Notes on variational properties in the DFT-KS method
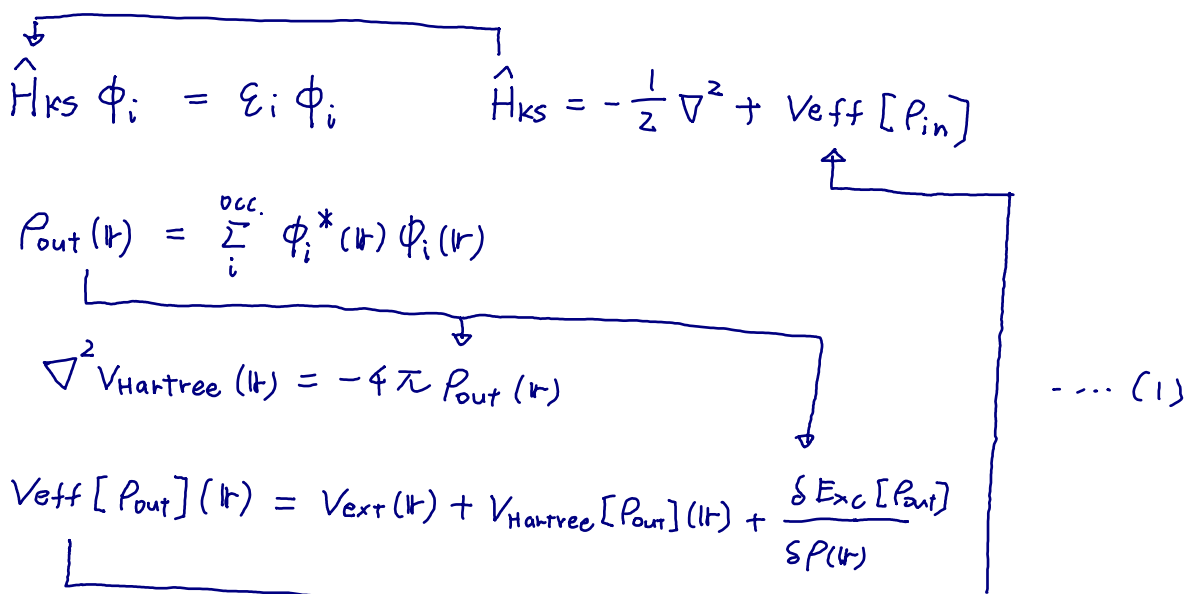
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✦ Algorithmic structure of the Kohn-Sham equation

$$\hat{H}_{KS}\,\phi_i = \varepsilon_i\,\phi_i \qquad\qquad \hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{eff}\,[\rho_{in}]$$

$$\rho_{out}(\mathbf{r}) = \sum_i^{occ.} \phi_i^*(\mathbf{r})\,\phi_i(\mathbf{r})$$

$$\nabla^2 V_{Hartree}(\mathbf{r}) = -4\pi\,\rho_{out}(\mathbf{r}) \qquad\qquad\qquad \cdots (1)$$

$$V_{eff}\,[\rho_{out}](\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[\rho_{out}](\mathbf{r}) + \frac{\delta E_{xc}[\rho_{out}]}{\delta\rho(\mathbf{r})}$$

This iteration is repeated until the self-consistency is achieved for ρ.

Variation of the total energy in the ks theory

✦ The total energy is given in the ks theory by

$$E_{KS}[\rho] = T_s + \int d\mathbf{r}^3\,V_{ext}(\mathbf{r})\,\rho_{out}(\mathbf{r}) + \underbrace{\frac{1}{2}\iint d\mathbf{r}^3 d\mathbf{r}'^3\,\frac{\rho_{out}(\mathbf{r})\,\rho_{out}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{``J[\rho_{out}]"} + E_{xc}[\rho_{out}] \qquad \cdots (2)$$

Now we consider the variation of E_{KS} for variation of ρ.

The electron density ρ is changed to $\rho + \delta\rho$.

