec{r}) \end{pmatrix}\right)}_{h(\vec{r})} \begin{pmatrix} \Psi(\vec{r}\uparrow) \\ \Psi(\vec{r}\downarrow) \end{pmatrix} = \epsilon \begin{pmatrix} \Psi(\vec{r}\uparrow) \\ \Psi(\vec{r}\downarrow) \end{pmatrix}$$

Let $\varphi_\uparrow$ and $\varphi_\downarrow$ be solutions to

$$\left(-\frac{1}{2}\nabla^2 + v_\uparrow(\vec{r})\right)\varphi_\uparrow(\vec{r}) = \epsilon_\uparrow \varphi_\uparrow(\vec{r})$$

$$\left(-\frac{1}{2}\nabla^2 + v_\downarrow(\vec{r})\right)\varphi_\downarrow(\vec{r}) = \epsilon_\downarrow \varphi_\downarrow(\vec{r})$$

with $\epsilon_\uparrow < \epsilon_\downarrow$

The ground state is given by $\Psi = \begin{pmatrix} \varphi_\uparrow(\vec{r}) \\ 0 \end{pmatrix}$

$\epsilon = \epsilon_\uparrow$

The ground state spin density matrix is

$$n_{\sigma\sigma'}(\vec{r}) = \begin{pmatrix} n_{\uparrow\uparrow}(\vec{r}) & 0 \\ 0 & 0 \end{pmatrix}$$

with $n_{\uparrow\uparrow}(\vec{r}) = \varphi^*(\vec{r})\varphi(\vec{r})$

Now if we consider

$$h'(\vec{r}) = h(\vec{r}) + \begin{pmatrix} 0 & 0 \\ 0 & v_0(\vec{r}) \end{pmatrix}$$

Then $h'(\vec{r}) \begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix} = h(\vec{r}) \begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix} = \epsilon_\uparrow \begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix}$

which will still be the ground state for $v_0(\vec{r})$ small enough. So we have

$$0 = \left(h'(\vec{r}) - h(\vec{r})\right)\begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & v_0(\vec{r}) \end{pmatrix}\begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix}$$

$$= -\frac{v_0(\vec{r})}{2}\left(\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right)\begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix} \qquad (*)$$

If we carry out an arbitrary spin rotation with unitary matrix $Q(\vec{r})$ then $(*)$ becomes

$$0 = -\frac{v_0(\vec{r})}{2}\left\{ Q(\vec{r})\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}Q^+(\vec{r}) - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right\}\begin{pmatrix} \tilde{\psi}(\vec{r}\uparrow) \\ \tilde{\psi}(\vec{r}\downarrow) \end{pmatrix} = 0$$

where $\begin{pmatrix} \tilde{\psi}(\vec{r}\uparrow) \\ \tilde{\psi}(\vec{r}\downarrow) \end{pmatrix} = Q(\vec{r})\begin{pmatrix} \varphi_\uparrow \\ 0 \end{pmatrix}$

Since $U = Q\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}Q^+$ must be Hermitian

and $\det U = -1$, $U^+ = U$

$\mathrm{tr}\, U = 0$

it must be of the form $\begin{pmatrix} u_3 & u_1 - iu_2 \\ u_1 + iu_2 & -u_3 \end{pmatrix}$

$= \vec{\sigma}\cdot\vec{u}$

So we obtain

$$0 = -\frac{V_0(\vec{r})}{2}\left((\vec{\sigma}\cdot\vec{u}) - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right)\begin{pmatrix} \tilde{\psi}(r\uparrow) \\ \tilde{\psi}(r\downarrow) \end{pmatrix} = 0$$

This is exactly the form of the von Barth-Hedin example

The freedom in the potential therefore arises from the possibility of choosing arbitrarily the potential for an unoccupied level of different spin.

What are the consequences for the variational equations of spin DFT?

