Coll. T2.

Ringium, ⊛ functionals for single excitations

What was the problem (initially)?

⊛ Comparing FCI and Hxc. HF and KS is the same? (even in boxium, I guess not).

* $T_s^{\underline{w}}[n] \neq$ ← linear in $\underline{w}$ (each state has a uniform density)

* Calculations in boxium. you used LIM, right?

$$\frac{\partial E^{\underline{w}}_{Hxc}[n]}{\partial w_I} \rightarrow$$ from the gas

$$F^{\underline{w}}(n) = (1-w_I)\, F_0(n) + \sum_{I>0} w_I F_I(n)$$

weight-independent!

$$n^w(r) = (1-w_I)\, \underbrace{n_0(r)}_{N/V} + \sum_{I>0} w_I\, \underbrace{n_I(r)}_{N/V}$$

$$F_I(n) - F_0(n) \xleftarrow{n = n^{\underline{w}}}$$

* Linearity of E^w: By construction, your functional is (explicitly) linear in $\underline{w}$!!)

$$E_{Hxc}([n] \longrightarrow E_{Hxc}[n^{\underline{w}}]$$

Generalized KS-eDF

$$F^{\underline{w}}_{HF}[n] = \min_{\hat{\Gamma}^{\underline{w}}_{HF} \to n} \mathrm{Tr}\, \hat{\Gamma}^{\underline{w}}_{HF} (\hat{T} + \hat{W}_{ee})$$

$$\mathcal{U}^{\underline{w}}_c[n] = F^{\underline{w}}[n] - F^{\underline{w}}_{HF}[n]$$

$$E^{\underline{w}} = \min_n \left\{ \min_{\hat{\Gamma}^{\underline{w}}_{HF} \to n} \left\{ \mathrm{Tr}\, \hat{\Gamma}^{\underline{w}}_{HF} (\hat{T} + \hat{W}_{ee}) + \mathcal{U}^{\underline{w}}_c [n_{\Gamma^{\underline{w}}_{HF}}] \right\} \right\}$$

$$\overset{(1)}{=} \min_{\Gamma^{\underline{w}}_{HF}} \left\{ \mathrm{Tr}\left[\hat{\Gamma}^{\underline{w}}_{HF} (\hat{T} + \hat{W}_{ee}) \right] + \mathcal{U}^{\underline{w}}_c [n_{\Gamma^{\underline{w}}_{HF}}] \right\}$$

$$= \min_{\kappa} \left\{ \mathrm{Tr}\left[\hat{\Gamma}^{\underline{w}}(\kappa) (\hat{T} + \hat{W}_{ee}) \right] + \mathcal{U}^{\underline{w}}_c [n_{\hat{\Gamma}^{\underline{w}}(\kappa)}] \right\}$$

$$\hat{\Gamma}^{\underline{w}}(\kappa) = e^{-\hat{\kappa}} \Gamma^{\underline{w}}_{HF} e^{\hat{\kappa}}$$

$$= \min_{\kappa} E^{\underline{w}}(\kappa)$$

minimizing DM op in (1) (K=0 is the solution by construction)

$$n_{\hat{\Gamma}^{\underline{w}}(\kappa)}(r) = \mathrm{Tr}\left[\hat{\Gamma}^{\underline{w}}(\kappa)\, \hat{n}(r) \right]$$

$$\frac{dE^{\underline{w}}}{dw_I} = \langle \Phi^{\underline{w}}_I | \hat{T} + \hat{W}_{ee} | \Phi^{\underline{w}}_I \rangle - \langle \Phi^{\underline{w}}_0 | \hat{T} + \hat{W}_{ee} | \Phi^{\underline{w}}_0 \rangle + \int dr\, \frac{\delta \mathcal{U}^{\underline{w}}_c [n^{\underline{w}}]}{\delta n(r)} \left(n_{\Phi^{\underline{w}}_I}(r) - n_{\Phi^{\underline{w}}_0}(r) \right) + \left. \frac{\partial \mathcal{U}^{\underline{w}}_c[n]}{\partial w_I} \right|_{n = n^{\underline{w}}}$$

