Electronic Excitation Energy Balance Sheet

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— Let $\{\phi_i\}$ be a set of Kohn-Sham (KS) orbitals in density functional theory (DFT). The total energy of an N-electron system is given by

$$E = \sum_{j=1}^{N} \int d\mathbf{r}\, \phi_j^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) \right) \phi_j(\mathbf{r})$$

$$+ \frac{1}{2} \sum_{j,k=1}^{N} \iint d\mathbf{r}\, d\mathbf{r}' \frac{\rho_j(\mathbf{r})\, \rho_k(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho] \tag{1}$$

where $v_{ext}(\mathbf{r})$ is the external potential, $E_{xc}[\rho]$ is the exchange-correlation energy functional, and the electron density is

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \rho_j(\mathbf{r}) = \sum_{j=1}^{N} |\phi_j(\mathbf{r})|^2 \tag{2}$$

Let

$$t_j = \int d\mathbf{r}\, \phi_j^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) \right) \phi_j(\mathbf{r}) \tag{3}$$

$$J_{jk} = [\rho_j | \tfrac{1}{r} | \rho_k] \tag{4}$$

$$= \iint d\mathbf{r}\, d\mathbf{r}' \frac{\rho_j(\mathbf{r})\, \rho_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \text{(Coulomb integral)} \tag{5}$$

then the total energy, Eq. (1), is expressed as

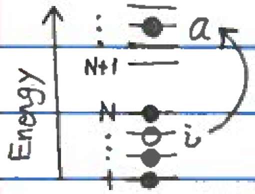
$$E = \sum_{j=1}^{N} t_j + \frac{1}{2} \sum_{j,k=1}^{N} J_{jk} + E_{xc}[\rho] \tag{6}$$

Single excitation

Let the KS orbitals be numbered in ascending order of energy. Then, the ground-state density is

$$\rho^{gr}(\mathbf{r}) = \sum_{j=1}^{N} \rho_j(\mathbf{r}) \tag{7}$$

We now consider single excitation, in which an electron is promoted from an occupied orbital, $i \in [1,N]$, to an unoccupied orbital, $a > N$.



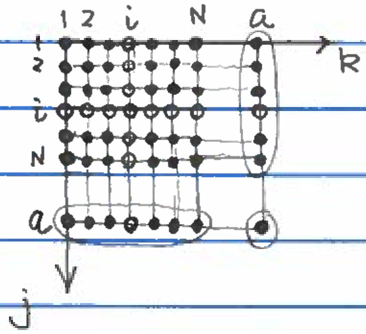
ΔSCF approximation

We evaluate the $i \to a$ excitation energy within ΔSCF approximation, neglecting the orbital relaxation effect.

(Single-particle term)

$$\Omega^{sp} = t_a - t_i \tag{8}$$

(Hartree term)



$$\Omega^{\text{Hartree}} = \Big(\overset{\checkmark}{\sum_{j=1}^{N} J_{aj}} - J_{ai}\Big) + \overset{\triangle}{\frac{1}{2} J_{aa}} - \Big(\overset{\checkmark}{\sum_{j=1}^{N} J_{ij}} - \overset{\triangle}{\frac{1}{2} J_{ii}}\Big)$$

$$= \sum_{j=1}^{N} (J_{aj} - J_{ij}) + \frac{1}{2}(J_{ii} + J_{aa}) - J_{ia} \qquad (9)$$

(xc term)

$$\Omega^{xc} = E_{xc}[\rho^{gr} + \rho_a - \rho_i] - E_{xc}[\rho^{gr}] \qquad (10)$$

Let us define

$$v_{xc}(\mathbf{r}) = \left.\frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho^{gr}} \qquad (11)$$

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \left.\frac{\delta^2 E_{xc}}{\delta \rho(\mathbf{r})\, \delta \rho(\mathbf{r}')}\right|_{\rho=\rho^{gr}} \qquad (12)$$