For the 1-particle system we have

$$E_{u_{\sigma\sigma'}}[n_{\sigma\sigma'}] = \langle \Psi[n_{\sigma\sigma'}] | \hat{T} + \hat{U} | \Psi[n_{\sigma\sigma'}] \rangle$$

$$= \underbrace{\langle \Psi[n_{\sigma\sigma'}] | \hat{T} | \Psi[n_{\sigma\sigma'}] \rangle}_{T_s[n_{\sigma\sigma'}]} + \sum_{\sigma\sigma'} \int d^3\vec{r}\; n_{\sigma\sigma'}(\vec{r}) u_{\sigma\sigma'}(\vec{r})$$

Requiring $\delta E_{u_{\sigma\sigma'}} = 0$ gives

$$0 = \delta T_s[n_{\sigma\sigma'}] + \sum_{\tau\tau'} \int d^3\vec{r}\; u_{\sigma\sigma'}(\vec{r})\, \delta n_{\tau\tau'}(\vec{r}) = 0$$

But for the 1-particle system

$$\delta n_{\sigma\sigma'}(\vec{r}) = \delta\left(\Psi^*(\vec{r}\sigma)\Psi(\vec{r}\sigma')\right)$$
$$= \delta\Psi^*(\vec{r}\sigma)\Psi(\vec{r}\sigma') + \Psi^*(\vec{r}\sigma)\delta\Psi(\vec{r}\sigma')$$

and therefore for the von Barth-Hedin potential

$$\sum_{\sigma\sigma'} \int d^3\vec{r}\; V_{\sigma\sigma'}(\vec{r})\, \delta n_{\sigma\sigma'}(\vec{r})$$

$$= \sum_{\sigma\sigma'} \int d^3\vec{r}\; \delta\Psi^*(\vec{r}\sigma) \underbrace{V_{\sigma\sigma'}(\vec{r})}_{0} \Psi(\vec{r}\sigma') + \text{c.c.} = 0$$

(c.c. = complex conjugate)

where we used $V_{\sigma\sigma'}(\vec{r}) = V_{\sigma'\sigma}(\vec{r})^*$

Therefore the condition

$$0 = \delta T_S[n] + \sum_{\sigma\sigma'} \int d^3\vec{r}\; u_{\sigma\sigma'}(\vec{r})\, \delta n_{\sigma\sigma'}(\vec{r}) = 0$$

gives the equation

$$\frac{\delta T_S}{\delta n_{\sigma\sigma'}(\vec{r})} = -u_{\sigma\sigma'}(\vec{r}) + \lambda\, v_{\sigma\sigma'}(\vec{r}) \qquad \lambda \in \mathbb{R} \qquad (**)$$

Each of the potentials on the right hand side gives the same solution for the spin-density matrix on the left hand side (provided λ is small enough).

Can this sort of degeneracy happen in the many-particle case?

The Schrödinger equation for noninteracting particles:

$$\hat{H} = \hat{T} + \hat{U} = \sum_{i=1}^{N} h_{\sigma\sigma'}(\vec{r}_i)$$

$$h_{\sigma\sigma'}(\vec{r}) = -\frac{\delta_{\sigma\sigma'}}{2}\nabla^2 + u_{\sigma\sigma'}(\vec{r})$$

$$\hat{H}\,\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N) = E\,\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N)$$

$$\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(\vec{r}_1\sigma_1) & \cdots & \Psi_1(\vec{r}_N\sigma_N) \\ \vdots & & \vdots \\ \Psi_N(\vec{r}_1\sigma_1) & \cdots & \Psi_N(\vec{r}_N\sigma_N) \end{vmatrix}$$

with $$\sum_{\sigma'} h_{\sigma\sigma'}(\vec{r})\,\Psi_j(\vec{r}\sigma') = \epsilon_j\,\Psi_j(\vec{r}\sigma)$$

$$E = \sum_{j}^{N} \epsilon_j$$

Let us take the case of a magnetic field $\vec{B}(\vec{r}) = (0, 0, B_z(\vec{r}))$. Then we have

$$\left[-\frac{1}{2}\nabla^2 + \begin{pmatrix} V_\uparrow(\vec{r}) & 0 \\ 0 & V_\downarrow(\vec{r}) \end{pmatrix} \right] \begin{pmatrix} \Psi_{j\uparrow}(\vec{r}) \\ \Psi_{j\downarrow}(\vec{r}) \end{pmatrix} = \epsilon_j \begin{pmatrix} \Psi_{j\uparrow}(\vec{r}) \\ \Psi_{j\downarrow}(\vec{r}) \end{pmatrix}$$

$$V_\uparrow(\vec{r}) = V(\vec{r}) + \mu B_z(\vec{r})$$
$$V_\downarrow(\vec{r}) = V(\vec{r}) - \mu B_z(\vec{r})$$