By noting that T_s can be transformed using the ks eq. as

$$(\hat{T} + V_{eff})\,\phi_i = \varepsilon_i\,\phi_i \;\longrightarrow\; \hat{T}\phi_i = \varepsilon_i\,\phi_i - V_{eff}\,\phi_i$$

$$\longrightarrow\quad T_s = \sum_i^{occ}\langle\phi_i|\hat{T}|\phi_i\rangle = \sum_i^{occ.}\varepsilon_i\langle\phi_i|\phi_i\rangle - \sum_i^{occ.}\int d\mathbf{r}^3\,\phi_i^*(\mathbf{r})\,V_{eff}(\mathbf{r})\,\phi_i(\mathbf{r})$$

$$= \sum_i^{occ.}\varepsilon_i[\rho_{in}] - \int d\mathbf{r}^3\,\underset{[\rho_{in}]}{V_{eff}(\mathbf{r})}\,\rho_{out}(\mathbf{r}) \qquad\qquad \cdots\cdots (3)$$

and inserting Eq. (3) into Eq. (2), we have

$$E_{KS}[\rho] = \sum_i^{occ}\varepsilon_i[\rho_{in}] - \int d\mathbf{r}^3\,\underset{[\rho_{in}]}{V_{eff}(\mathbf{r})}\,\rho_{out}(\mathbf{r}) + \int d\mathbf{r}^3\,V_{ext}(\mathbf{r})\,\underset{out}{\rho(\mathbf{r})} + \underset{out}{J[\rho]} + E_{xc}[\rho_{out}] \qquad \cdots (4)$$

The variation of the 3-rd term in Eq. (4) with respect to ρ ②

is given by

$$\delta\left(\int dr^3 \, V_{ext}(|r|) \, \rho_{out}(|r|)\right) = \int dr^3 \, V_{ext}(|r|) \, \delta\rho(|r|) \quad \cdots \cdots (5)$$

When the electron density $\rho(|r|)$ at a certain point r in real space

changes to $\rho(|r|) + \delta\rho(|r|)$, the effective potential V_{eff}

changes not only at the point r but also other points

into $V_{eff} + \delta V_{eff}$. Thus, the KS equation becomes

$$\left(-\frac{1}{2}\nabla^2 + V_{eff} + \delta V_{eff}\right)\left(\phi_i + \delta\phi_i\right) = \left(\varepsilon_i + \delta\varepsilon_i\right)\left(\phi_i + \delta\phi_i\right) \quad \cdots (6)$$

By expanding Eq. (6), and taking account of the first-order terms,

we can calculate as follows:

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\phi_i + \left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\delta\phi_i + \delta V_{eff}\,\phi_i = \varepsilon_i\phi_i + \varepsilon_i\,\delta\phi_i + \delta\varepsilon_i\,\phi_i$$

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\delta\phi_i + \delta V_{eff}\,\phi_i = \varepsilon_i\,\delta\phi_i + \delta\varepsilon_i\,\phi_i \quad \cdots (7)$$

Multiplying ϕ_i^* from the left-side, and integrating over space,

we have

$$\langle \phi_i |\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)| \delta\phi_i \rangle + \int dr^3 \, \delta V_{eff}(|r|) \, \phi_i^*(|r|)\, \phi_i(|r|)$$

$$= \varepsilon_i \, \langle \phi_i | \delta\phi_i \rangle + \delta\varepsilon_i \, \langle \phi_i | \phi_i \rangle$$

$$\varepsilon_i \, \cancel{\langle \phi_i | \delta\phi_i \rangle} + \int dr^3 \, \delta V_{eff}(|r|) \, \phi_i^*(|r|)\, \phi_i(|r|) = \varepsilon_i \, \cancel{\langle \phi_i | \delta\phi_i \rangle} + \delta\varepsilon_i$$

$$\cdots (8)$$

By summing up Eq. (8) over the occupied states, we obtain

$$\sum_i^{occ} \delta\varepsilon_i = \int dr^3 \, \delta V_{eff}[\rho_{in}](|r|) \, \rho_{out}(|r|) \quad \cdots\cdots (9)$$

Considering the change $\delta\rho$ for all the points in real space, we obtain the variation of the first term in Eq. (4) as

$$\delta\left(\sum_i^{occ.}\varepsilon_i\right) = \int d\vec{r}^3\,\delta\rho(\vec{r})\left[\int dr'^3\,\frac{\delta V_{eff}[\rho_{in}](\vec{r}')}{\delta\rho(\vec{r})}\rho_{out}(\vec{r}')\right] \qquad - - - - - (10)$$

The variation of the second term in Eq. (4) is given by

$$\delta\left(-\int d\vec{r}^3\,V_{eff}(\vec{r})\,\rho_{out}(\vec{r})\right) = -\int d\vec{r}^3\,\delta\rho(\vec{r})\left[\int d\vec{r}^3\,\frac{\overset{[\rho_{in}]}{\delta V_{eff}(\vec{r})}}{\delta\rho(\vec{r})}\rho_{out}(\vec{r}')\right] - \int d\vec{r}^3\,\overset{[\rho_{in}]}{V_{eff}(\vec{r})}\,\delta\rho(\vec{r}) \qquad - - - (11)$$