$$E_I = E_0 + \sum_{J>0} \delta_{IJ} (E_J - E_0)$$

$$= E^{\underline{w}} - \sum_{J>0} \frac{\partial E^{\underline{w}}}{\partial w_J} w_J + \sum_{J>0} \delta_{IJ} \frac{\partial E^{\underline{w}}}{\partial w_J}$$

$$= E^{\underline{w}} + \sum_{J>0} (\delta_{IJ} - w_J) \frac{\partial E^{\underline{w}}}{\partial w_J}$$

$$E^{\underline{w}}_{HF,I} = \langle \Phi_I^{\underline{w}} | \hat{T} + \hat{W}_{ee} | \Phi_I^{\underline{w}} \rangle + U_c^{\underline{w}}[n^{\underline{w}}]$$

if we do not want to introduce orbital energies

(but we could... nice only from a formal point of view (!))

$$E^{\underline{w}} \underset{\text{exact}}{=} \sum_{I\geq 0} w_I E^{\underline{w}}_{HF,I}$$

$$E_I = \left(1 - \sum_{I>0} w_I\right) \langle \hat{T} + \hat{W}_{ee} \rangle_{\Phi_0} + \sum_{I>0} w_I \langle \hat{T} + \hat{W}_{ee} \rangle_{\Phi_I}$$
$$+ U_c^{\underline{w}}[n^{\underline{w}}] + \sum_{J>0} (\delta_{IJ} - w_J) \left(\langle \hat{T} + \hat{W}_{ee} \rangle_{\Phi_J} - \langle \hat{T} + \hat{W}_{ee} \rangle_{\Phi_0} \right)$$
$$+ \int dr \frac{\delta U_c^{\underline{w}}[n^{\underline{w}}]}{\delta n(r)} \sum_{J>0} (\delta_{IJ} - w_J) \left(n_{\Phi_J}(r) - n_{\Phi_0}(r) \right)$$
$$+ \sum_{J>0} (\delta_{IJ} - w_J) \frac{\partial U_c^{\underline{w}}[n]}{\partial w_J} \bigg|_{n = n^{\underline{w}}}$$

$$\langle \hat{T} + \hat{W}_{ee} \rangle_{\Phi_I} + U_c^{\underline{w}}[n^{\underline{w}}] + \sum_{J>0} (\delta_{IJ} - w_J) \frac{\partial U_c^{\underline{w}}[n]}{\partial w_J} \bigg|_{n^{\underline{w}} = n}$$
$$+ \int dr \frac{\delta U_c^{\underline{w}}[n^{\underline{w}}]}{\delta n(r)} \boxed{\sum_{J>0} (\delta_{IJ} - w_J) \left(n_{\Phi_J}(r) - n_{\Phi_0}(r) \right)}$$

(1) $$\sum_{J>0} \delta_{IJ} \left(n_{\Phi_J} - n_{\Phi_0}\right) + n_{\Phi_0} = n_{\Phi_I} \qquad \forall I \geq 0$$

(2) $$\sum_{J>0} w_J \left(n_{\Phi_J} - n_{\Phi_0}\right) = n^w - \Big(1 - \sum_{J>0} w_J\Big) n_{\Phi_0} - \sum_{J>0} w_J n_{\Phi_0}$$

$$= n^w - n_{\Phi_0}$$

potential-dependent contribution:

$$\int dr \frac{\delta U_c^w}{\delta n(r)}[n^w] \times \left(n_{\Phi_I} - \cancel{n_{\Phi_0}} - n^w + \cancel{n_{\Phi_0}} \right)$$

Conclusion:

$$\boxed{\begin{aligned} E_I = {} & \Big\langle \Phi_I \Big| \hat{T} + \hat{W}_{ee} + \int dr \frac{\delta U_c^w}{\delta n(r)}[n^w]\, \hat{n}(r) \Big| \Phi_I \Big\rangle \\ & + U_c^w[n^w] - \int dr \frac{\delta U_c^w}{\delta n(r)}[n^w]\, n^w \\ & + \sum_{J>0} \left(\delta_{IJ} - w_J\right) \frac{\partial U_c^w}{\partial w_J}[n] \Big|_{n=n^w} \end{aligned}}$$

not the HF potential !

