Adiabatic connection

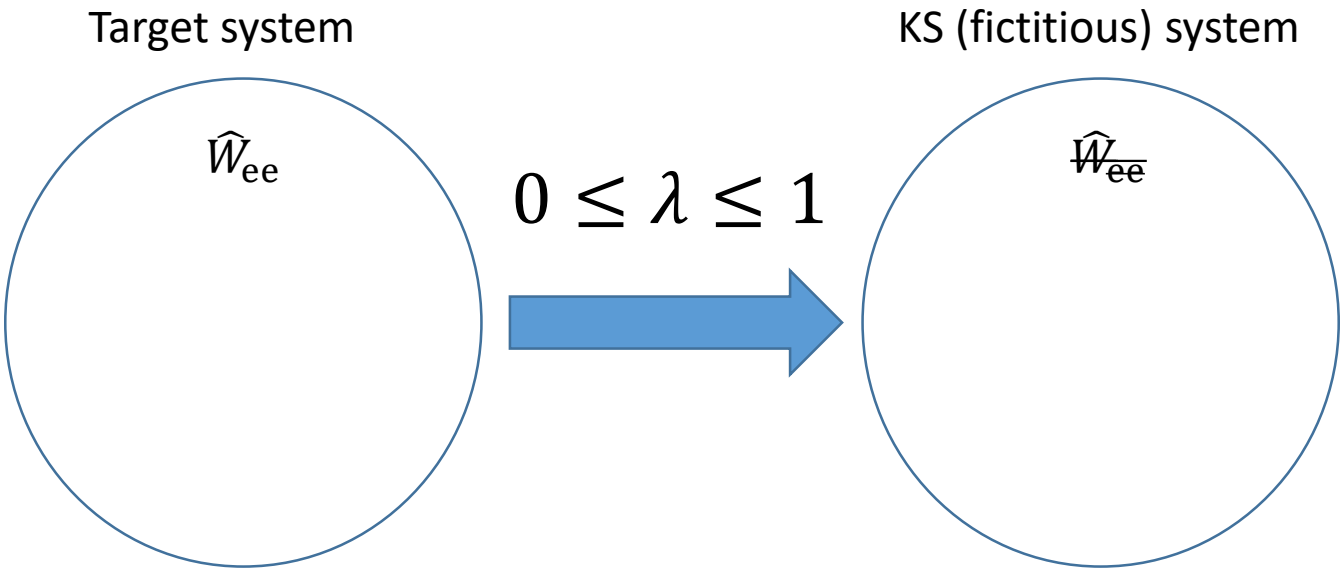
Towards rigorous DFT formulation

Adiabatic connection

- Adiabatically switch on the Coulomb interaction

$$\hat{H}^{\lambda} = \hat{T} + \lambda \hat{W}_{\mathrm{ee}} + \hat{\mathrm{V}}^{\lambda}, \qquad (2.18)$$

- Keep the density $n(\boldsymbol{r})$ constant!



Assume v-representability always

Adiabatic connection

- HK functional for the intermediate

$$F^{\lambda}[n] = \min_{\Psi \to n} \left\langle \Psi \middle| \hat{T} + \lambda \widehat{W}_{\mathrm{ee}} \middle| \Psi \right\rangle \qquad (2.19)$$

$$= T_s[n] + E_{\mathrm{H}}^{\lambda}[n] + E_{\mathrm{xc}}^{\lambda}[n] \qquad (2.20)$$

- Note the linear dependence for Hx!

$$E_{\mathrm{H}}^{\lambda}[n] = \frac{1}{2} \iint \frac{n(\boldsymbol{r}_1) n(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \lambda d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \lambda E_{\mathrm{H}}[n] \qquad (2.21)$$

$$E_{\mathrm{x}}^{\lambda}[n] = \left\langle \Phi[n] \middle| \lambda \widehat{W}_{\mathrm{ee}} \middle| \Phi[n] \right\rangle - E_{\mathrm{H}}^{\lambda}[n] = \lambda E_{\mathrm{x}}[n] \qquad (2.22)$$

$$E_{\mathrm{c}}^{\lambda}[n] = \left\langle \Psi^{\lambda}[n] \middle| \hat{T} + \lambda \widehat{W}_{\mathrm{ee}} \middle| \Psi^{\lambda}[n] \right\rangle - \left\langle \Phi[n] \middle| \hat{T} + \lambda \widehat{W}_{\mathrm{ee}} \middle| \Phi[n] \right\rangle \qquad (2.23)$$

Hellmann-Feynman theorem

$$\frac{\partial E_c^{\lambda}[n]}{\partial \lambda} = \left\langle \Psi^{\lambda}[n] \middle| \widehat{W}_{\mathrm{ee}} \middle| \Psi^{\lambda}[n] \right\rangle - \left\langle \Phi[n] \middle| \widehat{W}_{\mathrm{ee}} \middle| \Phi[n] \right\rangle \qquad (2.24)$$

$$E_c[n] = \int_0^1 \left\langle \Psi^{\lambda}[n] \middle| \widehat{W}_{\mathrm{ee}} \middle| \Psi^{\lambda}[n] \right\rangle d\lambda - \left\langle \Phi[n] \middle| \widehat{W}_{\mathrm{ee}} \middle| \Phi[n] \right\rangle \qquad (2.25)$$

- Correlation functional has been defined w/o the kinetic energy operator!

Averaged correlation hole

$$E_c[n] = \frac{1}{2}\int_0^1 d\lambda \iint \frac{n(\boldsymbol{r}_1)n_c^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r_1}-\boldsymbol{r}_2|}\,d\boldsymbol{r}_1 d\boldsymbol{r}_2 \qquad (2.26)$$

$$= \frac{1}{2}\iint \frac{n(\boldsymbol{r}_1)\bar{n}_c^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r_1}-\boldsymbol{r}_2|}\,d\boldsymbol{r}_1 d\boldsymbol{r}_2 \qquad (2.27)$$

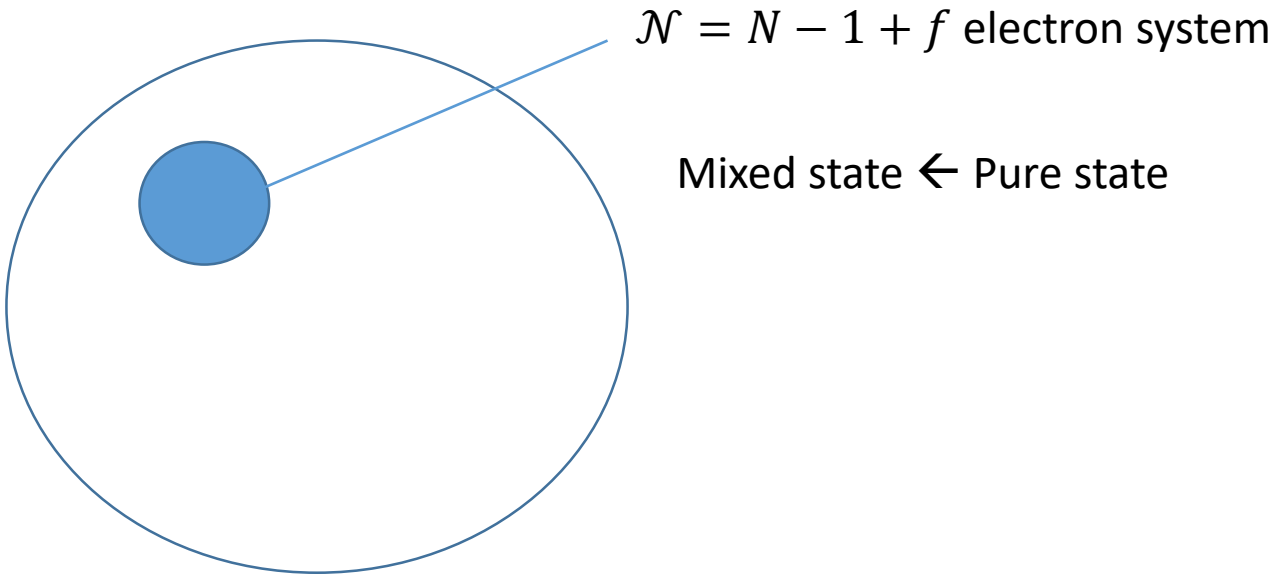
- Averaged correlation hole

$$\bar{n}_c^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2) = \int_0^1 d\lambda n_c^\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2)\,.$$

- This needs to be determined as a functional of the density!

Fractional number of electrons

- DFT is formulated for
  1. Subsystems (embedded in a large system)
  2. Finite temperatures = canonical ensembles
  3. Grand canonical ensembles



DFT for mixed states

$$E_0^{\mathcal{N}} = \min_{\hat{\Gamma}} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}}\right)\right], \qquad (2.30)$$

$$\hat{\Gamma} = (1-f)|\Psi^{N-1}\rangle\langle\Psi^{N-1}| + f|\Psi^{N}\rangle\langle\Psi^{N}|. \qquad (2.31)$$

- Consider only two states with different number of electrons, for simplicity

$$E_0^{\mathcal{N}} = (1-f)E_0^{N-1} + f E_0^{N}$$

Integer discontinuity

$$\frac{dE_0^{\mathcal{N}}}{d\mathcal{N}} = \begin{cases} E_0^N - E_0^{N-1} \equiv -I_N \text{ when } N-1 < \mathcal{N} < N \\ E_0^{N+1} - E_0^N \equiv -A_N \text{ when } N < \mathcal{N} < N+1 \end{cases}$$

- ionization I_N and the affinity A_N are different!
- $dE_0^{\mathcal{N}}/d\mathcal{N} \equiv \mu$ is discontinuous at the integer number
- The fundamental gap, or the HOMO-LUMO gap, is defined as

$$I_N - A_N \equiv E_{\text{gap}}^N.$$

Similarly for the KS-DFT

$$F[n] = \min_{\hat{\Gamma}\to n} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \hat{W}_{\mathrm{ee}}\right)\right] \qquad (2.38)$$

$$= T_s[n] + E_{\mathrm{Hxc}}[n] \qquad (2.39)$$

$$T_s[n] = \min_{\hat{\Gamma}_s\to n} \mathrm{Tr}[\hat{\Gamma}_s \hat{T}]$$

$$\hat{\Gamma}_s = (1-f)\,|\Phi^{N-1,f}\rangle\langle\Phi^{N-1,f}| + f|\Phi^{N,f}\rangle\langle\Phi^{N,f}| \qquad (2.41)$$

(Remember that this is a simplified description using only two states)

Then, we can formulate the KS eq.

$$E = \sum_i^N n_i \int \phi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r}) \right) \phi_i(\boldsymbol{r}) d\boldsymbol{r} + E_{\mathrm{Hxc}}[n] \qquad (2.42)$$

$$n(\boldsymbol{r}) = \sum_i^N n_i |\phi_i(\boldsymbol{r})|^2 . \qquad (2.43)$$

- $n_i = 1$ for $i \leq N - 1$ and $n_N = f$ when considering the two states.