The variation of the forth term in Eq. (4) is given by

$$\delta J[\rho_{out}] = \int d\vec{r}^3\,\delta\rho(\vec{r})\left[\int d\vec{r}^3\,\frac{\rho_{out}(\vec{r}')}{|\vec{r}-\vec{r}'|}\right] \qquad - - - - - (12)$$

The variation of the fifth term in Eq. (5) is given by

$$\delta E_{xc}[\rho_{out}] = \int d\vec{r}^3\,\delta\rho(\vec{r})\,\frac{\delta E_{xc}[\rho_{out}]}{\delta\rho(\vec{r})} \qquad - - - - - (13)$$

Summing up all the contributions of the variations given by Eqs. (5), (10), (11), (12), and (13), the variation of the total energy for $\delta\rho$ to the first order is found to be

$$\delta E_{KS} = \int d\vec{r}^3\,\delta\rho(\vec{r})\left(\int d\vec{r}^3\,\frac{\delta V_{eff}[\rho_{in}](\vec{r}')}{\delta\rho(\vec{r})}\rho_{out}(\vec{r}') - \int d\vec{r}^3\,\frac{\delta V_{eff}[\rho_{in}](\vec{r}')}{\delta\rho(\vec{r})}\rho_{out}(\vec{r}')\right.$$

$$\left. + V_{ext}(\vec{r}) - V_{eff}[\rho_{in}](\vec{r}) + \int d\vec{r}^3\,\frac{\rho_{out}(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{xc}[\rho_{out}]}{\delta\rho(\vec{r})}\right) \qquad - - (14)$$

To be $\delta E = 0$ for arbitrary $\delta\rho$, the sum in the parenthesis should be zero. Then, we have

$$V_{eff}[\rho_{in}](\vec{r}) = V_{ext}(\vec{r}) + \int d\vec{r}^3\,\frac{\rho_{out}(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{xc}[\rho_{out}]}{\delta\rho(\vec{r})} \qquad - - - (15)$$

Equation (15) looks the definition of the KS potential. However, the left hand side of Eq.(15) is evaluated by ρ_{in}, while the right hand side is evaluated by ρ_{out}. Therefore, for Eq.(15) to be valid, we need to have

the self-consistency condition:

$$\rho_{out} = \rho_{in} \quad \cdots (16)$$

In this case we have

$$\delta E[\rho] = 0 \quad \cdots (17)$$

Remembering that the KS eq. is derived by imposing

$$\frac{\delta E}{\delta \phi} = 0 \quad \cdots (18)$$

and solving the KS eq. self-consistently, one can achieve the two conditions of Eqs.(17) and (18) at the same time. This is a very nice aspect of the KS theory.

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* **Harris functional** J. Harris, Phys. Rev. B 31, 1770 (1985).

The Harris functional is given by

$$E_{Harris}[\rho_{in}] = \sum_i^{occ} \varepsilon_i[\rho_{in}] - \frac{1}{2}\iint dr\,dr'^3 \frac{\rho_{in}(r)\rho_{in}(r')}{|r-r'|} + E_{xc}[\rho_{in}] - \int dr^3 \rho_{in}(r) \frac{\delta E_{xc}[\rho_{in}]}{\delta \rho(r)}$$

where ρ_{in} is a trial input density. $\quad \cdots (18)$

We would like to show that the difference between E_{KS} and E_{Harris} is second order of $(\rho - \rho_{in})$.

It should be noted that the Harris functional E_{Harris} ⑤ can be obtained by replacing ρ_{out} with ρ_{in} in the KS functional E_{KS} of Eq. (4) as

$$E_{KS}[\rho_{out} \rightarrow \rho_{in}]$$

$$= \sum_{i}^{occ} \varepsilon_i[\rho_{in}] - \int d\vec{r}^3\, V_{eff}[\rho_{in}]\,\rho_{in}(\vec{r}) + \int d\vec{r}^3\, V_{ext}(\vec{r})\,\rho_{in}(\vec{r}) + J[\rho_{in}] + E_{xc}[\rho_{in}]$$