Levy shift-like term.

GOK-DFT - 3 states $\qquad \underline{w} = (w_1, w_2)$

$$E^{\underline{w}} = \min_{K} \left\{ \mathrm{Tr}\left[\hat{\Gamma}^{\underline{w}}(K)\hat{H}\right] + U_c^{\underline{w}}\left[n_{\hat{\Gamma}^{\underline{w}}(K)}\right] \right\}$$

From the uniform model

$$U_c^{\underline{w}}[n] \longrightarrow \left(1 - \sum_{I>0} w_I\right) U_{c,0}[n] + \sum_{I>0} w_I U_{c,I}[n]$$

$$U_{c,K}[n] = \langle \Psi_K[n] | \hat{T} + \hat{V}_{ee} | \Psi_K[n] \rangle$$

$$- \langle \Phi_K[n] | \hat{T} + \hat{V}_{ee} | \Phi_K[n] \rangle$$

KS or HF (same, right?)

$$\left.\frac{\partial U_c^{\underline{w}}[n]}{\partial w_I}\right|_{n=n^{\underline{w}}} = \left.\left(U_{c,I}[n] - U_{c,0}[n]\right)\right|_{n=n^{\underline{w}}}$$

If the 2nd is not well described in boxium, one could try to increase the weight w_2 that is assigned to the 2nd excitation.

N-centred eDFT / hybrid functionals

$$E_0^{\underline{\xi}} = \min_{\kappa} \left\{ \mathrm{Tr}\left[\hat{\Gamma}^{\underline{\xi}}(\kappa)\hat{H}\right] + U_c^{\underline{\xi}}\left[n_{\hat{\Gamma}^{\underline{\xi}}(\kappa)}\right] \right\} \quad \text{(A)}$$

$$\hat{\Gamma}^{\underline{\xi}}(\kappa) = e^{-\hat{\kappa}}\hat{\Gamma}^{\underline{\xi}} e^{\hat{\kappa}} \qquad \boxed{\underline{\xi} = (\xi_-, \xi_+)}$$

$$\hat{\Gamma}^{\underline{\xi}} = \xi_- |\Phi^{N-1}\rangle\langle\Phi^{N-1}| + \xi_+ |\Phi^{N+1}\rangle\langle\Phi^{N+1}| + \left[1 - \frac{\xi_-}{N}(N-1) - \frac{\xi_+(N+1)}{N}\right]|\Phi^N\rangle\langle\Phi^N|$$

all constructed from the same set of (KS) orbitals.

$$\boxed{E_0^{\underline{\xi}} = \xi_- E_0^{N-1} + \xi_+ E_0^{N+1} + \left[1 - \frac{\xi_-(N-1)}{N} - \frac{\xi_+(N+1)}{N}\right]E_0^N}$$

$$\boxed{E_0^N = E^{\underline{\xi}} - \xi_+ \frac{\partial E^{\underline{\xi}}}{\partial \xi_+} - \xi_- \frac{\partial E^{\underline{\xi}}}{\partial \xi_-}} \quad \text{(B)}$$

$$\frac{\partial E^{\underline{\xi}}}{\partial \xi_+} = -\frac{(N+1)}{N}E_0^N + E_0^{N+1} \quad (1)$$

$$\frac{\partial E^{\underline{\xi}}}{\partial \xi_-} = E_0^{N-1} - \frac{(N-1)}{N}E_0^N \quad (2)$$

$$(1) \quad \boxed{E_0^{N+1} = \frac{(N+1)}{N}E_0^N + \frac{\partial E^{\underline{\xi}}}{\partial \xi_+}} \quad \text{(C)}$$

$$(2) \quad \boxed{E_0^{N-1} = \frac{(N-1)}{N}E_0^N + \frac{\partial E^{\underline{\xi}}}{\partial \xi_-}} \quad \text{(D)}$$