This way, partial occupation number has been justified.

Note on the KS-eq.

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r}) \tag{2.44}$$

$$v_{\mathrm{s}}(\boldsymbol{r}) = v_{\mathrm{ne}}(\boldsymbol{r}) + \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\boldsymbol{r})}. \tag{2.45}$$

- KS equation is unchanged
- Be careful about the exchange-correlation potential, $\delta E/\delta n(\boldsymbol{r})$!

$$\delta E_{\mathrm{Hxc}}[n] = \int\left(\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\boldsymbol{r})} + \mathrm{const}\right)\delta n(\boldsymbol{r})d\boldsymbol{r} \tag{2.46}$$

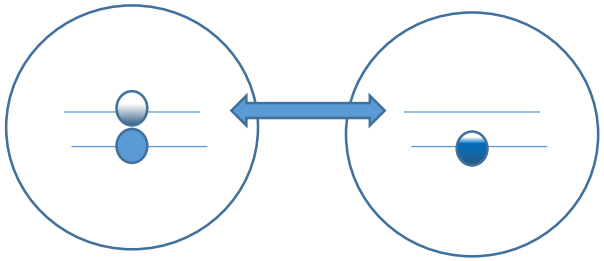
- Derivative with and without $\int \delta n(\boldsymbol{r})d\boldsymbol{r} = N$ are different by a constant.

  This is related to the constant appeared in HK theorem.

- Janak theorem applies, which is different from the Koopmans.

$$\frac{\partial E}{\partial n_i} = \varepsilon_i \tag{2.47}$$

More about Janak



- HOMO of $N+\delta$ electron system

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}\right)_{N+\delta} = \varepsilon_{\mathrm{HOMO}}^{N+\delta}, \tag{2.54}$$

$$\varepsilon_{\mathrm{HOMO}}^{N+\delta} = -A_N \tag{2.55}$$

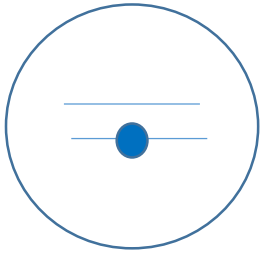
$$= \int \phi_{\mathrm{HOMO}}^{N+\delta}(\boldsymbol{r})^* \left(-\frac{1}{2}\nabla^2 + v_s^{N+\delta}(\boldsymbol{r})\right) \phi_{\mathrm{HOMO}}^{N+\delta}(\boldsymbol{r}) d\boldsymbol{r}. \tag{2.56}$$

- LUMO of $N-\delta$ electron system

$$\varepsilon_{\mathrm{LUMO}}^{N-\delta} = \int \phi_{\mathrm{LUMO}}^{N-\delta}(\boldsymbol{r})^* \left(-\frac{1}{2}\nabla^2 + v_s^{N-\delta}(\boldsymbol{r})\right) \phi_{\mathrm{LUMO}}^{N-\delta}(\boldsymbol{r}) d\boldsymbol{r}. \tag{2.57}$$

$$v_s^{N+\delta}(\boldsymbol{r}) - v_s^{N-\delta}(\boldsymbol{r}) \equiv \Delta_{\mathrm{xc}}^{N}$$

More about Janak (cont'd)



$$\varepsilon_{\mathrm{HOMO}}^{N+\delta} = \varepsilon_{\mathrm{LUMO}}^{N-\delta} + \Delta_{\mathrm{xc}}^{N} \qquad (2.58)$$

- After taking the limit,
  $\varepsilon_{\mathrm{LUMO}}^{N} = -A_N - \Delta_{\mathrm{xc}}^{N}.$ (2.60)
- Therefore
  $E_{\mathrm{gap}}^{N} = \varepsilon_{\mathrm{LUMO}}^{N} - \varepsilon_{\mathrm{HOMO}}^{N} + \Delta_{\mathrm{xc}}^{N}.$ (2.63)

HOMO-LUMO gap is not necessarily the fundamental gap ($I_N - A_N$)!

Existing functionals

LDA

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int n(r)\varepsilon_{\mathrm{xc}}^{\text{uniform gas}}\big(n(\boldsymbol{r})\big)d\boldsymbol{r}\,.$$

$$-\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}(\boldsymbol{r}) + \varepsilon_c\left(r_s\big(n(\boldsymbol{r})\big)\right) \qquad \text{where} \quad r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}$$

$$\varepsilon_c(r_s) = \begin{cases} A\ln r_s + B + C\, r_s \ln r_s & \text{when } r_s \le r_{s,0} \\ \dfrac{a}{r_s} + \dfrac{b}{r_s^{3/2}} & \text{when } r_s > r_{s,0} \end{cases}$$

GGA

$$E_{\mathrm{xc}}^{\mathrm{GEA}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}[n] + \int C_{\mathrm{xc}}\big(n(\boldsymbol{r})\big) n(\boldsymbol{r})^{\frac{4}{3}} \left(\frac{\nabla n(\boldsymbol{r})}{n(\boldsymbol{r})^{\frac{4}{3}}} \right)^2 d\boldsymbol{r}, \quad (3.10)$$

- Correction term can be larger, e.g., at infinity where the density low.

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int f\big(n(\boldsymbol{r}), \nabla n(\boldsymbol{r})\big) d\boldsymbol{r} \quad (3.11)$$

Becke 88	Correct the asymptotic behavior of the exchange energy Local approximation to the nonlocal exchange of rare gas
LYP	Local approximation to the HF pair density
PW91	Local modeling of the exchange hole and the averaged correlation hole
PBE	Simplified PW91. Probably the most popular PBE

Meta-GGA

$$E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int_N f\left(n(\boldsymbol{r}), \nabla n(\boldsymbol{r}), \nabla^2 n(\boldsymbol{r}), \tau(\boldsymbol{r})\right) d\boldsymbol{r} \tag{3.13}$$

$$\tau(\boldsymbol{r}) = \frac{1}{2}\sum_i |\nabla \phi_i(\boldsymbol{r})|^2 \tag{3.14}$$

$$E_0 = \min_{\Phi} \left\langle \Phi \middle| \hat{T} + \hat{V}_{\mathrm{ne}} \middle| \Phi \right\rangle + E_{\mathrm{H}}[n_\Phi] + E_{\mathrm{xc}}[n_\Phi, \tau_\Phi] .$$

- Strictly, this is not the KS-DFT because of $\tau(\boldsymbol{r})$

Hybrid DFT

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{\sigma}^{N_\sigma}\sum_{ij}\iint \frac{\phi_{i\sigma}^{*}(\boldsymbol{r}_1)\phi_{j\sigma}(\boldsymbol{r_1})\phi_{j\sigma}^{*}(\boldsymbol{r}_2)\phi_{i\sigma}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2, \quad (3.18)$$

$$E_{\mathrm{xc}}^{3\mathrm{H}} = aE_{\mathrm{x}}^{\mathrm{HF}} + bE_{x}^{\mathrm{GGA}} + (1-a-b)E_{x}^{\mathrm{LDA}} + cE_{\mathrm{c}}^{\mathrm{GGA}} + (1-c)E_{\mathrm{c}}^{\mathrm{LDA}}. \quad (3.17)$$

The most famous parameterization is known as B3LYP, which was constructed by using the B88 exchange for the GGA exchange and the LYP correlation for the GGA correlation.

$$E_{\mathrm{xc}}^{1\mathrm{H}} = aE_{\mathrm{x}}^{HF} + (1-a)E_{\mathrm{x}}^{\mathrm{DFA}} + E_{\mathrm{c}}^{\mathrm{DFA}}, \quad (3.19)$$

where DFA stands for any semilocal density functional approximation (DFA). The most famous one is called PBE0 where the fitting parameter was set to be 0.25.