$$= \sum_{i}^{occ} \varepsilon_i[\rho_{in}] - \int d\vec{r}^3\left(V_{ext}(\vec{r}) + V_H[\rho_{in}](\vec{r}) + \frac{\delta E_{xc}[\rho_{in}]}{\delta \rho(\vec{r})}\right)\rho_{in}(\vec{r})$$

$$+ \int d\vec{r}^3\, V_{ext}(\vec{r})\,\rho_{in}(\vec{r}) + \frac{1}{2}\int d\vec{r}^3\, V_H[\rho_{in}](\vec{r})\,\rho_{in}(\vec{r}) + E_{xc}[\rho_{in}]$$

$$= \sum_{i}^{occ} \varepsilon_i[\rho_{in}] - \frac{1}{2}\int d\vec{r}^3\, V_H[\rho_{in}](\vec{r})\,\rho_{in}(\vec{r}) + E_{xc}[\rho_{in}] - \int d\vec{r}^3\, \frac{\delta E_{xc}[\rho_{in}]}{\delta \rho(\vec{r})}\,\rho_{in}(\vec{r})$$

$$= E_{Harris}[\rho_{in}] \qquad \text{----- (19)}$$

Then, using Eqs. (5), (10), (11), (12), and (13) with the replacement: $\rho_{out} \rightarrow \rho_{in}$, we obtain the variation of E_{Harris} for $\delta\rho$ as follows:

$$\delta E_{Harris} = \int d\vec{r}^3\, \delta\rho(\vec{r})\left(\int d\vec{r}'^3\, \frac{\delta V_{eff}[\rho_{in}](\vec{r}')}{\delta \rho(\vec{r})}\,\rho_{in}(\vec{r}') - \int d\vec{r}^3\, \frac{\delta V_{eff}[\rho_{in}](\vec{r}')}{\delta \rho(\vec{r})}\,\rho_{in}(\vec{r}')\right.$$

$$\left. + V_{ext}(\vec{r}) - V_{eff}[\rho_{in}](\vec{r}) + \boxed{\int d\vec{r}'^3\, \frac{\rho_{in}(\vec{r}')}{|\vec{r}-\vec{r}'|}} + \frac{\delta E_{xc}[\rho_{in}]}{\delta \rho(\vec{r})}\right)$$

$$\underset{\text{(boxed term labeled } V_H(\vec{r}))}{}$$

The sum in the parenthesis is always zero by the $\qquad$----(20)

the definition of $V_{eff}[\rho_{in}]$ as

$$V_{eff}[\rho_{in}](\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + \frac{\delta E_{xc}[\rho_{in}]}{\delta \rho(\vec{r})} \qquad \text{--- (21)}$$

Considering $\delta\rho = \rho - \rho_{in}$ where ρ is the ground state density, we obtain $\qquad E_{KS}[\rho] = E_{Harris}[\rho_{in}] + O((\rho-\rho_{in})^2) \quad \text{--- (22)}$

☆ Local force theorem :

> A.R. Mackintosh and O.k. Andersen, in Electrons at the Fermi surface, edited by M. Springford (Cambridge Univ. Press, 1980)

Let's consider again the total energy in the KS theory given by

$$E_{KS}[\rho] = T_s[n] + A[\rho] \quad ---- \quad (23)$$

$$A[\rho] = \int dr^3 \, V_{ext}(\mathbf{r}) \, \rho(\mathbf{r}) + J[\rho] + E_{xc}[\rho] \quad --- \quad (24)$$

$$T_s[\rho] = \overset{occ.}{\underset{i}{\sum}} \varepsilon_i - \int dr^3 \, V_{eff}(\mathbf{r}) \, \rho(\mathbf{r}) \quad ---- \quad (25)$$

From Eqs. (10) and (11), we have

$$\delta T_s[\rho] = - \int dr^3 \, V_{eff}(\mathbf{r}) \, \delta\rho(\mathbf{r}) \quad ---- \quad (26)$$

Up to here, we considered that V_{eff} is a functional of ρ such as

$$V_{eff}[\rho] \quad ----- \quad (27)$$

Now we assume that V_{eff} is an independent variable from ρ. Then, T_s can be written as

$$T_s[\rho, V_{eff}] = \overset{occ}{\underset{i}{\sum}} \varepsilon_i[V_{eff}] - \int dr^3 \, V_{eff}(\mathbf{r}) \, \rho(\mathbf{r}) \quad --- \quad (28)$$