We expand Eq.(10) around ρ^{gr}:

$$\Omega^{xc} = \cancel{E_{xc}[\rho^{gr}]} + \int d\mathbf{r}\, v_{xc}(\mathbf{r}) [\rho_a(\mathbf{r}) - \rho_i(\mathbf{r})]$$

$$+ \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}' [\rho_a(\mathbf{r}) - \rho_i(\mathbf{r})] f_{xc}(\mathbf{r}, \mathbf{r}') [\rho_a(\mathbf{r}') - \rho_i(\mathbf{r}')] + \cdots - \cancel{E_{xc}[\rho^{gr}]}$$

$$\simeq \int d\mathbf{r}\, v_{xc}(\mathbf{r}) [\rho_a(\mathbf{r}) - \rho_i(\mathbf{r})]$$

$$+ \frac{1}{2} \iint d\mathbf{r}\, d\mathbf{r}' [\rho_a(\mathbf{r}) - \rho_i(\mathbf{r})] f_{xc}(\mathbf{r}, \mathbf{r}') [\rho_a(\mathbf{r}') - \rho_i(\mathbf{r}')] \qquad (13)$$

Combining Eqs. (8), (9) and (13), the ΔSCF excitation energy is

$$\Omega^{\Delta SCF} = \overset{\checkmark}{t_a} - \overset{\Delta}{t_i} + \sum_{j=1}^{N} (\overset{\checkmark}{J_{aj}} - \overset{\Delta}{J_{ij}}) + \frac{1}{2}(J_{ii} + J_{aa}) - J_{ia}$$
$$+ \int d\mathbf{r}\, v_{xc}(\mathbf{r}) [\overset{\checkmark}{\rho_a(\mathbf{r})} - \overset{\Delta}{\rho_i(\mathbf{r})}] + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' [\rho_a(\mathbf{r}) - \rho_i(\mathbf{r})] f_{xc}(\mathbf{r}, \mathbf{r}') [\rho_a(\mathbf{r}') - \rho_i(\mathbf{r}')] \quad (14)$$

Now, consider the ground-state KS equation:

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + \sum_{j=1}^{N} \int d\mathbf{r}' \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}) \right] \phi_k(\mathbf{r}) = \epsilon_k^{KS} \phi_k(\mathbf{r}) \quad (15)$$

where ϵ_k^{KS} is the k-th KS energy.

$\int d\mathbf{r}\, \phi_k^*(\mathbf{r}) \times$ Eq. (15)

$$t_k + \sum_{j=1}^{N} J_{kj} + \int d\mathbf{r}\, v_{xc}(\mathbf{r}) \rho_k(\mathbf{r}) = \epsilon_k^{KS} \quad (16)$$

Using Eq. (16) in (14),

$$\Omega^{\Delta SCF} = \epsilon_a^{KS} - \epsilon_i^{KS} + \frac{1}{2}(J_{ii} + J_{aa}) - J_{ia}$$
$$+ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' [\rho_a(\mathbf{r}) - \rho_i(\mathbf{r})] f_{xc}(\mathbf{r}, \mathbf{r}') [\rho_a(\mathbf{r}') - \rho_i(\mathbf{r}')] \quad (17)$$

Here, we consider a local xc functional:

$$f_{xc}(\mathbf{r}, \mathbf{r}') = f_{xc}^{local}(\mathbf{r})\, \delta(\mathbf{r} - \mathbf{r}') \quad (18)$$

Then, the ΔSCF excitation energy becomes

$$\Omega^{\Delta SCF} = \overset{\checkmark}{\epsilon_a^{KS}} - \overset{\triangle}{\epsilon_i^{KS}} + \frac{1}{2}(\overset{\triangle}{J_{ii}} + \overset{\checkmark}{J_{aa}}) - J_{ia} + \frac{1}{2}\int d\mathbf{r}\, f_{xc}^{local}(\mathbf{r})\,[\overset{\checkmark}{\rho_a}(\mathbf{r}) - \overset{\checkmark}{\rho_i}(\mathbf{r})]^2 \tag{19}$$