Double hybrid

$$E_{\mathrm{xc}}^{\mathrm{2DH}} = a_{\mathrm{x}} E_{\mathrm{x}}^{HF} + (1 - a_{\mathrm{x}}) E_{\mathrm{x}}^{\mathrm{DFA}} + (1 - a_{\mathrm{c}}) E_{\mathrm{c}}^{\mathrm{DFA}} + a_{\mathrm{c}} E_{\mathrm{c}}^{\mathrm{MP2}}, (3.22)$$

where MP2 stands for the second order approximation to the correlation energy

$$E_{\mathrm{c}}^{\mathrm{MP2}} = -\frac{1}{4} \sum_{ij=1}^{N} \sum_{ab=N+1}^{2M} \frac{\left| \langle \psi_i \psi_j | \psi_a \psi_b \rangle - \langle \psi_i \psi_j | \psi_b \psi_a \rangle \right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, (3.23)$$

where the bracket appearing in the numerator indicates the Coulomb integral

$$\langle \psi_i \psi_j | \psi_a \psi_b \rangle = \iint \frac{\psi_i^*(\boldsymbol{r}_1) \psi_j^*(\boldsymbol{r_2}) \psi_a(\boldsymbol{r}_1) \psi_b(\boldsymbol{r_2})}{|\boldsymbol{r}_1 - \boldsymbol{r_2}|} d\boldsymbol{x}_1 d\boldsymbol{x}_2. (3.24)$$

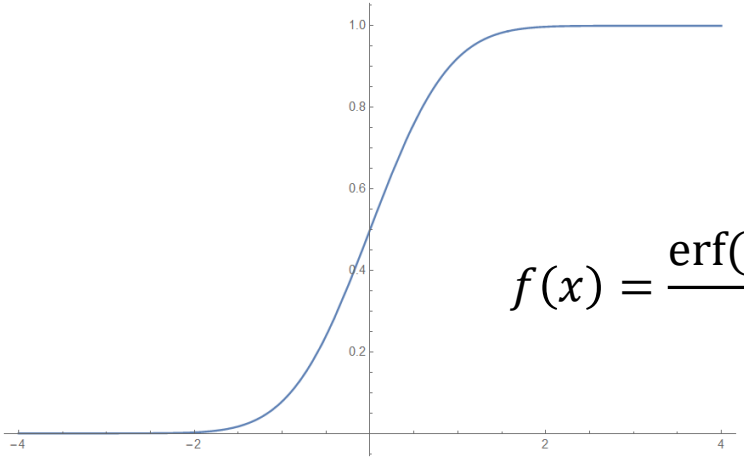
Range separated hybrid DFT

$$E_{\mathrm{xc}}^{\mathrm{LC}} = E_{\mathrm{x}}^{\text{long range,HF}} + E_{\mathrm{x}}^{\text{short range,DFA}} + E_{\mathrm{c}}^{\mathrm{DFA}}.$$

The range-separation is done using the error function as

$$E_{\mathrm{x}}^{\text{long range,HF}}$$

$$= -\frac{1}{2}\sum_{\sigma}^{N_\sigma}\sum_{ij}\iint \frac{\phi_{i\sigma}^{*}(\boldsymbol{r}_1)\phi_{j\sigma}(\boldsymbol{r_1})f(\mu(|\boldsymbol{r}_1-\boldsymbol{r}_2|-r_c))\phi_{j\sigma}^{*}(\boldsymbol{r}_2)\phi_{i\sigma}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \quad (3.27)$$



$$f(x) = \frac{\mathrm{erf}(x)+1}{2}$$

Exact exchange with OEP

$$E_{\mathrm{x}} = -\frac{1}{2}\sum_{\sigma}\sum_{ij}^{N_\sigma}\iint \frac{\phi_{i\sigma}^{*}(\boldsymbol{r}_1)\phi_{j\sigma}(\boldsymbol{r_1})\phi_{j\sigma}^{*}(\boldsymbol{r}_2)\phi_{i\sigma}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{r}_1 d\boldsymbol{r}_2, \quad (3.18)$$

$$\frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\boldsymbol{r})} = \int \frac{\delta E_{\mathrm{x}}}{\delta n(\boldsymbol{r}')}\frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})}d\boldsymbol{r}' \equiv \int v_{\mathrm{x}}(\boldsymbol{r}')\chi_0(\boldsymbol{r}',\boldsymbol{r})d\boldsymbol{r}'\,. \quad (4.2)$$

where

$$\chi_0(\boldsymbol{r}',\boldsymbol{r}) = -\sum_{\sigma}\sum_{i=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}\iint \frac{\phi_{i\sigma}^{*}(\boldsymbol{r}')\phi_{a\sigma}(\boldsymbol{r})\phi_{a\sigma}^{*}(\boldsymbol{r})\phi_{i\sigma}(\boldsymbol{r}')}{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}}d\boldsymbol{r}_1 d\boldsymbol{r}_2 + \mathrm{c.c.} \quad (4.5)$$

and

$$\frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\boldsymbol{r})} = \sum_{i\sigma}\frac{\delta E_{\mathrm{x}}}{\delta \phi_{i\sigma}(\boldsymbol{r}')}\frac{\delta \phi_{i\sigma}(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})}d\boldsymbol{r}'$$

$$= \sum_{\sigma}\sum_{ij=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}\left(\phi_{a\sigma}\phi_{j\sigma}\middle|\phi_{j\sigma}\phi_{i\sigma}\right)\frac{\phi_{a\sigma}(\boldsymbol{r})\phi_{i\sigma}^{*}(\boldsymbol{r})}{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}} + \mathrm{c.c.} \quad (4.6)$$

Second-order Görling-Levy perturbation theory

$$\hat{H}^{\lambda} = \hat{T} + \lambda\hat{W}_{\mathrm{ee}} + \hat{\mathrm{V}}^{\lambda}$$

Effective KS potential

is rewritten as

$$\hat{\mathrm{V}}^{\lambda} = \hat{V}_{\mathrm{s}} - \lambda\hat{V}_{\mathrm{Hx}} - \hat{V}_{\mathrm{c}}^{\lambda}$$

External potential at $\lambda = 1$

so that we start from

$$\hat{H}^{\lambda} = \left(\hat{T} + \hat{V}_{\mathrm{s}}\right) + \lambda\left(\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}\right) - \hat{V}_{\mathrm{c}}^{\lambda}$$

Apply perturbation $\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}$ to the reference KS state Φ

$$|\Psi^{(1)}\rangle = -\sum_{n\neq 0} |\Phi_n\rangle \frac{\langle\Phi_n|\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}|\Phi_n\rangle}{\mathcal{E}_n - \mathcal{E}_0}$$

The perturbed WF is inserted into the correlation energy

$$E_{\mathrm{c}}^{\lambda} = \langle\Psi^{\lambda}|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Psi^{\lambda}\rangle - \langle\Phi|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Phi\rangle$$

The second order (the lowest order) correlation energy is then

$$E_{\mathrm{c}}^{(2)} = \langle\Phi|\hat{W}_{\mathrm{ee}}|\Psi^{(1)}\rangle = \langle\Phi|\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}|\Psi^{(1)}\rangle = -\sum_{n\neq 0} |\frac{\left|\langle\Phi|\hat{W}_{\mathrm{ee}} - \hat{V}_{\mathrm{Hx}}|\Phi_n\rangle\right|^2}{\mathcal{E}_n - \mathcal{E}_0}.$$

Summary and outlook

- The empirically determined correlation functionals are improving in the accuracy year by year.
- But is not systematic!

- Density-density correlation is difficult to formulate but density response is easier to access.

Fluctuation dissipation theorem

(Kubo formula for density-density correlation)

$$\chi(\boldsymbol{r}'t', \boldsymbol{r}t) = \frac{\delta n(\boldsymbol{r}'t')}{\delta v_{\mathrm{ne}}(\boldsymbol{r}t)}$$

Density operators

Introduction of the density operator

$$\hat{n}_1(\boldsymbol{r}) = \sum_i^N \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

$$n(\boldsymbol{r}) = \langle \Psi | \hat{n}_1(\boldsymbol{r}) | \Psi \rangle$$

Pair density operator

$$\hat{n}_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \hat{n}_1(\boldsymbol{r}_1)\hat{n}_1(\boldsymbol{r}_2) - \hat{n}_1(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2).$$

- Those are used to obtain

$$\hat{T} = -\frac{1}{2}\int \left[\nabla^2_{\boldsymbol{r}} \hat{n}_1\left(\boldsymbol{r}, \boldsymbol{r}'\right)\right]_{\boldsymbol{r}'=\boldsymbol{r}} d\boldsymbol{r}$$

$$\widehat{W}_{\mathrm{ee}} = \frac{1}{2}\iint w_{\mathrm{ee}}(\boldsymbol{r}_1, \boldsymbol{r}_2)\hat{n}_2(\boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$\hat{V}_{\mathrm{ne}} = \int v_{\mathrm{ne}}\,(\boldsymbol{r})\hat{n}(\boldsymbol{r}) d\boldsymbol{r}$$

Correlation energy via density operator

$$E_{\mathrm{c}} = \int_0^1 d\lambda \left\langle \Psi^\lambda \middle| \widehat{W}_{\mathrm{ee}} \middle| \Psi^\lambda \right\rangle - \left\langle \Phi \middle| \widehat{W}_{\mathrm{ee}} \middle| \Phi \right\rangle = \frac{1}{2} \int_0^1 d\lambda \iint \frac{n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \,, \quad (4.15)$$

where

$$n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2) = n_2^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2) - n_{2,\mathrm{KS}}(\boldsymbol{r}_1, \boldsymbol{r}_2).$$

This can be described as

$$\begin{aligned} n_2^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2) &= \left\langle \Psi^\lambda \middle| \hat{n}_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \middle| \Psi^\lambda \right\rangle \\ &= \left\langle \Psi^\lambda \middle| \hat{n}_1(\boldsymbol{r}_1) \hat{n}_1(\boldsymbol{r}_2) \middle| \Psi^\lambda \right\rangle - \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) \left\langle \Psi^\lambda \middle| \hat{n}_1(\boldsymbol{r}_1) \middle| \Psi^\lambda \right\rangle \\ n_{2,\mathrm{KS}}(\boldsymbol{r}_1, \boldsymbol{r}_2) &= \langle \Phi | \hat{n}_1(\boldsymbol{r}_1) \hat{n}_1(\boldsymbol{r}_2) | \Phi \rangle - \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) \langle \Phi | \hat{n}_1(\boldsymbol{r}_1) | \Phi \rangle \end{aligned} \quad (4.16,17)$$

and using the fact that the density is independent of λ, we have

$$n_{2,\mathrm{c}}^\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left\langle \Psi^\lambda \middle| \hat{n}_1(\boldsymbol{r}_1) \hat{n}_1(\boldsymbol{r}_2) \middle| \Psi^\lambda \right\rangle - \langle \Phi | \hat{n}_1(\boldsymbol{r}_1) \hat{n}_1(\boldsymbol{r}_2) | \Phi \rangle. \quad (4.18)$$