Since ε_i depends on only V_{eff} in this case, similar to the derivation of Eq. (9), we can derive $\delta(\overset{occ}{\underset{i}{\sum}}\varepsilon_i)$ to the first order as

$$\delta \left(\overset{occ}{\underset{i}{\sum}} \varepsilon_i \right) = \int dr^3 \, \delta V_{eff}(\mathbf{r}) \, \rho(\mathbf{r}) \quad ----- \quad (29)$$

The variation of the second term in Eq. (28) is given by

$$\delta \left(- \int dr^3 \, V_{eff}(\mathbf{r}) \, \rho(\mathbf{r}) \right) = - \int dr^3 \, \delta V_{eff}(\mathbf{r}) \, \rho(\mathbf{r}) - \int dr^3 \, V_{eff}(\mathbf{r}) \, \delta\rho(\mathbf{r})$$

$$--- (30)$$

Therefore

$$\delta T_s[\rho, V_{eff}] = - \int dr^3 \, V_{eff}(\mathbf{r}) \, \delta\rho(\mathbf{r}) \quad ---- \quad (31)$$

Comparing Eq. (31) with Eq. (26), we see that

$\delta T_s [\rho, V_{eff}]$ is equivalent to $\delta T_s [\rho]$ even if

V_{eff} is treated as independent variable.

Since $A[\rho]$ is a functional of only ρ, we find

that

$$\delta E [\rho, V_{eff}] = \delta \left(T_s [\rho, V_{eff}] + A[\rho] \right)$$

$$= \int d\vec{r}^3 \, \delta \rho (\vec{r}) \left(-V_{eff} (\vec{r}) + V_{ext} (\vec{r}) + V_H [\rho] (\vec{r}) + \frac{\delta E_{xc} [\rho]}{\delta \rho (\vec{r})} \right) \quad \cdots \cdot (32)$$

If V_{eff} and ρ are the ground state ones, the sum

in the parenthesis becomes zero. Therefore, we obtain

the following relation:

$$\boxed{E \left[\rho + \delta\rho, V_{eff} + \delta V_{eff} \right] = E \left[\rho, V_{eff} \right] + O \left(\delta\rho^2, \delta V_{eff}^2, \delta\rho\delta V_{eff} \right)}$$

$$\cdots (33)$$

By inserting Eq. (28) into Eq. (23), we have

$$E [\rho, V_{eff}] = \sum_i^{occ.} \varepsilon_i [V_{eff}] - \int d\vec{r}^3 V_{eff} (\vec{r}) \rho (\vec{r}) + A [\rho] \qquad \cdots \cdots (34)$$

For $V_{eff} \to V_{eff} + \delta V_{eff}$, the variation of the first two terms in Eq. (34)

to the first order is given by

$$\int d\vec{r}^3 \delta V_{eff} (\vec{r}) \rho (\vec{r}) + O(\delta V_{eff}^2) - \int d\vec{r}^3 \delta V_{eff} (\vec{r}) \rho (\vec{r}) = O(\delta V_{eff}^2)$$

$$\cdots (35)$$

Therefore, the variation of E for δV_{eff} is contributed

by only the first term of Eq. (34), and it is second order

of δV_{eff}^2 as $\boxed{E [\rho, V_{eff} + \delta V_{eff}] - E [\rho, V_{eff}] = \sum_i^{occ.} \varepsilon_i [V_{eff} + \delta V_{eff}] - \sum_i^{occ} \varepsilon_i [V_{eff}]} \cdots (36)$

Take only the second order term

In the right-hand side of Eq. (36), we only have to consider the second order term. The first order term is canceled out by the first order term arising from the second term of Eq. (34).

Note that the higher order terms from the second term of Eq. (34) are zero, since Veff is treated as an independent variable.

This is a very important consequence when we investigate how the system respondes for the perturbed potential $(V_{eff} + \delta V_{eff})$, and Eq. (36) allows us to focus on only the band energy.

We have already discussed that Eq. (33) is valid only if ρ and Veff are the ground state ones. However, we can further extend the condition.

In order to vanish the sum in the parenthesis of the R.H.S in Eq. (32), the Harris condition:

$$V_{eff}[\rho_{in}](\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H[\rho_{in}](\mathbf{r}) + \frac{\delta E_{xc}[\rho_{in}]}{\delta \rho(\mathbf{r})} \quad \cdots (37)$$

can also be considered. In this case we can hold Eqs. (33) and (36).

Equation (36) will be utilized when we analyze magnetic interactions to derive effective exchange coupling parameters.