$$= \left[\epsilon_a^{KS} + \frac{1}{2}J_{aa} + \frac{1}{2}\int d\mathbf{r}\, f_{xc}^{local}(\mathbf{r})\,\rho_a^2(\mathbf{r})\right] - \left[\epsilon_i^{KS} - \frac{1}{2}J_{ii} - \frac{1}{2}\int d\mathbf{r}\, f_{xc}^{local}(\mathbf{r})\,\rho_i^2(\mathbf{r})\right] - J_{ia} - \int d\mathbf{r}\,\rho_i(\mathbf{r})\, f_{xc}^{local}(\mathbf{r})\,\rho_a(\mathbf{r}) \tag{20}$$

$$\therefore \Omega^{\Delta SCF} = [\epsilon_a^{KS} + U_a] - [\epsilon_i^{KS} - U_i] - J_{ia} - \int d\mathbf{r}\,\rho_i(\mathbf{r})\, f_{xc}^{local}(\mathbf{r})\,\rho_a(\mathbf{r}) \tag{21}$$

where the self-interaction correction (SIC) terms are defined as

$$U_k = \frac{1}{2}\left[J_{kk} + \int d\mathbf{r}\,\rho_k(\mathbf{r})\, f_{xc}^{local}(\mathbf{r})\,\rho_k(\mathbf{r})\right] \tag{22}$$

$\Omega^{\Delta SCF}$ entails, even at the RPA level (i.e., $E_{xc}=0$), two correct physics:

(1) SIC band-broadening by pushing $\begin{matrix}\text{up } \epsilon_a^{KS} \text{ by } \frac{1}{2}J_{aa} \\ \text{down } \epsilon_i^{KS} \text{ by } \frac{1}{2}J_{ii}\end{matrix}$.

(2) Electron-hole binding, $-J_{ia}$, that narrows the gap.

※ Note the conventional SIC only push down occupied level i, instead.

– Linear-response TDDFT

In linear-response (LR) time-dependent density functional theory (TDDFT), the electronic excitation energy is obtained by solving Casida's eigenvalue problem:

$$\Omega(\omega_I)\,\vec{F}_I = \omega_I^2\,\vec{F}_I \tag{23}$$

where

$$\Omega_{ia\sigma,i'a'\sigma'}(\omega) = \delta_{\sigma\sigma'}\delta_{ii'}\delta_{aa'}(\epsilon^{KS}_{a\sigma}-\epsilon^{KS}_{ia})^2 + 2\sqrt{(f_{i\sigma}-f_{a\sigma})(\epsilon^{KS}_{a\sigma}-\epsilon^{KS}_{i\sigma})}\,K_{ia\sigma,i'a'\sigma'}(\omega)\sqrt{(f_{i'\sigma'}-f_{a'\sigma'})(\epsilon^{KS}_{a'\sigma'}-\epsilon^{KS}_{i'\sigma'})} \tag{24}$$

and the coupling matrix is

$$K_{ia\sigma,i'a'\sigma'}(\omega) = [\phi^*_{a\sigma}\phi_{i\sigma}|\tfrac{1}{r}|\phi^*_{a'\sigma'}\phi_{i'\sigma'}] + [\phi^*_{a\sigma}\phi_{i\sigma}|f_{xc}(\mathbf{r},\mathbf{r}';\omega)|\phi^*_{a'\sigma'}\phi_{i'\sigma'}] \tag{25}$$

In Eq. (25), the Coulomb-like integral is define as

$$[f|h(r)|g] \equiv \iint d\mathbf{r}\,d\mathbf{r}'\,f(\mathbf{r})\,h(|\mathbf{r}-\mathbf{r}'|)\,g(\mathbf{r}') \tag{26}$$

Here, we denote the electron-hole excitation wave function

$$\Phi_\nu(\mathbf{r}) = \phi^*_{a\sigma}(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}), \tag{27}$$

with the corresponding excitation energy

$$\omega^{KS}_\nu = \epsilon^{KS}_{a\sigma} - \epsilon^{KS}_{i\sigma}, \tag{28}$$

where $\nu = i \to a$.