Let the potentials $V_\uparrow(\vec{r})$ and $V_\downarrow(\vec{r})$ be such that the lowest N states are of the form

$$\Psi_j(\vec{r}) = \begin{pmatrix} \varphi_{j\uparrow}(\vec{r}) \\ 0 \end{pmatrix} \qquad j = 1 \ldots N$$

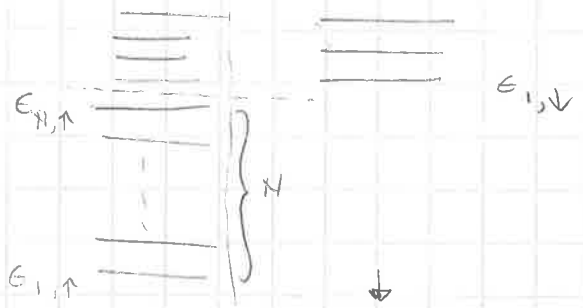
where

$$\left(-\frac{1}{2}\nabla^2 + V_\uparrow(\vec{r})\right) \varphi_{j\uparrow}(\vec{r}) = \epsilon_{j\uparrow}\, \varphi_{j\uparrow}(\vec{r})$$

and that only unoccupied states can be of the the form

$$\Psi_j(\vec{r}) = \begin{pmatrix} 0 \\ \varphi_{j\downarrow}(\vec{r}) \end{pmatrix} \qquad \left(-\frac{1}{2}\nabla^2 + V_\downarrow(\vec{r})\right) \varphi_{j\downarrow}(\vec{r}) = \epsilon_{j\downarrow} \varphi_{j\downarrow}(\vec{r})$$

i.e. $\epsilon_{j\uparrow} < \epsilon_{j\downarrow} \qquad j = 1 \ldots N$



This corresponds to a fully polarized state with

$$S_z \Psi = m_z \Psi \qquad m_z = \frac{N}{2}$$

and

$$n_{\sigma\sigma'}(\vec{r}) = \begin{pmatrix} n_{\uparrow\uparrow}(\vec{r}) & 0 \\ 0 & 0 \end{pmatrix}$$

$$n_{\uparrow\uparrow}(\vec{r}) = \sum_{j=1}^{N} \varphi^*_{j\uparrow}(\vec{r})\, \varphi_{j\uparrow}(\vec{r})$$

It is clear that also for this state $V_{\downarrow}(\vec{r})$ can be chosen arbitrarily as long as $\epsilon_{j,\uparrow} < \epsilon_{j,\downarrow}$ for $j = 1 \cdots N$. (See K. Capelle, G. Vignale, Phys. Rev. Lett. 86, 5546 (2001))

Can we construct for this case an example of the von Barth-Hedin type?

The potential $V_{xc}(\vec{r})$ of the von Barth-Hedin example contains the vector $\hat{u}_i(\vec{r})$ which is constructed in terms of the eigenstate $\Psi_i(\vec{r}\sigma)$. Since we want the potential to be the same for all orbitals we must have

$$\hat{u}_i(\vec{r}) = \hat{u}_j(\vec{r}) \qquad \forall\, i,j \le N$$

This will, however, in general not be the case. (See: H. Eschrig, W.E. Pickett, Solid State Comm. 118, 123 (2001))

Symmetry related nonuniqueness

There is also another nonuniqueness in spin DFT. This is a consequence of the symmetry of the many-particle Hamiltonian for certain choices of the magnetic field

Consider a homogeneous magnetic field in the z-direction $\vec{B} = (0, 0, B_z)$. Then

$$\hat{U} = \sum_{i}^{N} v(\vec{r}_i) - \mu \vec{\sigma}^{(i)} \cdot \vec{B}$$

$$= \sum_{i}^{N} v(\vec{r}_i) - 2\mu B_z \hat{S}_z$$

$$\hat{S}_z = \frac{1}{2} \sum_{i=1}^{N} \sigma^{(i)}$$

Consider further the interaction system

$$\hat{H}_u = \hat{T} + \hat{U} + \hat{W} \qquad , \qquad \hat{H}\Psi = E\Psi$$

It is clear that $[\hat{H}, \hat{S}_z] = 0$ and therefore the eigenstates of $\hat{H}$ can also be chosen to be eigenstates of $\hat{S}_z$.