From (A)

$$\frac{\partial E^{\xi}}{\partial \xi_-} = \mathrm{Tr}\left(\partial_{\xi_-}\hat{\Gamma}^{\xi}_s \hat{H}\right) + \int \frac{\delta U_c^{\xi}[n^{\xi}]}{\delta n(r)}\, n_{\partial_{\xi}\hat{\Gamma}^{\xi}_s}(r)\, dr$$

$$+ \left.\frac{\partial U_c^{\xi}[n]}{\partial \xi_-}\right|_{n=n^{\xi}}$$

$$\partial_{\xi_-}\hat{\Gamma}^{\xi}_s = \underbrace{|\Phi^{N-1}\rangle\langle\Phi^{N-1}|}_{\hat{\Gamma}^{N-1}_s} - \frac{N-1}{N}\hat{\Gamma}^N_s$$

(say $K=0$ gives the minimizing solution)

$$\frac{\partial E^{\xi}}{\partial \xi_+} = \text{same with } \partial_{\xi_+}\hat{\Gamma}^{\xi}_s = \hat{\Gamma}^{N+1}_s - \frac{(N+1)}{N}\hat{\Gamma}^N_s$$

true Hamiltonian!

$$\hat{H}^{\xi} = \hat{H} + \int \left.\frac{\delta U_c^{\xi}[n]}{\delta n(r)}\right|_{n=n^{\xi}} \hat{n}(r)\, dr$$

$$\begin{cases} \dfrac{\partial E^{\xi}}{\partial \xi_+} = \mathrm{Tr}\left[\left(\hat{\Gamma}^{N+1}_s - \dfrac{(N+1)}{N}\hat{\Gamma}^N_s\right)\hat{H}^{\xi}\right] + \left.\dfrac{\partial U_c^{\xi}[n]}{\partial \xi_+}\right|_{n=n^{\xi}} \\ \dfrac{\partial E^{\xi}}{\partial \xi_-} = \mathrm{Tr}\left[\left(\hat{\Gamma}^{N-1}_s - \dfrac{(N-1)}{N}\hat{\Gamma}^N_s\right)\hat{H}^{\xi}\right] + \left.\dfrac{\partial U_c^{\xi}[n]}{\partial \xi_-}\right|_{n=n^{\xi}} \end{cases}$$

(A)

$$\hookrightarrow E^{\xi} = \mathrm{Tr}\left[\hat{\Gamma}^{\xi}_s \hat{H}^{\xi}\right] + U_c^{\xi}[n^{\xi}] - \underbrace{\int dr \frac{\delta U_c^{\xi}[n^{\xi}]}{\delta n(r)} n^{\xi}(r)}_{\text{analog of Levy-Zahariev's shift}}$$

Since a) $\hat{\Gamma}^{\xi}_s - \xi_+\left(\cancel{\hat{\Gamma}^{N+1}_s} - \frac{(N+1)}{N}\hat{\Gamma}^N_s\right) - \xi_-\left(\cancel{\hat{\Gamma}^{N-1}_s} - \frac{(N-1)}{N}\hat{\Gamma}^N_s\right) = \hat{\Gamma}^N_s$

Final expressions:

$$E_0^N = \underbrace{\mathrm{Tr}\left[\hat{\Gamma}_s^N \hat{H}^{\xi}\right]}_{\langle \Phi^N | \hat{H}^{\xi} | \Phi^N \rangle} + \underbrace{U_c^{\xi}[n^{\xi}] - \int dr \frac{\delta U_c^{\xi}[n^{\xi}]}{\delta n(r)} n^{\xi}(r)}_{N C^{\xi}} - \xi_+ \frac{\partial U^{\xi}[n]}{\partial \xi_+}\bigg|_{n=n^{\xi}} - \xi_- \frac{\partial U^{\xi}[n]}{\partial \xi_-}\bigg|_{n=n^{\xi}}$$

$$\underbrace{\hat{\overline{H}}^{\xi}}_{\text{shifted Hamiltonian}} = \hat{H}^{\xi} + \int dr\, c^{\xi} \hat{n}(r)$$

$$\boxed{E_0^N = \underbrace{\mathrm{Tr}\left[\hat{\Gamma}_s^N \hat{\overline{H}}^{\xi}\right]}_{\langle \Phi^N | \hat{\overline{H}}^{\xi} | \Phi^N \rangle} - \xi_+ \frac{\partial U^{\xi}[n]}{\partial \xi_+}\bigg|_{n=n^{\xi}} - \xi_- \frac{\partial U^{\xi}[n]}{\partial \xi_-}\bigg|_{n=n^{\xi}}}$$