Correlation has been related to the density fluctuation

Response functions

Static response of the KS system

$$\chi_0(\boldsymbol{r}', \boldsymbol{r}) = \frac{\delta n(\boldsymbol{r}')}{\delta v_s(\boldsymbol{r})}$$

time-dependent response

$$\chi_0(\boldsymbol{r}'t', \boldsymbol{r}t) = \frac{\delta n(\boldsymbol{r}'t')}{\delta v_s(\boldsymbol{r}t)}.$$

Rather, we need response of the interacting systems

$$\chi(\boldsymbol{r}'t', \boldsymbol{r}t) = \frac{\delta n(\boldsymbol{r}'t')}{\delta v_{\mathrm{ne}}(\boldsymbol{r}t)}.$$

1. Many-body perturbation theory
2. Time-dependent density functional theory

Many-body perturbation theory

Quantum field theory (non relativistic)

Many-body Green's function

$$\hat{H} = \int d\boldsymbol{x}\, \hat{\psi}^{\dagger}(\boldsymbol{x}) \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\boldsymbol{r}) \right) \hat{\psi}(x) \qquad h(\boldsymbol{r})$$

$$+ \frac{1}{2} \iint d\boldsymbol{x}_1 d\boldsymbol{x}_2\, \hat{\psi}^{\dagger}(\boldsymbol{x}_1)\hat{\psi}^{\dagger}(\boldsymbol{x}_2) v(\boldsymbol{r}_1, \boldsymbol{r}_2) \hat{\psi}(\boldsymbol{x}_2)\hat{\psi}(\boldsymbol{x}_1)$$

$1/|\boldsymbol{r}_1 - \boldsymbol{r}_2|$

$$\psi(\boldsymbol{x}) \equiv \sum\nolimits_{\mathrm{i}} \psi_i(\boldsymbol{x}) \hat{c}_i$$

Heisenberg representation

$$\psi(1) \equiv \psi(\boldsymbol{x}_1, t_1) = e^{i\hat{H}t_1} \psi(\boldsymbol{x}_1) e^{-i\hat{H}t_1}$$

$$\mathrm{i}G(1,2) = \langle N | T\left[\hat{\psi}(1)\hat{\psi}^{\dagger}(2)\right] | N \rangle = \begin{cases} \langle N | \hat{\psi}(1)\hat{\psi}^{\dagger}(2) | N \rangle & \text{when } \mathrm{t}_1 > t_2 \\ -\langle N | \hat{\psi}^{\dagger}(2)\hat{\psi}(1) | N \rangle & \text{when } \mathrm{t}_1 < t_2 \end{cases} \qquad (2)$$

Time ordered Green's function

Equation of motion

$$\left(\mathrm{i}\frac{\partial}{\partial t}+\frac{\nabla^2}{2}\right)G(1,2)=\delta(1-2)-i\sum_{\sigma_3}v(3,1)\left\langle N\left|T\left[\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)\hat{\psi}^{\dagger}(2)\right]\right|N\right\rangle$$

$$\frac{\partial\hat{\psi}(1)}{\partial t_1}=-\mathrm{i}e^{\mathrm{i}\hat{H}t_1}\left[\hat{\psi}(\boldsymbol{x}_1),\hat{H}\right]e^{-\mathrm{i}\hat{H}t_1}$$

$$=h(\boldsymbol{r}_1)\hat{\psi}(\boldsymbol{x}_1)+\int d\boldsymbol{x}_2\,\hat{\psi}^{\dagger}(\boldsymbol{x}_2)v(\boldsymbol{r}_1,\boldsymbol{r}_2)\hat{\psi}(\boldsymbol{x}_2)\psi(\boldsymbol{x}_1)$$

$$\frac{\partial\hat{\psi}(1)}{\partial t_1}=-\mathrm{i}h(1)\hat{\psi}(1)-i\int d3\hat{\psi}(3)v(1,3)\hat{\psi}(3)\hat{\psi}(1)$$

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1,2)$$

$$=\delta(t_1-t_2)\left\langle N\left|\hat{\psi}(1)\hat{\psi}^{\dagger}(2)\right|N\right\rangle+\theta(t_1-t_2)\left\langle N\left|\frac{\partial\hat{\psi}(1)}{\partial t_1}\hat{\psi}^{\dagger}(2)\right|N\right\rangle$$

$$-\delta(t_1-t_2)\left\langle N\left|\hat{\psi}^{\dagger}(2)\hat{\psi}(1)\right|N\right\rangle-\theta(t_1-t_2)\left\langle N\left|\hat{\psi}^{\dagger}(2)\frac{\partial\hat{\psi}(1)}{\partial t_1}\right|N\right\rangle$$

Equation of motion

$$\left(\mathrm{i}\frac{\partial}{\partial t}+\frac{\nabla^2}{2}\right)G(1,2)=\delta(1-2)-i\sum_{\sigma_3}v(3,1)\left\langle N\middle|T\left[\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)\hat{\psi}^{\dagger}(2)\right]\middle|N\right\rangle$$

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1,2)$$

$$=\delta(1,2)+h(1)G(1,2)-i\int d3\,v(1,3)[\theta(t_1-t_2)\left\langle N\middle|\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)\hat{\psi}^{\dagger}(2)\middle|N\right\rangle$$

$$-\theta(t_2-t_1)\left\langle N\middle|\hat{\psi}^{\dagger}(2)\hat{\psi}^{\dagger}(3)\hat{\psi}(3)\hat{\psi}(1)\middle|N\right\rangle$$

$$\mathrm{i}^2G_2(1,2;1',2')=\left\langle N\middle|T\left[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^{\dagger}(1')\hat{\psi}^{\dagger}(2')\right]\middle|N\right\rangle$$

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1,2)$$

$$=\delta(t_1-t_2)\left\langle N\middle|\hat{\psi}(1)\hat{\psi}^{\dagger}(2)\middle|N\right\rangle+\theta(t_1-t_2)\left\langle N\middle|\frac{\partial\hat{\psi}(1)}{\partial t_1}\hat{\psi}^{\dagger}(2)\middle|N\right\rangle$$

$$-\delta(t_1-t_2)\left\langle N\middle|\hat{\psi}^{\dagger}(2)\hat{\psi}(1)\middle|N\right\rangle-\theta(t_1-t_2)\left\langle N\middle|\hat{\psi}^{\dagger}(2)\frac{\partial\hat{\psi}(1)}{\partial t_1}\middle|N\right\rangle$$

Equation of motion

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1,2) = \delta(1,2) + h(1)G(1,2) + \mathrm{i}\int d3v(1,3)G_2(1,3^+;2,3^{++})$$

$$t_3^{++} > t_3^+ > t_3$$

Once the EOM has been solved,,,

$$n_1(\boldsymbol{x}_1,\boldsymbol{x}_2) = \langle N|\hat{\psi}^\dagger(\boldsymbol{x}_2)\hat{\psi}(\boldsymbol{x}_1)|N\rangle = -\mathrm{i}G(\boldsymbol{x}_1 t_1,\boldsymbol{x}_2 t_1^+) \qquad (3)$$

$$n_1(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\mathrm{i}\sum\nolimits_\sigma G(\boldsymbol{r}_1\sigma t_1,\boldsymbol{r}_2\sigma t_1^+)\,. \qquad (4)$$

Lehman representation

$$
\begin{aligned}
&\mathrm{i}G(\boldsymbol{x}_1, \boldsymbol{x}_2, \tau) \\
&= \theta(\tau) \sum\nolimits_a \langle N|\hat{\psi}(\boldsymbol{x}_1)|N+1, a\rangle\langle N+1, a|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N\rangle e^{-\mathrm{i}(E_{N+1,a}-E_N)\tau} \\
&- \theta(-\tau) \sum\nolimits_a \langle N|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N-1, a\rangle\langle N-1, a|\hat{\psi}(\boldsymbol{x}_1)|N\rangle e^{-\mathrm{i}(E_N-E_{N-1,a})\tau},
\end{aligned} \tag{5}
$$

$$
\begin{aligned}
&G(\boldsymbol{x}_1, \boldsymbol{x}_2, \omega) \\
&= \sum\nolimits_a \frac{\langle N|\hat{\psi}(\boldsymbol{x}_1)|N+1, a\rangle\langle N+1, a|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N\rangle}{\omega - E_{N+1,a} + E_N + i0^+} \\
&+ \sum\nolimits_a \frac{\langle N|\hat{\psi}^\dagger(\boldsymbol{x}_2)|N-1, a\rangle\langle N-1, a|\hat{\psi}(\boldsymbol{x}_1)|N\rangle}{\omega - E_{N-1,a} + E_N - i0^+}
\end{aligned}
$$

$$
= \sum\nolimits_a \frac{f_a(\boldsymbol{x}_1) f_a^*(\boldsymbol{x}_2)}{\omega + A_a + i0^+} + \sum\nolimits_i \frac{f_i(\boldsymbol{x}_1) f_i^*(\boldsymbol{x}_2)}{\omega - I_i - i0^+}, \tag{6}
$$

Wave function of the quasi-particle

Linear response of many-body

$$\hat{H}'(\mathrm{t}) = \int \hat{n}(\boldsymbol{r}) V_{\mathrm{ext}}(\boldsymbol{r}, t) d\boldsymbol{r}$$

$$\mathrm{i}\frac{\partial U_I(t, t_0)}{\partial t} = \hat{H}'_I(t) U_I(t, t_0)$$

This is solved as

$$U_I(t, t_0) \simeq 1 - \mathrm{i}\int_{\mathrm{t_0}}^{\mathrm{t}} dt'\, \hat{H}'_I(t') = 1 - \mathrm{i}\int_{\mathrm{t_0}}^{\mathrm{t}} dt'\, e^{\mathrm{i}\hat{H}_0 t'} \hat{H}(t') e^{-\mathrm{i}\hat{H}_0 t'}.$$