So if we have a ground state Ψ_0 of

$$\hat{H}_v = \hat{T} + \hat{V} + \hat{W} \qquad \hat{V} = \sum_{i=1}^{N} v(\vec{r}_i)$$

$$\hat{H}_v \Psi_0 = E_0 \Psi_0$$

Then $\hat{H}_u \Psi_0 = \left(\hat{H}_v - 2\mu B_z \hat{S}_z \right) \Psi_0$

$$= \left(E_0 - 2\mu B_z m_z \right) \Psi_0 = E_0' \Psi_0$$

therefore Ψ_0 is also eigenstate of $\hat{H}_u$!

For small enough B_z is will also be ground state of $\hat{H}_u$.

Therefore, knowledge of the ground state wave function $\Psi_0(\vec{r}_1 \sigma_1, \ldots \vec{r}_N \sigma_N)$ does not determine the applied magnetic field. Therefore also $n_{\uparrow\downarrow}(\vec{r})$ does not determine the applied magnetic field.

For noninteracting particles this reduces to the equations

$$\left(-\frac{1}{2}\nabla^2 + \begin{pmatrix} v(\vec{r}) - \mu B_z & 0 \\ 0 & v(\vec{r}) + \mu B_z \end{pmatrix} \right) \begin{pmatrix} \Psi_j(\vec{r}\uparrow) \\ \Psi_j(\vec{r}\downarrow) \end{pmatrix} = \epsilon_j \begin{pmatrix} \Psi_j(\vec{r}\uparrow) \\ \Psi_j(\vec{r}\downarrow) \end{pmatrix}$$

The solutions are of the form

$$\Psi_j(\vec{r}) = \begin{pmatrix} \varphi_j(\vec{r}) \\ 0 \end{pmatrix}, \quad \epsilon_j = \epsilon_j^0 + \mu B_z$$

$$\Psi_j(\vec{r}) = \begin{pmatrix} 0 \\ \varphi_j(\vec{r}) \end{pmatrix}, \quad \epsilon_j = \epsilon_j^0 - \mu B_z$$

$$\left(-\frac{1}{2}\nabla^2 + v(\vec{r}) \right) \varphi_j(\vec{r}) = \epsilon_j^0 \varphi_j(\vec{r})$$

The density matrix $n_{\sigma\sigma'}(\vec{r})$ is of the form

$$n_{\sigma\sigma'}(\vec{r}) = \begin{pmatrix} n_{\uparrow\uparrow}(\vec{r}) & 0 \\ 0 & n_{\downarrow\downarrow}(\vec{r}) \end{pmatrix}$$

$$n_{\uparrow\uparrow}(\vec{r}) = \sum_{j=1}^{N_\uparrow} \varphi_j^*(\vec{r})\,\varphi_j(\vec{r})$$

$$n_{\downarrow\downarrow}(\vec{r}) = \sum_{j=1}^{N_\downarrow} \varphi_j^*(\vec{r})\,\varphi_j(\vec{r})$$

The indeterminacy in B_z is then a consequence of the fact that the orbitals φ_j do not determine the arbitrary constant that can be added to the potential $v(\vec{r})$.

It is clear that there is nothing special about the z-axis. The kind of nonuniqueness that we encountered here occurs for any quantization axis that we prefer to choose

We will see that the kind of nonuniqueness described here does not prevent the construction of a useful Kohn-Sham scheme.