Then, Casida's matrix elements become

$$\Omega_{ia\sigma,i'a'\sigma'}(\omega) = \delta_{\sigma\sigma'}\delta_{ii'}\delta_{aa'}\,\omega^{KS\,2}_{ia\sigma} + 2\sqrt{(f_{i\sigma}-f_{a\sigma})\omega^{KS}_{ia\sigma}}\,K_{ia\sigma,i'a'\sigma'}(\omega)\sqrt{(f_{i'\sigma'}-f_{a'\sigma'})\omega^{KS}_{i'a'\sigma'}} \qquad (29)$$

$$K_{ia\sigma,i'a'\sigma'}(\omega) = [\Phi_{ia\sigma}|\tfrac{1}{r}|\Phi_{i'a'\sigma'}] + [\Phi_{ia\sigma}|f_{xc}(\mathbf{r},\mathbf{r}';\omega)|\Phi_{i'a'\sigma'}] \qquad (30)$$

(Diagonal approximation)

$$\omega^{KS\,2}_{ia\sigma} + 2\omega^{KS}_{ia\sigma}\left\{[\Phi_{ia\sigma}|\tfrac{1}{r}|\Phi_{ia\sigma}] + [\Phi_{ia\sigma}|f_{xc}(\mathbf{r},\mathbf{r}';\omega_I)|\Phi_{ia\sigma}]\right\} = \omega_I^2 \qquad (31)$$

or

$$\omega^{KS\,2}_{\nu} + 2\omega^{KS}_{\nu}\left\{K_\nu + [\Phi_\nu|f_{xc}(\mathbf{r},\mathbf{r}';\omega_I)|\Phi_\nu]\right\} = \omega_I^2 \qquad (32)$$

where the <u>exchange integral</u> is

$$K_\nu = [\Phi_\nu|\tfrac{1}{r}|\Phi_\nu] = \iint d\mathbf{r}\,d\mathbf{r}'\,\phi_a^*(\mathbf{r})\phi_i(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_a^*(\mathbf{r}')\phi_i(\mathbf{r}') \qquad (33)$$

(Weak-coupling, adiabatic limit)

In the weak-coupling limit, where the Coulombic interaction is small, we expand Eq.(32). We also assume that f_{xc} is frequency independent.

$$\omega_I = \omega^{KS}_\nu\left[1 + \frac{2}{\omega^{KS}_\nu}\left\{K_\nu + [\Phi_\nu|f_{xc}(\mathbf{r},\mathbf{r}')|\Phi_\nu]\right\}\right]^{1/2}$$

$$\simeq \omega^{KS}_\nu\left[1 + \frac{1}{\cancel{2}}\cdot\frac{\cancel{2}}{\omega^{KS}_\nu}\left\{K_\nu + [\Phi_\nu|f_{xc}(\mathbf{r},\mathbf{r}')|\Phi_\nu]\right\}\right]$$

$$\therefore\ \omega_I \simeq \omega_\nu^{KS} + K_\nu + [\Phi_\nu | f_{xc}(\mathbb{r},\mathbb{r}') | \Phi_\nu] \qquad (34)$$

With local xc approximation,

$$[\Phi_\nu | f_{xc}(\mathbb{r},\mathbb{r}') | \Phi_\nu] = \int d\mathbb{r}\, \phi_a^*(\mathbb{r})\, \phi_i(\mathbb{r})\, f_{xc}^{local}(\mathbb{r})\, \phi_a^*(\mathbb{r})\, \phi_i(\mathbb{r})$$

$$= \int d\mathbb{r}\, \rho_a(\mathbb{r})\, f_{xc}^{local}(\mathbb{r})\, \rho_i(\mathbb{r}) \qquad (35)$$

Here, we assumed that KS orbitals are real.