Therefore, the expectation value of the density is given as

$$\delta n(\boldsymbol{r}t) = \langle U_I^{\dagger}(t, t_0) \hat{n}_I(\boldsymbol{r}t) U_I(t, t_0) \rangle$$

$$= i\int_{t_0}^{t} dt' \int d\boldsymbol{r}' \, \langle [\hat{n}_I(\boldsymbol{r}t), \hat{n}_I(\boldsymbol{r}'t')] \rangle V_{\mathrm{ext}}(\boldsymbol{r}', t')$$

From the definition of the response function, we have

$$\chi(\boldsymbol{r}t, \boldsymbol{r}'t') = \mathrm{i}\langle [\hat{n}_I(\boldsymbol{r}t), \hat{n}_I(\boldsymbol{r}'t')] \rangle$$

Two-body Green's function

$$\mathrm{i}^2 G_2(1,2;1',2') = \langle N|T[\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(1')\hat{\psi}^\dagger(2')]|N\rangle, \quad (7)$$

propagation of a pair of particles; electrons, holes, or electron-hole

We define the four-point linear response function as

$$\mathrm{i}\chi(1,2;1',2') = \mathrm{i}^2 G_2(1,2;1',2') - iG(1,1')iG(2,2'). \quad (8)$$

Because the special case

$$\mathrm{i}\chi(1,2;\boldsymbol{x}'_1 t_1^+, \boldsymbol{x}'_2 t_2^+) = \langle N|T[\hat{\psi}^\dagger(1')\hat{\psi}(1)\hat{\psi}^\dagger(2')\hat{\psi}(2)]|N\rangle - \langle N|\hat{\psi}^\dagger(1')\hat{\psi}(1)|N\rangle\langle N|\hat{\psi}^\dagger(2')\hat{\psi}(2)|N\rangle \quad (9)$$

can be regarded as a natural extension of the (one-body) response function.
Lehman representation is

$$\chi(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}'_1,\boldsymbol{x}'_2;\omega) = \sum_{n\neq 0}\left[\frac{\langle N|\hat{\psi}^\dagger(1')\hat{\psi}(1)|N,n\rangle\langle N,n|\hat{\psi}^\dagger(2')\hat{\psi}(2)|N\rangle}{\omega-(E_{N,n}-E_N)+i0^+} - \frac{\langle N|\hat{\psi}^\dagger(2')\hat{\psi}(2)|N,n\rangle\langle N,n|\hat{\psi}^\dagger(1')\hat{\psi}(1)|N\rangle}{\omega+(E_{N,n}-E_N)-i0^+}\right] \quad (11)$$

For independent electron-hole pairs

$$\chi_{\mathrm{IP}}(1,2;1',2') = -iG(1,1')G(2,2') \tag{12}$$

or

$$\chi_{\mathrm{IP}}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1',\boldsymbol{x}_2';\tau) = -iG(\boldsymbol{x}_1,\boldsymbol{x}_2';\tau)G(\boldsymbol{x}_2,\boldsymbol{x}_1';-\tau) \tag{13}$$

$$\chi_{\mathrm{IP}}(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1',\boldsymbol{x}_2';\omega) = \sum_{i\le N<a}\left[\frac{f_i^*(\boldsymbol{x}_1')f_a(\boldsymbol{x}_1)f_a^*(\boldsymbol{x}_2')f_i(\boldsymbol{x}_2)}{\omega-(\mathcal{E}_a-\mathcal{E}_i)+i0^+} - \frac{f_i^*(\boldsymbol{x}_2')f_a(\boldsymbol{x}_2)f_a^*(\boldsymbol{x}_1')f_i(\boldsymbol{x}_1)}{\omega+(\mathcal{E}_a-\mathcal{E}_i)-i0^+}\right]. \tag{14}$$

In this approximation, the response function can be described by the wave function of quasiparticles

Let us return to the ACFD formalism

Adiabatic connection fluctuation dissipation theorem

The response function at finite λ

$$
\begin{aligned}
&\mathrm{i}\chi_\lambda(\boldsymbol{r}_1 t_1, \boldsymbol{r}_2 t_2) \\
&= \left\langle \Psi^\lambda \middle| T[\hat{n}^\lambda(\boldsymbol{r}_1 t_1)\hat{n}^\lambda(\boldsymbol{r}_2 t_2)] \middle| \Psi^\lambda \right\rangle - \left\langle \Psi^\lambda \middle| T\left[\hat{n}^\lambda(\boldsymbol{r}_1 t_1)\right] \middle| \Psi^\lambda \right\rangle \left\langle \Psi^\lambda \middle| T\left[\hat{n}^\lambda(\boldsymbol{r}_2 t_2)\right] \middle| \Psi^\lambda \right\rangle \\
&= \left\langle \Psi^\lambda \middle| T[\hat{n}^\lambda(\boldsymbol{r}_1 t_1)\hat{n}^\lambda(\boldsymbol{r}_2 t_2)] \middle| \Psi^\lambda \right\rangle - \left\langle \Psi^\lambda \middle| \hat{n}(\boldsymbol{r}_1) \middle| \Psi^\lambda \right\rangle \left\langle \Psi^\lambda \middle| \hat{n}(\boldsymbol{r}_2) \middle| \Psi^\lambda \right\rangle
\end{aligned}
\tag{4.19}
$$

If we set $t_2 = t_1 + 0^+$, the Heisenberg phase factor is canceled out and

$$
\mathrm{i}\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-) = \left\langle \Psi^\lambda \middle| \hat{n}(\boldsymbol{r}_1)\hat{n}(\boldsymbol{r}_2) \middle| \Psi^\lambda \right\rangle - \left\langle \Psi^\lambda \middle| \hat{n}(\boldsymbol{r}_1) \middle| \Psi^\lambda \right\rangle \left\langle \Psi^\lambda \middle| \hat{n}(\boldsymbol{r}_2) \middle| \Psi^\lambda \right\rangle. \tag{4.20}
$$

Comparing with a similar one for non-interacting case

$$
\mathrm{i}\chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-) = \langle \Phi | \hat{n}(\boldsymbol{r}_1)\hat{n}(\boldsymbol{r}_2) | \Phi \rangle - \langle \Phi | \hat{n}(\boldsymbol{r}_1) | \Phi \rangle \langle \Phi | \hat{n}(\boldsymbol{r}_2) | \Phi \rangle. \tag{4.21}
$$

We obtain

$$
n^\lambda_{2,\mathrm{c}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \mathrm{i}[\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-) - \chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \tau = 0^-)], \tag{4.22}
$$

$$
= -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi\mathrm{i}} e^{i\omega 0^+} [\chi_\lambda(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) - \chi_0(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega)], \tag{4.23}
$$

The response function at finite λ

$$n_{2,\mathrm{c}}^{\lambda}(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi\mathrm{i}}e^{i\omega 0^+}[\chi_\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)-\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)], \qquad (4.23)$$

$$E_{\mathrm{c}} = -\frac{1}{2}\int_0^1 d\lambda \int_{-\infty}^{\infty}\frac{d\omega}{2\pi\mathrm{i}}e^{i\omega 0^+}\iint\frac{\chi_\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)-\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

Correlation energy has been related to the response function

Time-dependent DFT

Runge Gross theory

- there exists a one-to-one correspondence between the time-dependent density $n(\boldsymbol{r}, t)$ and the time-dependent effective potential $v_{\mathrm{s}}(\boldsymbol{r}, t)$, so that $n(\boldsymbol{r}, t)$ can be obtained by solving the time-dependent Kohn-Sham equation:

$$i\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r}, t) = \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\boldsymbol{r}, t)\right]\varphi_i(\boldsymbol{r}, t),$$

and

$$n(\boldsymbol{r}, t) = \sum_i^N |\varphi_i(\boldsymbol{r}, t)|^2$$

TD-DFT within linear response

$$\delta n_\lambda(\boldsymbol{r},t)=\int_0^\infty dt'\int d\boldsymbol{r}'\,\chi_\lambda\left(\boldsymbol{r}t,\boldsymbol{r}'t'\right)\delta v_{\mathrm{ext}}^\lambda(\boldsymbol{r}'t')$$

where

$$\chi_\lambda\left(\boldsymbol{r}t,\boldsymbol{r}'t'\right)=\frac{\delta n(\boldsymbol{r}t)}{\delta v_{\mathrm{ext}}^\lambda\left(\boldsymbol{r}'t'\right)}$$

The (general) response function can be given (from the definition) as

$$\chi_\lambda\left(\boldsymbol{r},\boldsymbol{r}',\omega\right)=\sum_{m\neq 0}\left[\frac{\langle\Psi^\lambda|\hat{n}(\boldsymbol{r})|\Psi_m^\lambda\rangle\langle\Psi_m^\lambda|\hat{n}\left(\boldsymbol{r}'\right)|\Psi^\lambda\rangle}{\omega-\omega_m+i0^+}-\frac{\langle\Psi^\lambda|\hat{n}\left(\boldsymbol{r}'\right)|\Psi_m^\lambda\rangle\langle\Psi_m^\lambda|\hat{n}(\boldsymbol{r})|\Psi^\lambda\rangle}{\omega+\omega_m+i0^+}\right].$$

TD-DFT within linear response

$$\delta n(\boldsymbol{r},t)=\int_0^\infty dt'\int dr'\,\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t,\boldsymbol{r}'t')\delta v_{\mathrm{s}}^{\lambda}(\boldsymbol{r}'t'),$$