The fact that there could be more KS potentials yielding a given spin-density matrix $n_{\sigma\sigma'}(\vec{r})$ does not matter, since the corresponding Kohn-Sham eigenstates are identical (due to the $n_{\sigma\sigma'} \leftrightarrow \pm\{n_{\sigma\sigma'}\}$ mapping that we proved). Therefore all quantities expressed in terms of Kohn-Sham states are well-defined.

The only thing we have to be careful with are functional derivatives, are they maybe defined up to a class of additional potentials (see (**)).

Spin Kohn-Sham theory

Due to the $n_{\sigma\sigma'}(\vec{r}) \longleftrightarrow \Psi[n_{\sigma\sigma'}]$ mapping we can consider a noninteracting system with given spin-density matrix $n_{\sigma\sigma'}(\vec{r})$

$$\hat{H}_S = \hat{T} + \hat{V}_S$$

$$\hat{H}_S \Phi_S[n_{\sigma\sigma'}] = E_S \Phi_S[n_{\sigma\sigma'}]$$

$$\Phi_S[n_{\sigma\sigma'}] = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \cdots & \psi_1(\vec{r}_N\sigma_N) \\ \vdots & & \\ \psi_N(\vec{r}_1\sigma_1) & \cdots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix}$$

$$n_{\sigma\sigma'}(\vec{r}) = \sum_{i=1}^{N} \psi_i^*(\vec{r}\sigma) \psi_i(\vec{r}\sigma')$$

$$\sum_{\sigma'} h_{\sigma\sigma',S}(\vec{r}) \psi_i(\vec{r}\sigma') = \epsilon_i \psi_i(\vec{r}\sigma)$$

$$h_{\sigma\sigma',S}(\vec{r}) = -\frac{\delta_{\sigma\sigma'}}{2}\nabla^2 + v_{S,\sigma\sigma'}(\vec{r})$$

The Kohn-Sham kinetic energy is then defined as

$$T_S[n_{\sigma\sigma'}] = \langle \Phi_S[n_{\sigma\sigma'}] | \hat{T} | \Phi_S[n_{\sigma\sigma'}] \rangle$$

$$= \sum_{i=1}^{N} \sum_{\sigma=\pm 1} -\frac{1}{2} \int d^3\vec{r}\, \psi_i^*(\vec{r}\sigma) \nabla^2 \psi_i(\vec{r}\sigma)$$

The total density $n(\vec{r}) = \sum_\sigma n_{\sigma\sigma}(\vec{r}) = n_{\uparrow\uparrow}(\vec{r}) + n_{\downarrow\downarrow}(\vec{r})$

such that we define the Hartree energy as usual

$$E_H[n_{\sigma\sigma'}] = \frac{1}{2} \int d^3\vec{r}\, d^3\vec{r}\,' \frac{n(\vec{r}) n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

The exchange-correlation energy is then defined as

$$E_{xc}[n_{\sigma\sigma'}] = F_{HK}[n_{\sigma\sigma'}] - T_s[n_{\sigma\sigma'}] - E_H[n_{\sigma\sigma'}]$$

We can therefore write the total energy as

$$E_u[n_{\sigma\sigma'}] = T_s[n_{\sigma\sigma'}] + \sum_{\sigma\sigma'} \int d^3\vec{r}\; u_{\sigma\sigma'}(\vec{r})\, n_{\sigma\sigma'}(\vec{r}) + E_H[n_{\sigma\sigma'}] + E_{xc}[n_{\sigma\sigma'}]$$

We can now simply copy the proofs for the nonmagnetic case. The spin-density matrix is determined by

$$0 = \frac{\delta E_u}{\delta n_{\sigma\sigma'}(\vec{r})} = \frac{\delta T_s}{\delta n_{\sigma\sigma'}(\vec{r})} + u_{\sigma\sigma'}(\vec{r}) + \delta_{\sigma\sigma'} V_H[n_{\sigma\sigma'}](\vec{r}) + V_{xc}[n_{\sigma\sigma'}](\vec{r})$$

$$\| \frac{\delta E_{xc}}{\delta n_{\sigma\sigma'}(\vec{r})}$$

where $V_H[n_{\sigma\sigma'}](\vec{r}) = \delta_{\sigma\sigma'} \int d^3\vec{r}\; \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}$