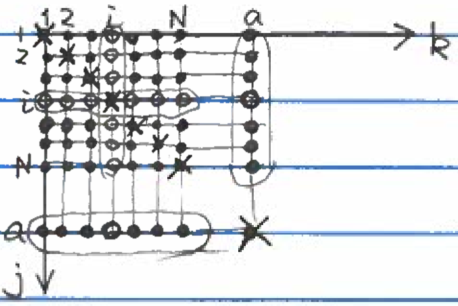
$$\boxed{\therefore\ \Omega^{\text{LR-TDDFT, local}} = \omega_\nu^{KS} + K_\nu + \int d\mathbb{r}\, \rho_i(\mathbb{r})\, f_{xc}^{local}(\mathbb{r})\, \rho_a(\mathbb{r})} \qquad (36)$$

$\Omega^{\text{LR-TDDFT, local}}$ has (1) no SIC nor (2) electron-hole binding. The band gap is widened by the exchange integral and xc interaction.

— Hartree-Fock approximation (ΔHF)

$$E_{HF} = \sum_{j=1}^{N} t_j + \frac{1}{2}\sum_{j,k=1}^{N}\left([jj|kk] - [jk|kj]\right) \tag{37}$$

Note that there is no self interaction.



$$\Omega^{\Delta HF} = \overset{\checkmark}{t_a} - \overset{\Delta}{t_i} + \sum_{j=1}^{N}\overset{\checkmark}{\left([aa|jj] - [aj|ja]\right)}$$

$$- \left([aa|ii] - [ai|ia]\right)$$

$$- \sum_{j=1}^{N}\overset{\Delta}{\left([ii|jj] - [ij|ji]\right)} \tag{38}$$

Now consider the ground-state HF equation

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + \sum_{j=1}^{N}\int d\mathbf{r}' \frac{\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi_k(\mathbf{r})$$

$$- \sum_{j=1}^{N}\int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r}) = \epsilon_k^{HF}\phi_k(\mathbf{r}) \tag{39}$$

$\int d\mathbf{r}\,\phi_k^*(\mathbf{r}) \times$ Eq. (39)

$$t_k + \sum_{j=1}^{N}[jj|kk] - \sum_{j=1}^{N}[jk|kj] = \epsilon_k^{HF} \tag{40}$$

Using Eq. (40) in (38),

$$\boxed{\begin{aligned} \Omega^{\Delta HF} &= \epsilon_a^{HF} - \epsilon_i^{HF} - [\rho_a|\tfrac{1}{r}|\rho_i] + [\Phi_{ia}|\tfrac{1}{r}|\Phi_{ia}] && (41) \\ &= \omega_\nu^{HF} - J_\nu + K_\nu && (42) \end{aligned}}$$

— Hybrid exact-exchange (exx) LR-TDDFT

Casida's eigenvalue equation in this case becomes

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} X_I \\ Y_I \end{pmatrix} = \omega_I \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} X_I \\ Y_I \end{pmatrix} \tag{43}$$

$$A_{ia\sigma,i'a'\sigma'} = \delta_{\sigma\sigma'}\delta_{ii'}\delta_{aa'}(\epsilon^{exx}_{a\sigma} - \epsilon^{exx}_{i\sigma}) + K_{ia\sigma,i'a'\sigma'} \tag{44}$$

$$B_{ia\sigma,i'a'\sigma'} = K_{ia\sigma,a'i'\sigma'} \tag{45}$$

$$\begin{aligned} K_{ia\sigma,i'a'\sigma'} = {} & [\Phi_{ia\sigma}|\tfrac{1}{r}|\Phi^*_{i'a'\sigma'}] - \delta_{\sigma\sigma'}[\rho_{ii'\sigma}|\frac{\mathrm{erf}(\mu r)}{r}|\rho^*_{aa'\sigma'}] \\ & + \iint d\mathbf{r}\, d\mathbf{r}'\, \Phi_{ia\sigma}(\mathbf{r})(f_{xc} - f^{LR}_{x})(\mathbf{r},\mathbf{r}';\omega)\,\Phi_{i'a'\sigma'}(\mathbf{r}') \end{aligned} \tag{46}$$