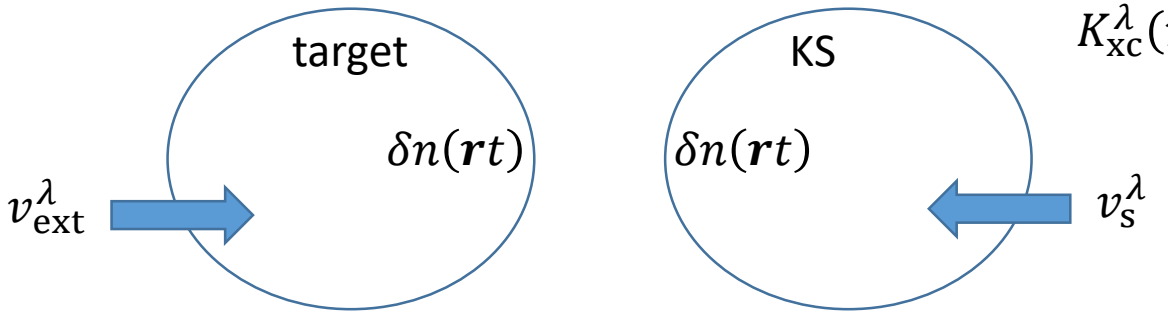
$$\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t,\boldsymbol{r}'t')=\frac{\delta n(\boldsymbol{r}t)}{\delta v_{\mathrm{s}}^{\lambda}(\boldsymbol{r}'t')},$$

and

$$\chi_{\lambda,\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}',\omega)=\sum_{kj}\frac{\varphi_k^{\lambda*}(\boldsymbol{r})\varphi_j^{\lambda}(\boldsymbol{r})\varphi_j^{\lambda*}(\boldsymbol{r}')\varphi_k^{\lambda}(\boldsymbol{r}')}{\omega-\omega_{jk}+i\eta}$$

$$\delta v_{\mathrm{s}}^{\lambda}(\boldsymbol{r}t)=\delta v_{\mathrm{ext}}^{\lambda}(\boldsymbol{r}t)+\int \mathrm{d}\mathbf{r}'\frac{\delta n(\boldsymbol{r}'t)}{|\mathbf{r}-\mathbf{r}'|}+\int d\,\boldsymbol{r}'dt'\mathrm{K}_{\mathrm{xc}}^{\lambda}(\boldsymbol{r}t,\mathbf{r}'\mathrm{t}')\delta n(\boldsymbol{r}'t')$$

$$K_{\mathrm{xc}}^{\lambda}(\boldsymbol{r}t,\boldsymbol{r}'t')\equiv\frac{\delta v_{\mathrm{xc}}^{\lambda}(\boldsymbol{r}t)}{\delta n(\boldsymbol{r}'t')}$$



$$\delta v_{\mathrm{s}}^{\lambda}(\boldsymbol{r}t) = \delta v_{\mathrm{ext}}^{\lambda}(\boldsymbol{r}t) + \int \mathrm{d}\mathbf{r}' \frac{\delta n(\boldsymbol{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + \int d\,\boldsymbol{r}'dt' \mathrm{K}_{\mathrm{xc}}^{\lambda}(\boldsymbol{r}t, \mathbf{r}'\mathrm{t}')\delta n(\boldsymbol{r}'t')$$

TD-DFT within linear response

$$\delta n_{\lambda}(\boldsymbol{r},t) = \int_0^{\infty} dt' \int d\boldsymbol{r}'\, \chi_{\lambda}(\boldsymbol{r}t, \boldsymbol{r}'t')\delta v_{\mathrm{ext}}^{\lambda}(\boldsymbol{r}'t')$$

$$= \int_0^{\infty} dt' \int dr'\, \chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t, \boldsymbol{r}'t')\delta v_{\mathrm{s}}^{\lambda}(\boldsymbol{r}'t')$$

Then we arrive at a Dyson equation

$$\chi_{\lambda}(\boldsymbol{r}t, \boldsymbol{r}'t')$$
$$= \chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t, \boldsymbol{r}'t') + \iiint \chi_{\lambda,\mathrm{KS}}(\boldsymbol{r}t, \boldsymbol{r}_1t_1)\left[\frac{\delta(t_1-t_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} + K_{\mathrm{xc}}^{\lambda}(\boldsymbol{r}_1t_1, \boldsymbol{r}_2t_2)\right]\chi_{\lambda}\,(\boldsymbol{r}_2t_2, \boldsymbol{r}'t')$$

Once the exchange-correlation kernel $K_{\mathrm{xc}}^{\lambda}$ has been given a functional form, one can obtain the response function by solving the Dyson equation.

Many-body approach to the response function

Random phase approximation and beyond

Self-energy

$$\mathrm{i}\frac{\partial}{\partial t_1}G(1,2) = \delta(1,2) + h(1)G(1,2) + \mathrm{i}\int d3v(1,3)G_2(1,3^+;2,3^{++})\,, \qquad (15)$$

Assume existence of the self-energy

$$\int d3\Sigma_{\mathrm{Hxc}}(1,3)G(3,2) = -i\int d3v(1,3)G_2(1,3^+;2,3^{++}) \qquad (17)$$

or

$$\Sigma_{\mathrm{Hxc}}(1,4) = -i\int d3v(1,3)G_2(1,3^+;2,3^{++})G^{-1}(2,4)\,. \qquad (18)$$

Then the EOM has a closed form

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right]G(1,2) = \delta(1,2) + \int d3\Sigma_{\mathrm{Hxc}}(1,3)G(3,2)\,. \qquad (16)$$

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right] G(1,2) = \delta(1,2) + \int d3\,\Sigma_{\mathrm{Hxc}}(1,3)G(3,2)\,. \qquad (16)$$

Green's function for independent electrons

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right] G_{\mathrm{indep}}(1,2) = \delta(1,2) \qquad (19)$$

- Using $G(1,2) = \int G_{\mathrm{indep}}(1,4)G^{-1}_{\mathrm{indep}}(4,3)G(3,2)$ in (16), we get

$$\int d3\left[G^{-1}_{\mathrm{indep}}(1,3) - \Sigma_{\mathrm{Hxc}}(1,3)\right]\mathrm{G}(3,2) = \delta(1,2) \qquad (20)$$

- This is rewritten as

$$G(1,2) = G_{\mathrm{indep}}(1,2) + \iint G_{\mathrm{indep}}(1,3)\,\Sigma_{\mathrm{Hxc}}(3,4)G(4,2), \qquad (21)$$

- or as

$$G^{-1}(1,2) = G^{-1}_{\mathrm{indep}}(1,2) - \Sigma_{\mathrm{Hxc}}(3,4). \qquad (22)$$

Dyson equation for the one-body Green's function

Quasi particle equation

Fourie transform is (assuming homogeneity in time) given as

$$[\omega - h(\boldsymbol{r}_1)]G(\boldsymbol{x}_1, \boldsymbol{x_2}; \omega) = \delta(\boldsymbol{x}_1, \boldsymbol{x}_2) + \int d\boldsymbol{x}_3 \Sigma_{\mathrm{Hxc}}(\boldsymbol{x}_1, \boldsymbol{x}_3; \omega) G(\boldsymbol{x}_3, \boldsymbol{x}_2; \omega) \quad (23)$$

Using the pole $\mathcal{E}_k$ and the wave function $f_k(\boldsymbol{x})$ of the Green's function, we can rewrite Eq. (23) at the pole as

$$[\mathcal{E}_k - h(\boldsymbol{r}_1)] f_k(\boldsymbol{x}_1) f_k^*(\boldsymbol{x}_2) = \int d\boldsymbol{x}_3 \, \Sigma_{\mathrm{Hxc}}(\boldsymbol{x}_1, \boldsymbol{x}_3; \mathcal{E}_k) f_k(\boldsymbol{x}_3) f_k^*(\boldsymbol{x}_2) = 0, \quad (24)$$

when there is no degeneracy. This can be further simplified as

$$h(\boldsymbol{r}_1) f_k(\boldsymbol{x}_1) + \int d\boldsymbol{x}_3 \, \Sigma_{\mathrm{Hxc}}(\boldsymbol{x}_1, \boldsymbol{x}_3; \mathcal{E}_k) f_k(\boldsymbol{x}_3) = \mathcal{E}_k f_k(\boldsymbol{x}_1). \quad (25)$$

The wave function follows a Schrodinger like equation, where the "potential" is time-dependent and complex.

Exchange-correlation from first-principles

Hedin's equation

Green's function in the interaction representation

$$H'(t_1) = \int d1\, u(1) n(1)$$

The Green's function can be described using the interaction representation

$$G(1,1') = -\mathrm{i}\frac{\langle N|T\left[S\hat{\psi}(1)\hat{\psi}^{\dagger}(1')\right]|N\rangle}{\langle N|T[S]|N\rangle},$$

where S is the time-evolution operator in the interaction representation

$$S(t_a, t_b) = \exp\left[-\mathrm{i}\int_{t_b}^{t_a} dt_1 H'_I(1)\right]; \quad \mathrm{S} = \mathrm{S}(-\infty, \infty).$$

The two-body Green's function is also

$$G_2\left(1,1';2,2'\right) = (-\mathrm{i})^2\frac{\langle N|T\left[S\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^{\dagger}(2')\hat{\psi}^{\dagger}(1')\right]|N\rangle}{\langle N|T[S]|N\rangle}$$

Schwinger's trick

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1) - u(1)\right] G(1,1') + i\int d2v(1,2) G_2\left(1,1',2^+,2^{++}\right) = \delta\left(1,1'\right).$$

Differentiate with respect to the perturbation

$$\frac{\delta G\left(1,1'\right)}{\delta u(2)} = -G_2\left(1,1',2,2^+\right) + iG\left(1,1'\right)G(2,2^+)$$
$$= -G_2\left(1,1',2,2^+\right) + iG\left(1,1'\right)\langle\hat{n}(2)\rangle$$

