

Spin-polarized DFT

Lecture 32

CHM 652 / PHY 626

Electronic Structure of Materials

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Lecture Plan

- Spin density as a variable
- Spin-polarized systems
- Spin-restricted vs unrestricted Kohn-Sham systems
- Spin-scaling of functionals

Spin Density as a Variable

In principle, the density (spinless) is the basic variable in DFT. However, in some applications it is quite useful to think of this arising from two contributions.

$$n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$$
$$n_{\uparrow/\downarrow}(\mathbf{r}) = n(\mathbf{r}, \sigma = \pm \frac{1}{2})$$

So that each spin-density is allowed to vary subject to the normalisation of their sum to N . This makes the energy a functional of both.

$$E \equiv E[n_{\uparrow}, n_{\downarrow}]$$

The H-K Theorems can easily be reformulated in terms of the spin-density functionals.

$$E_0 = \min_{\rho} E[\rho] = \min_{\rho} \left\{ q_e \int \rho(\mathbf{r}) v_{\text{nuc}}(\mathbf{r}) d^3r + \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle \right\}$$
$$= \min_{\rho} \left\{ q_e \int \rho(\mathbf{r}) v_{\text{nuc}}(\mathbf{r}) d^3r + \min_{\rho^{\alpha}, \rho^{\beta} \rightarrow \rho} \left[\min_{\Psi \rightarrow \rho^{\alpha}, \rho^{\beta}} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle \right] \right\}$$

Spin-polarized systems

When the ground-state of an electronic system corresponds to

$$n_{\uparrow}(\mathbf{r}) \neq n_{\downarrow}(\mathbf{r})$$

The system is said to be spin-polarized or, since this is often the case, magnetised.

We define the spin-polarisation as

$$\zeta(\mathbf{r}) \equiv \frac{n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})}{n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})} \quad \longrightarrow \quad n_{\uparrow/\downarrow} = \frac{(1 \pm \zeta)}{2}$$

Along with $n(\mathbf{r})$, this variable now can describe the energy functionals.

$$E \equiv E[n_{\uparrow}, n_{\downarrow}] \equiv E[n, \zeta]$$

Spin-restricted vs. Unrestricted KS systems

It can be shown that an analogous treatment yields the Spin-polarized KS equations

$$\left(\frac{-\nabla^2}{2} + v_s^\uparrow(\mathbf{r}) \right) \phi_{i,\uparrow} = \epsilon_{i,\uparrow} \phi_{i,\uparrow}$$
$$\left(\frac{-\nabla^2}{2} + v_s^\downarrow(\mathbf{r}) \right) \phi_{i,\downarrow} = \epsilon_{i,\downarrow} \phi_{i,\downarrow}$$

$$v_s^\tau(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^\tau[n_\uparrow, n_\downarrow](\mathbf{r})$$

$$v_{xc}^\tau[n_\uparrow, n_\downarrow](\mathbf{r}) = \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\tau(\mathbf{r})}$$

Spin-restricted vs. Unrestricted KS systems

The polarised and unpolarised equations can be connected but are not the same.

Table 2. Definition of the noninteracting kinetic energy, exchange–correlation energy, and exchange–correlation potential in the spin-restricted and spin-unrestricted formulations of KS-DFT.

	Spin-restricted KS-DFT	Spin-unrestricted KS-DFT
Noninteracting kinetic energy	$T_s[\rho] = \min_{\Psi_s \rightarrow \rho} \langle \Psi_s \hat{T} \Psi_s \rangle$	$T_s^{(u)}[\rho, Q] = \min_{\Psi_s^{(u)} \rightarrow \rho, Q} \langle \Psi_s^{(u)} \hat{T} \Psi_s^{(u)} \rangle$
Decomposition of HK functional	$F_{\text{HK}}[\rho, Q] = T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho, Q]$	$F_{\text{HK}}[\rho, Q] = T_s^{(u)}[\rho, Q] + J[\rho] + E_{\text{xc}}^{(u)}[\rho, Q]$
Exchange–correlation energy	$E_{\text{xc}}[\rho, Q] = F_{\text{HK}}[\rho, Q] - T_s[\rho] - J[\rho]$	$E_{\text{xc}}^{(u)}[\rho, Q] = F_{\text{HK}}[\rho, Q] - T_s^{(u)}[\rho, Q] - J[\rho]$
Exchange–correlation potential	$v_{\text{xc}}[\rho] = \frac{1}{q_e} \frac{\delta E_{\text{xc}}[\rho, Q]}{\delta \rho(\mathbf{r})}$	$v_{\text{xc}}^{\text{tot}}[\rho, Q] = \frac{1}{q_e} \frac{\delta E_{\text{xc}}^{(u)}[\rho, Q]}{\delta \rho(\mathbf{r})}$ $v_{\text{xc}}^{\text{spin}}[\rho, Q] = \frac{1}{q_e} \frac{\delta E_{\text{xc}}^{(u)}[\rho, Q]}{\delta Q(\mathbf{r})}$

Spin-restricted vs. Unrestricted KS systems

Spin-restricted or polarised calculations become essential in some cases.

Table 1. Comparison of the spin-restricted and spin-unrestricted formulations of KS-DFT. "Correct" indicates that the quantity calculated for the noninteracting reference system agrees with the corresponding one of the fully interacting system.