Moreover $\frac{\delta T_s}{\delta n_{\sigma\sigma'}(\vec{r})} = -V_{s,\sigma\sigma'}(\vec{r})$

$$\Rightarrow V_{s,\sigma\sigma'}(\vec{r}) = u_{\sigma\sigma'}(\vec{r}) + \delta_{\sigma\sigma'} V_H[n_{\sigma\sigma'}](\vec{r}) + V_{xc}[n_{\sigma\sigma'}](\vec{r})$$

The main task is therefore to find approximations for $E_{xc}[n_{\sigma\sigma'}]$ and $V_{xc}[n_{\sigma\sigma'}](\vec{r})$

In the following we consider the special case that the potential is of the form

$$U_{\sigma\sigma'}(\vec{r}) = \begin{pmatrix} V_\uparrow(\vec{r}) & 0 \\ 0 & V_\downarrow(\vec{r}) \end{pmatrix}$$

(Magnetic field in the z-direction).

The spin-density matrix is then of the form

$$n_{\sigma\sigma'}(\vec{r}) = \begin{pmatrix} n_\uparrow(\vec{r}) & 0 \\ 0 & n_\downarrow(\vec{r}) \end{pmatrix}$$

(we use the notation $n_\sigma(\vec{r}) \equiv n_{\sigma\sigma}(\vec{r})$)

Then we write $\Psi[n_{\sigma\sigma'}] = \Psi[n_\uparrow, n_\downarrow]$.
The KS-potential attains the form,

$$V_{s,\sigma}(\vec{r}) = V_\sigma(\vec{r}) + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc,\sigma}[n_\uparrow, n_\downarrow](\vec{r})$$

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

and the KS-equations are given by

$$\left(-\frac{1}{2}\nabla^2 + \begin{pmatrix} V_{s,\uparrow}(\vec{r}) & 0 \\ 0 & V_{s,\downarrow}(\vec{r}) \end{pmatrix}\right) \begin{pmatrix} \psi_j(\vec{r}\uparrow) \\ \psi_j(\vec{r}\downarrow) \end{pmatrix} = \epsilon_j \begin{pmatrix} \psi(\vec{r}\uparrow) \\ \psi(\vec{r}\downarrow) \end{pmatrix}$$

$$n_\uparrow(\vec{r}) = \sum_{j=1}^{N_\uparrow} \psi_j^*(\vec{r}\uparrow)\,\psi_j(\vec{r}\uparrow)$$

$$n_\downarrow(\vec{r}) = \sum_{j=1}^{N_\downarrow} \psi_j^*(\vec{r}\downarrow)\,\psi_j(\vec{r}\downarrow)$$

Due to the diagonal form of the potential the Kohn-Sham orbitals are of the form

$$\Psi_j(\vec{r}) = \begin{pmatrix} \varphi_{j,\uparrow}(\vec{r}) \\ 0 \end{pmatrix}, \quad \Psi_j(\vec{r}) = \begin{pmatrix} 0 \\ \varphi_{j,\downarrow}(\vec{r}) \end{pmatrix}$$

$j = 1 \dots N_\uparrow$ $\qquad$ $j = 1 \dots N_\downarrow$ $\qquad$ $N = N_\uparrow + N_\downarrow$

We summarize these equations in a form they often appear in the literature

$$\left(-\frac{1}{2}\nabla^2 + V_{s,\sigma}(\vec{r})\right)\varphi_{j,\sigma}(\vec{r}) = \epsilon_\sigma \varphi_{j,\sigma}(\vec{r})$$

$$n_\sigma(\vec{r}) = \sum_{j=1}^{N_\sigma} |\varphi_{j,\sigma}(\vec{r})|^2$$

$$V_{s,\sigma}(\vec{r}) = V_\sigma(\vec{r}) + \int d^3\vec{r}\, \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc,\sigma}(\vec{r})$$