Then,

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1) - u(1) - \int d2v(1,2)\langle\hat{n}(2)\rangle\right] G(1,1') - i\int d2v(1^+,2)\frac{\delta G\left(1,1'\right)}{\delta u(2)}$$
$$= \delta\left(1,1'\right).$$

$$\Sigma(1,1') = \int d2v(1,2)\langle\hat{n}(2)\rangle\,\delta(1,1') + i\iint d23\ \ v(1^+,2)\frac{\delta G(1,3)}{\delta u(2)}G^{-1}(3,1')$$
$$\equiv \Sigma^{\mathrm{H}}(1,1') + \Sigma^{\mathrm{xc}}(1,1')$$

Dyson equation

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1) - u(1)\right] G\left(1,1^{'}\right) - i\int d2\Sigma(1,2)G\left(2,1^{'}\right) = \delta\left(1,1^{'}\right).$$

When unperturbed Green's function is defined from

$$\left[\mathrm{i}\frac{\partial}{\partial t_1} - h(1)\right] G^{(0)}\left(1,1^{'}\right) = \delta\left(1,1^{'}\right),$$

we have the equation of Dyson type

$$G\left(1,1^{'}\right) = G^{(0)}\left(1,1^{'}\right) + \iint d23\, G^{(0)}(1,2)\Sigma(2,3)G\left(3,1^{'}\right).$$

We need to perform the differentiation with respect to u to get the self-energy

Vertex function

- Hartree-potential (total potential)

$$V(1) = u(1) + \int d2v(1,2)\langle\hat{n}(2)\rangle$$

- Consider the response of the Green's function to the change in the total potential;

$$-\frac{\delta \mathrm{G}^{-1}(1,2)}{\delta V(3)} \mapsto \Gamma(1,2;3)$$

- The vertex function $\Gamma(1,2;3)$ can be rewritten in a Dyson form as

$$\Gamma(1,2;3) = \delta(1,2)\delta(2,3) + \iiint d4567 \frac{\delta \Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)} \mathrm{G}(4,6)\mathrm{G}(7,5)\Gamma(6,7;3),$$

This will be used eliminate the u-derivative

Exchange correlation self-energy

$$\Sigma^{\mathrm{xc}}(1,1') = i \iint d23 \; v(1^+,2) \frac{\delta G(1,3)}{\delta u(2)} G^{-1}(3,1')$$

The definition can be rewritten as

$$\Sigma^{\mathrm{xc}}(1,2) = \mathrm{i} \iint d3456 \, v(1^+,3) \frac{\delta V(4)}{\delta u(3)} G(1,6) \Gamma(6,2;5)$$

Note that dielectric function is, by definition,

$$\epsilon^{-1}(4,3) = \frac{\delta V(4)}{\delta u(3)}$$

Then, defining the screened Coulomb as

$$W(1^+,4) = \int d3 \; v(1^+,3) \epsilon^{-1}(4,3)$$

We get

$$\Sigma^{\mathrm{xc}}(1,2) = \mathrm{i} \iint d56 \, W(1^+,3) G(1,6) \Gamma(6,2;5)$$

Dyson equation for W

$$W(1^+,2) = v(1^+,2) + \int d34\ v(1^+,4)\frac{\delta G(4,4^+)}{\delta V(5)}\frac{\delta V(5)}{\delta u(3)}v(3,2)$$

$$= v(1^+,2) + \int d34\ v(1^+,4)\frac{\delta G(4,4^+)}{\delta V(5)}W(5,2)$$

$$= v(1^+,2) + \int d34\ v(1^+,4)\frac{\delta\langle\hat{\rho}(2)\rangle}{\delta V(5)}W(5,2)$$

- The final derivative, appearing in the last line, is the polarization and can be eliminated as

$$P(1,2) = \mathrm{i}\int d34\, G(1,3)\frac{\delta G^{-1}(3,4)}{\delta V(2)}G(4,1^+)$$ Chain rule

$$= -i\int d34\, G(1,3)G(4,1^+)\Gamma(3,4;2)$$

$$W(1^+,2) = v(1^+,2) + \int d34\ v(1^+,4)P(2,5)W(5,2)$$

Final equation

$$G(1,2) = G^0(1,2) + \int d34 G^0(1,3)\Sigma(3,4)G(4,2)$$
$$\Sigma^{\mathrm{xc}}(1,2) = i\int d34 W(1^+,3)G(1,4)\Gamma(4,2;3)$$
$$P(1,2) = -i\int d34\, G(1,3)G(4,1^+)\Gamma(3,4;2)$$
$$W(1,2) = V_C(1,2) + \int d34 V_C(1,3)P(3,4)W(4,2)$$
$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d4567 \frac{\delta\Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(6,7;3)$$

- When the equations are solved self-consistently, you have done. If, on the other hand, you approximate G^0, for example, using KS orbital, it can be regarded as an advanced DFT.

$$\Sigma^{\mathrm{xc}}(1,2) = i\int d34 W(1^+,3)G(1,4)$$
$$P(1,2) = -i\int d34\, G(1,3)G(4,1^+)$$

- This approximation is called as GW approximation (GWA).

Bethe-Salpeter equation

- When using

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + \int d4567 \frac{\delta\Sigma^{\mathrm{xc}}(1,2)}{\delta G(4,5)} G(4,6)G(7,5)$$

- You can take into account the interaction of quasi particles

Now we derive the Dyson equation

BSE from Schwinger's trick

- Four point response function

$$\chi(1,2;1',2') = L(1,1',2,2') = \mathrm{i}G_2(1,1',2,2') - G(1,1')G'2',2)$$

- nonlocal external potential $u(2,2)$ is introduced to yield

$$L(1,1',2,2') = -\mathrm{i}\frac{\delta \mathrm{G}(1,1')}{\delta \mathrm{u}(2,2)}.$$

- Using the identity of the functional derivative,

$$\frac{\delta F(1,1')}{\delta G(3)} = -\int F(1,3)\frac{\delta F^{-1}(3,3')}{\delta G(2)}F(3',1')d3d3',$$

- we obtain

$$\frac{\delta \mathrm{G}(1,1')}{\delta \mathrm{u}(2,2')} = -\int G(1,3)G(3',1')\frac{\delta \mathrm{G}^{-1}(3,3')}{\delta \mathrm{u}(2,2')}d3d3'.$$

BSE

$$\frac{\delta G(1,1')}{\delta u(2,2')} = -\int G(1,3)G(3',1')\frac{\delta G^{-1}(3,3')}{\delta u(2,2')}d3d3'$$

- When this is substituted into the Dyson equation

$$G^{-1}(3,3') = G_0^{-1}(3,3') - u(3,3') - \Sigma(3,3'),$$

- we obtain

$$\frac{\delta G(1,1')}{\delta u(2,2')} = G(1,2)G(2',1) + \int G(1,3)G(3',1')\frac{\delta \Sigma(3,3')}{\delta u(2,2')}d3d3'$$

$$= \underbrace{G(1,2)G(2',1)}_{= L_0(1,1',2,2')} + \int G(1,3)G(3',1')\underbrace{\frac{\delta \Sigma(3,3')}{\delta G(4,4')}}\frac{\delta G(4,4')}{\delta u(2,2')}d3d3'd4d4'.$$

$$K(3,3',4,4') = \mathrm{i}\frac{\delta \Sigma(3,3')}{\delta G(4,4')}$$

e-h interaction kernel

$$L(1,1',2,2')$$

$$= L_0(1,1',2,2') + \int L_0(1,1',3,3')K(3,3',4,4')L(4,4',2,2')d3d3'd4d4'$$

Interaction kernel

$$K^{\mathrm{x}}\left(3,3',4'\right) \equiv i\frac{\delta\Sigma^{\mathrm{H}}\left(3,3'\right)}{\delta\mathrm{G}\left(4,4'\right)}$$

- is called bare Coulomb exchange interaction and can be described as

$$K^{\mathrm{x}}\left(3,3',4'\right) = \delta\left(3,3'\right)\delta\left(4,4'\right)v(3,4).$$

- While the rest yields, within the GW approximation,

$$i\frac{\delta\Sigma^{GW}\left(3,3'\right)}{\delta\mathrm{G}\left(4,4'\right)} = -\delta(3,4)\delta\left(3',4'\right)W\left(3^{+},3'\right) - G\left(3,3'\right)\frac{\delta\mathrm{W}\left(3^{+},3'\right)}{\delta\mathrm{G}\left(4,4'\right)}.$$

- Using the polarization, $W = v + vPW$, which replaces $\delta W/\delta G = W\,\delta P/\delta G\,W$ with

$$i\frac{\delta\Sigma^{GW}\left(3,3'\right)}{\delta\mathrm{G}\left(4,4'\right)} = -\delta(3,4)\delta\left(3',4'\right)W\left(3^{+},3'\right) - \int G\left(3,3'\right)W(3^{+},5)\frac{\delta P(5,6)}{\delta G\left(4,4'\right)}W\left(6,3'\right)d5d6\,.$$

GW + BSE

- Using the approximation $P = -GG$,

$$\mathrm{i}\frac{\delta\Sigma^{GW}(3,3')}{\delta \mathrm{G}(4,4')}$$

$$= -\delta(3,4)\delta(3',4')W(3^+,3') + \mathrm{i}\int G(3,3')W(3^+,5)\frac{\delta\left(G(5,6)G(6,5^+)\right)}{\delta G(4,4')}W(6,3')d5d6\,,$$

- and further,

$$\mathrm{i}\frac{\delta\Sigma^{GW}(3,3')}{\delta \mathrm{G}(4,4')}$$

$$= -\delta(3,4)\delta(3',4')W(3^+,3') + \mathrm{i}W(3^+,4)G(4',4^+)W(4',3') + \mathrm{i}W(3^+,4')G(4',4^+)W(4,3')$$

$$K^{\mathrm{x}}(3,3',4,4') = \delta(3,3')\delta(4,4')v(3,4)$$
$$K^{\mathrm{d}}(3,3',4,4') = -\delta(3,4)\delta(3'4')W(3^+,3')$$
$$K'^{(3,3',4,4')} = -G(3,3')\frac{\delta W(3,3^+)}{\delta G(4,4')}$$