	Spin-restricted KS-DFT	Spin-unrestricted KS-DFT
Correct $\rho_s(\mathbf{r})$?	Yes	Yes
Correct $Q_s(\mathbf{r})$?	No	Yes
Ψ_s is eigenfunction of $\hat{\mathbf{S}}^2$?	Yes	No
Correct $\langle \hat{\mathbf{S}}^2 \rangle$?	Maybe	No
Ψ_s is eigenfunction of \hat{S}_z ?	Yes	Yes
Correct $\langle \hat{S}_z \rangle$?	Maybe	Yes

Spin-scaling of functionals

Kinetic energy functional

We first note that by their very definitions the kinetic energy functionals for the spin-unpolarised and the spin-polarised cases are different.

$$T_s^{(0)}[n] = \min_{\Psi_D \rightarrow n} \left\langle \Psi_D \left| \hat{T} \right| \Psi_D \right\rangle \quad \text{Spin-unpolarized KE functional}$$

$$T_s[n_\uparrow, n_\downarrow] = \min_{\Psi_D \rightarrow n_\uparrow, \downarrow} \left\langle \Psi_D \left| \hat{T} \right| \Psi_D \right\rangle \quad \text{Spin-polarized KE functional}$$

$$T_s^{(0)}[n] \neq T_s[n_\uparrow, n_\downarrow]$$

Spin-scaling of functionals

Kinetic energy functional

In terms of the Kohn-Sham orbitals we can write

$$T_s^{(0)}[n] = 2 \sum_{i=1}^{N/2} \left\langle \phi_i \left| \frac{-\nabla^2}{2} \right| \phi_i \right\rangle$$

Spin-unpolarized KE functional

$$\begin{aligned} T_s[n_\uparrow, n_\downarrow] &= \sum_{i=1}^{N_\uparrow} \left\langle \phi_{i,\uparrow} \left| \frac{-\nabla^2}{2} \right| \phi_{i,\uparrow} \right\rangle + \sum_{i=1}^{N_\downarrow} \left\langle \phi_{i,\downarrow} \left| \frac{-\nabla^2}{2} \right| \phi_{i,\downarrow} \right\rangle \\ &\equiv T_s[n_\uparrow, 0] + T_s[0, n_\downarrow] \end{aligned}$$

Spin-polarized KE functional

Where the last two terms refer to the KE functionals of fully polarised systems.

Spin-scaling of functionals

Kinetic energy functional

Applying the spin-density functional for a spin-unpolarised system yields

$$\begin{aligned} T_s[n/2, n/2] &= T_s[n/2, 0] + T_s[0, n/2] \\ &= 2T_s[n/2, 0] && \text{Since the KE is spin-independent} \\ &= T_s^{(0)}[n] \end{aligned}$$

In other words, $T_s[n/2, 0] = \frac{1}{2}T_s^{(0)}[n]$

We have derived a general property of the functional albeit by considering a special case. This gives us the scaling relation

$$T_s[n_{\uparrow}, n_{\downarrow}] = \frac{1}{2} \left(T_s^{(0)}[2n_{\uparrow}] + T_s^{(0)}[2n_{\downarrow}] \right)$$

Spin-scaling of functionals

Kinetic energy functional

As an example consider the Thomas-Fermi KE functional

$$T_s^{(0)}[n] = C_f \int n(\mathbf{r})^{\frac{5}{3}} d^3r$$

The spin-polarised functional is then

$$T_s[n_\uparrow, n_\downarrow] = 2^{\frac{2}{3}} C_F \left(\int n_\uparrow(\mathbf{r})^{\frac{5}{3}} d^3r + \int n_\downarrow(\mathbf{r})^{\frac{5}{3}} d^3r \right)$$

Spin-scaling of functionals

Exchange-correlation energy functional

First we split up the E_{xc} into an exchange and a correlation functional.

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

Similar considerations as the KE functional can be applied to the exchange functional remembering its definition (from Hartree-Fock theory)

$$\begin{aligned} E_x[n_{\uparrow}, n_{\downarrow}] &= -\frac{1}{2} \int dx \int dx' \frac{|\gamma_1(x, x')|^2}{|\mathbf{r} - \mathbf{r}'|} \\ &= -\frac{1}{2} \int d^3r \int d^3r' \frac{|\rho^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \int d^3r \int d^3r' \frac{|\rho^{\beta\beta}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \\ &\equiv E_x[n_{\uparrow}, 0] + E_x[0, n_{\downarrow}] \end{aligned}$$

$$\gamma_1(x, x') = \sum_{i=1}^N \sum_{j=1}^N \psi_i(x) \psi_j(x')$$

$$\rho^{\tau\tau}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_{\tau}} \sum_{j=1}^{N_{\tau}} \phi_{i,\tau}(\mathbf{r}) \phi_{j,\tau}(\mathbf{r}')$$

Spin-scaling of functionals

Exchange-correlation energy functional

This gives the following scaling relation for the exchange functional

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} \left(E_x^{(0)}[2n_\uparrow] + E_x^{(0)}[n_\downarrow] \right)$$
$$E_x^{(0)} = E_x[n/2, n/2]$$

Here $E_x^{(0)}[n]$ is the spin-unpolarised functional. As an example, the *local spin density approximation* for the exchange using the Dirac functional is

$$E_x^{LSD}[n_\uparrow, n_\downarrow] = 2^{\frac{1}{3}} C_x \int d^3r \left(n(\mathbf{r})_{\uparrow}^{\frac{4}{3}} + n(\mathbf{r})_{\downarrow}^{\frac{4}{3}} \right)$$
$$= \frac{1}{2} C_x \int d^3r n(\mathbf{r}) \left[(1 + \zeta(\mathbf{r}))^{\frac{4}{3}} + (1 - \zeta(\mathbf{r}))^{\frac{4}{3}} \right]$$