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

We can now define the exchange functional as we did before

$$E_x[n_\uparrow, n_\downarrow] = -\frac{1}{2}\sum_\sigma \int d^3\vec{r}\, d^3\vec{r}'\, \frac{|\gamma_s(\vec{r}\sigma, \vec{r}'\sigma)|^2}{|\vec{r}-\vec{r}'|}$$

$$\left(= \langle \Phi_s[n_\uparrow, n_\downarrow] | \hat{W} | \Phi_s[n_\uparrow, n_\downarrow] \rangle - E_H[n] \right)$$

where

$$\gamma_s(\vec{r}\sigma, \vec{r}'\sigma) = \sum_{j=1}^{N} \psi_j^*(\vec{r}\sigma)\, \psi_j(\vec{r}'\sigma)$$

So

$$\gamma_s(\vec{r}\uparrow, \vec{r}'\uparrow) = \sum_{j=1}^{N_\uparrow} \varphi_{j,\uparrow}^*(\vec{r})\, \varphi_{j,\uparrow}(\vec{r}') = \gamma_{s,\uparrow}(\vec{r}, \vec{r}')$$

$$\gamma_s(\vec{r}\downarrow, \vec{r}'\downarrow) = \sum_{j=1}^{N_\downarrow} \varphi_{j,\downarrow}^*(\vec{r})\, \varphi_{j,\downarrow}(\vec{r}') = \gamma_{s,\downarrow}(\vec{r}, \vec{r}')$$

Therefore the exchange functional attains the form

$$E_x[n_\uparrow, n_\downarrow] = -\frac{1}{2}\int d^3\vec{r}\, d^3\vec{r}'\, \frac{|\gamma_{s,\uparrow}(\vec{r}, \vec{r}')|^2}{|\vec{r}-\vec{r}'|}$$

$$-\frac{1}{2}\int d^3\vec{r}\, d^3\vec{r}'\, \frac{|\gamma_{s,\downarrow}(\vec{r}, \vec{r}')|^2}{|\vec{r}-\vec{r}'|}$$

We see that

$$E_x[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, 0] + E_x[0, n_\downarrow] \qquad (***)$$

On the other hand for a spin-unpolarized system we have

$$E_x[n] = E_x\left[\frac{n}{2}, \frac{n}{2}\right] = 2E_x\left[\frac{n}{2}, 0\right] = 2E_x\left[0, \frac{n}{2}\right]$$

$$\Rightarrow E_x[n, 0] = \frac{1}{2}E_x[2n] = E_x[0, n]$$

So Eq. (***) becomes

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}\left(E_x[2n_\uparrow] + E_x[2n_\downarrow]\right)$$

In this way we immediately obtain the spin-polarized form for all the exchange-functionals such as LDA, GGA that we derived before.

For example

$$E_x^{LSDA}[n_\uparrow, n_\downarrow] = \frac{1}{2}\left(E_x^{LDA}[2n_\uparrow] + E_x^{LDA}[2n_\downarrow]\right)$$

$$= \frac{A_x}{2}\int d^3\vec{r}\left\{(2n_\uparrow(\vec{r}))^{4/3} + (2n_\downarrow(\vec{r}))^{4/3}\right)$$

$$= A_x 2^{1/3}\int d^3\vec{r}\left(n_\uparrow^{4/3}(\vec{r}) + n_\downarrow^{4/3}(\vec{r})\right)$$

$$A_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

LSDA = Local Spin Density Approximation

For the correlation functional defined as

$$E_c[n_\uparrow, n_\downarrow] = E_{xc}[n_\uparrow, n_\downarrow] - E_x[n_\uparrow, n_\downarrow]$$

do such simple relations to the unpolarized case not exist

Nevertheless, on the basis of many-body theory for the homogeneous and weakly inhomogeneous electron gas, one can derive expressions for LDA and GGA correlation functionals in the same way as we described earlier

Final remark:

Spin DFT also applies in the limit of zero magnetic field

For that case it can be used to predict the spin densities $n_\uparrow$ and $n_\downarrow$ rather than the total density $n_\uparrow + n_\downarrow$ for a system for which the expectation value $\langle S_z \rangle$ does not vanish.

This is generally the case for systems with an odd number of electrons, such as the H or Li atoms (in for example the $1s\uparrow$ and $1s\uparrow, 1s\downarrow, 2s\uparrow$ states).