$$E_0^{N+1} = \frac{N+1}{N} E_0^N + \frac{\partial E^{\xi}}{\partial \xi_+} = \underbrace{\mathrm{Tr}\left(\hat{\Gamma}_s^{N+1} \hat{H}^{\xi}\right) + (N+1) C^{\xi}}_{\langle \Phi^{N+1} | \hat{\overline{H}}^{\xi} | \Phi^{N+1} \rangle} + \left(1 - \frac{(N+1)}{N}\xi_+\right) \frac{\partial U^{\xi}[n]}{\partial \xi_+}\bigg|_{n=n^{\xi}} - \frac{(N+1)}{N}\xi_- \frac{\partial U^{\xi}[n]}{\partial \xi_-}\bigg|_{n=n^{\xi}}$$

$$E_0^{N-1} = \frac{(N-1)}{N} E_0^N + \frac{\partial E^{\xi}}{\partial \xi_-} = \underbrace{\mathrm{Tr}\left(\hat{\Gamma}_s^{N-1} \hat{H}^{\xi}\right) + (N-1) C^{\xi}}_{\langle \Phi^{N-1} | \hat{\overline{H}}^{\xi} | \Phi^{N-1} \rangle} - \frac{(N-1)}{N}\xi_+ \frac{\partial U^{\xi}[n]}{\partial \xi_+}\bigg|_{n=n^{\xi}} + \left(1 - \frac{(N-1)}{N}\xi_-\right) \frac{\partial U^{\xi}[n]}{\partial \xi_-}\bigg|_{n=n^{\xi}}$$

Fund. gap expression:

$$E_g = \langle \Phi^{N+1} | \hat{H}^{\xi} | \Phi^{N+1}\rangle + \langle \Phi^{N-1} | \hat{H}^{\xi} | \Phi^{N-1}\rangle$$

$$- 2\langle \Phi^{N} | \hat{H}^{\xi} | \Phi^{N}\rangle$$

$$+ \underbrace{\left(1 - \frac{(N+1)\xi_+}{N} - \frac{(N-1)\xi_+}{N} + 2\xi_+\right)}_{1} \frac{\partial U_c^{\xi}[n]}{\partial \xi_+}$$

$$+ \underbrace{\left(1 - \frac{(N-1)\xi_-}{N} - \frac{(N+1)\xi_-}{N} + 2\xi_-\right)}_{1} \frac{\partial U_c^{\xi}[n]}{\partial \xi_-}$$

$$E_g = \mathrm{Tr}\left(\left[\hat{\Gamma}_s^{N+1} + \hat{\Gamma}_s^{N-1} - 2\hat{\Gamma}_s^{N}\right] \underbrace{\hat{H}^{\xi}}_{\text{without shift!}}\right) + \underbrace{\frac{\partial U_c^{\xi}[n]}{\partial \xi_+} + \frac{\partial U_c^{\xi}[n]}{\partial \xi_-}}_{\left.\frac{\partial U_c^{\xi}[n]}{\partial \xi}\right|_{n=n^{\xi}}}$$

In the particular case $\xi_+ = \xi_- = \xi$

$$U_c^{\xi}[n] = U_c^{(\xi,\xi)}[n]$$

Construction of the functional: for the uniform system

$$U_c^{\xi}[n] = \xi_+ \underbrace{U_{c,(N+1)}[n]}_{\langle \Psi^{N+1}[n] | \hat{T} + \hat{W}_{ee} | \Psi^{N+1}[n]\rangle - \langle \Phi^{N+1}[n] | \;''\; | \Phi^{N+1}[n]\rangle} + \xi_- \underbrace{U_{c,(N-1)}[n]}_{\text{Same for } (N-1)e^-} + \left[1 - \frac{\xi_+(N+1)}{N} - \frac{\xi_-(N-1)}{N}\right] \underbrace{U_{c,N}[n]}_{\text{Same for } Ne^-}$$