=GW + BSE

Application to ACFD

DFT-RPA

Direct RPA

- When using the direct term only,

$$K_{\mathrm{Hxc}}^{\lambda}(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) \simeq K_{\mathrm{H}}^{\lambda}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \lambda v(\boldsymbol{r}_1,\boldsymbol{r}_2). \qquad (4.28)$$

- When this is used, the resulting equation for the response function is

$$\chi_\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) = \chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) + \lambda \iiint \chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega) v(\boldsymbol{r}_3,\boldsymbol{r}_4) \chi_\lambda(\boldsymbol{r}_4,\boldsymbol{r}_2;\omega)\,. \qquad (4.29)$$

- By this we can define the correlation functional within this approximation called direct RPA as

$$E_{\mathrm{c}}^{\mathrm{dRPA}} = -\frac{1}{2}\int_0^1 d\lambda \int_\infty^\infty \frac{d\omega}{2\pi \mathrm{i}} e^{-\mathrm{i}\omega 0^+} \left[\lambda \iiint \frac{\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega)\chi_0(\boldsymbol{r}_4,\boldsymbol{r}_2;\omega)}{|\boldsymbol{r}_1-\boldsymbol{r}_2||\boldsymbol{r}_3-\boldsymbol{r}_4|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 \right.$$
$$+ \lambda^2 \iiint \frac{\chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega)\chi_0(\boldsymbol{r}_4,\boldsymbol{r}_5;\omega)\chi_0(\boldsymbol{r}_6,\boldsymbol{r}_2;\omega)}{|\boldsymbol{r}_1-\boldsymbol{r}_2||\boldsymbol{r}_3-\boldsymbol{r}_4||\boldsymbol{r}_5-\boldsymbol{r}_6|} d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 d\boldsymbol{r}_4 d\boldsymbol{r}_5 d\boldsymbol{r}_6$$
$$\left. + \cdots \right] \qquad (4.30)$$

Practical dRPA

$$\chi_\lambda(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) = \chi_0(\boldsymbol{r}_1,\boldsymbol{r}_2;\omega) + \lambda\iiint \chi_0(\boldsymbol{r}_1,\boldsymbol{r}_3;\omega)v(\boldsymbol{r}_3,\boldsymbol{r}_4)\chi_\lambda(\boldsymbol{r}_4,\boldsymbol{r}_2;\omega)\,. \quad (4.29)$$

- Within dRPA the Dyson equation for the response function is

$$\chi_\lambda^{\mathrm{dRPA}}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_1',\boldsymbol{x}_2';\omega) = \chi_0(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_1',\boldsymbol{x}_2';\omega) + \iiint d\boldsymbol{x}_3 d\boldsymbol{x}_4 d\boldsymbol{x}_5 d\boldsymbol{x}_6 \chi_0(\boldsymbol{x}_1,\boldsymbol{x}_4,\boldsymbol{x}_1',\boldsymbol{x}_3;\omega)K_{\mathrm{H}}^{\lambda}(\boldsymbol{x}_3,\boldsymbol{x}_6;\boldsymbol{x}_4,\boldsymbol{x}_5) \times \chi_\lambda^{\mathrm{dRPA}}(\boldsymbol{x}_5,\boldsymbol{x}_2,\boldsymbol{x}_6,\boldsymbol{x}_2';\omega) \quad (4.36)$$

- with the kernel being given by

$$K_{\mathrm{H}}^{\lambda}(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{x}_1',\boldsymbol{x}_2') = \lambda v(|\boldsymbol{r}_1-\boldsymbol{r}_2|)\delta(\boldsymbol{x}_1-\boldsymbol{x}_1')\delta(\boldsymbol{x}_2-\boldsymbol{x}_2')$$

Basis representation

- With

$$f_{ia}(\boldsymbol{x}_1, \boldsymbol{x}_1') = \phi_i^*(\boldsymbol{x}_1')\phi_a(\boldsymbol{x}_1)$$
$$f_{ai}(\boldsymbol{x}_1, \boldsymbol{x}_1') = \phi_a^*(\boldsymbol{x}_1')\phi_i(\boldsymbol{x}_1).$$

- χ_0 can be expanded as

$$\chi_0(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_1', \boldsymbol{x}_2'; \omega) \sum_{pq} [\chi_0]_{pq} f_p(\boldsymbol{x}_1, \boldsymbol{x}_1') f_q^*(\boldsymbol{x}_2, \boldsymbol{x}_2')$$

- where

$$[\chi_0(\omega)]_{ia,jb} = \frac{\delta_{ij}\delta_{ab}}{\omega - (\varepsilon_a - \varepsilon_i) + \mathrm{i}0^+}$$
$$[\chi_0(\omega)]_{ai,bj} = \frac{\delta_{ij}\delta_{ab}}{\omega + (\varepsilon_a - \varepsilon_i) - \mathrm{i}0^+}$$
$$[\chi_0(\omega)]_{ia,bj} = [\chi_0(\omega)]_{ai,jb} = 0.$$

Matrix representation

- The previous equation can be rewritten as

$$(\chi_0)^{-1}(\omega) = -\left[\begin{pmatrix} \boldsymbol{\Delta\varepsilon} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Delta\varepsilon} \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix}\right] \qquad (4.39)$$

- with

$$\Delta\varepsilon_{ia,jb} \equiv (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}.$$

- Then

$$\left(\chi_\lambda^{\mathrm{dRPA}}\right)^{-1}(\omega) = -\left[\begin{pmatrix} \mathbf{A}_\lambda & \boldsymbol{B}_\lambda \\ \boldsymbol{B}_\lambda^* & \mathbf{A}_\lambda^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix}\right] \qquad (4.40)$$

- with

$$(A_\lambda)_{ia,jb} = \Delta\varepsilon_{ia,jb} + \lambda\langle\phi_a\phi_j|\phi_i\phi_b\rangle$$
$$(B)_{ia,jb} = \lambda\langle\phi_a\phi_b|\phi_i\phi_j\rangle. \qquad (4.41)$$

To take the inverse in Eq. (4.40), we solve the generalized eigenvalue problem

- $$\begin{pmatrix} \mathbf{A}_\lambda & \boldsymbol{B}_\lambda \\ \boldsymbol{B}_\lambda^* & \mathbf{A}_\lambda^* \end{pmatrix} \begin{pmatrix} \boldsymbol{X}_{n,\lambda} \\ \boldsymbol{Y}_{n,\lambda} \end{pmatrix} = \omega_n^\lambda \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix} \begin{pmatrix} \boldsymbol{X}_{n,\lambda} \\ \boldsymbol{Y}_{n,\lambda} \end{pmatrix} \qquad (4.42)$$

Matrix Representation

- Under the normalization condition for the eigenvectors (X ,Y), the response function is

$$\boldsymbol{\chi}_{\lambda}^{\mathrm{dRPA}}(\omega)=\sum_{n}\left[\frac{1}{\omega-\omega_{n}^{\lambda}+i0^{+}}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}\\ \boldsymbol{Y}_{n,\lambda}\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}^{\dagger} & \boldsymbol{Y}_{n,\lambda}^{\dagger}\end{pmatrix}-\frac{1}{\omega+\omega_{n}^{\lambda}-i0^{+}}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}^{*}\\ \boldsymbol{Y}_{n,\lambda}^{*}\end{pmatrix}\begin{pmatrix}\boldsymbol{X}_{n,\lambda}^{*\dagger} & \boldsymbol{Y}_{n,\lambda}^{*\dagger}\end{pmatrix}\right],$$

- and the correlation part of the two-body density matrix is then

$$\boldsymbol{n}_{2,\mathrm{c}}^{\lambda,\mathrm{dRPA}}=-\int_{\infty}^{\infty}\frac{d\omega}{2\pi\mathrm{i}}e^{\mathrm{i}\omega0^{+}}[\boldsymbol{\chi}_{\lambda}(\omega)-\boldsymbol{\chi}_{0}(\omega)]=\sum_{n}\left[\begin{pmatrix}\boldsymbol{Y}_{n,\lambda}^{*}\boldsymbol{Y}_{n,\lambda}^{*\dagger} & \boldsymbol{Y}_{n,\lambda}^{*}\boldsymbol{X}_{n,\lambda}^{*\dagger}\\ \boldsymbol{X}_{n,\lambda}^{*}\boldsymbol{Y}_{n,\lambda}^{*\dagger} & \boldsymbol{X}_{n,\lambda}^{*}\boldsymbol{X}_{n,\lambda}^{*\dagger}\end{pmatrix}-\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathbf{1}\end{pmatrix}\right]$$

- Finally the dRPA correlation functional is given by

$$E_{\mathrm{c}}^{\mathrm{dRPA}}=\frac{1}{2}\int_{0}^{1}d\lambda\sum_{ij\leq N<ab}\left\{\sum_{n}\begin{aligned}&\langle\phi_i\phi_b|\phi_a\phi_j\rangle\left(Y_{n,\lambda}\right)_{ia}^{*}\left(Y_{n,\lambda}\right)_{jb}+\langle\phi_i\phi_j|\phi_a\phi_b\rangle\left(X_{n,\lambda}\right)_{ia}^{*}(X)_{jb}\\&+\langle\phi_a\phi_b|\phi_i\phi_j\rangle\left(X_{n,\lambda}\right)_{ia}^{*}\left(Y_{n,\lambda}\right)_{jb}\\&+\langle\phi_i\phi_b|\phi_a\phi_j\rangle\left[(X)_{ia}^{*}\left(X_{n,\lambda}\right)_{jb}-\delta_{ij}\delta_{ab}\right]\end{aligned}\right\}$$

dRPA is known to work well for metallic system, but for insulators, self-interaction error remains. One should include more terms.