(Diagonal approximation) $A, X \gg B, Y$

$$\begin{aligned} & \epsilon^{exx}_{a\sigma} - \epsilon^{exx}_{i\sigma} + [\Phi_{ia\sigma}|\tfrac{1}{r}|\Phi_{ia\sigma}] - [\rho_{i\sigma}|\frac{\mathrm{erf}(\mu r)}{r}|\rho_{a\sigma}] \\ & \quad + [\Phi_{ia\sigma}|(f_{xc} - f^{LR}_{x})|\Phi_{ia\sigma}] \simeq \omega_I \end{aligned} \tag{47}$$

$$\boxed{\begin{aligned} \therefore \Omega^{LR\text{-}TDDFT,exx} = {} & \underbrace{\omega^{exx}_{\nu}}_{\text{wide gap}} + K_\nu - \underbrace{[\rho_i|\frac{\mathrm{erf}(\mu r)}{r}|\rho_a]}_{\text{long-range } J_\nu} \\ & + [\Phi_\nu|(f_{xc} - f^{LR}_{x})|\Phi_\nu] \end{aligned}} \tag{48}$$

$\downarrow$ for local

$$\int d\mathbf{r}\, \rho_i(\mathbf{r})\, (f_{xc} - f^{LR}_{x})^{local}(\mathbf{r})\,\rho_a(\mathbf{r}) \tag{49}$$

– In summary,

$$\begin{array}{l|l|l|l}
\Omega^{\Delta SCF} = \tilde{\omega}_\nu^{KS} & -J_\nu & & -\int d\mathbf{r}\,\rho_i(\mathbf{r})\, f_{xc}^{local}(\mathbf{r})\, \rho_a(\mathbf{r}) \quad (21') \\
\Omega^{\Delta HF} = \omega_\nu^{HF} & -J_\nu & +K_\nu & \quad (42) \\
\Omega^{LR\text{-}TDDFT,\,local} = \omega_\nu^{KS} & & +K_\nu & +\int d\mathbf{r}\,\rho_i(\mathbf{r})\, f_{xc}^{local}(\mathbf{r})\, \rho_a(\mathbf{r}) \quad (36) \\
\Omega^{LR\text{-}TDPFT,\,exx} = \omega_\nu^{exx} & -[\rho_i|\frac{\mathrm{erf}(\mu r)}{r}|\rho_a] & +K_\nu & +\int d\mathbf{r}\,\rho_i(\mathbf{r})\,(f_{xc}-f_x^{LR})^{local}(\mathbf{r})\, \rho_a(\mathbf{r}) \quad (49) \\
\text{e-h excitation} & \text{e-h Coulomb} & \text{RPA} &
\end{array}$$

In Eq. (21′), we have introduced the SIC-KS excitation energy,

$$\tilde{\omega}_\nu^{KS} = \underbrace{\epsilon_a^{KS} + U_a}_{\tilde{\epsilon}_a^{KS}} - (\underbrace{\epsilon_i^{KS} - U_i}_{\tilde{\epsilon}_i^{KS}}) \qquad (50)$$

\- Occupation-number integration

According to the Janak's theorem,

$$\frac{\partial E_{tot}}{\partial f_i} = \epsilon_i^{KS} \qquad (51)$$

where f_i is the occupation of the i-th KS orbital.

Now consider gradual promotion of electron from $i \to a$, with a fraction $f_a = 0 \to 1$ (or $f_i = 1 - f_a = 1 \to 0$). Then,

$$\frac{\partial E_{tot}}{\partial f_a} = \epsilon_a^{KS} - \epsilon_i^{KS} = \omega_\nu^{KS} \qquad (52)$$

$\int_0^1 df_a \times$ Eq.(52)

$$\underbrace{E_{tot}(f_a=1) - E_{tot}(f_a=0)}_{} = \int_0^1 df_a \frac{\partial E_{tot}}{\partial f_a} = \int_0^1 df_a\, \omega_\nu^{KS} \qquad (53)$$

$$= \Omega^{\Delta SCF}$$

$$\therefore \langle \omega_\nu^{KS} \rangle \equiv \int_0^1 df_a\, \omega_\nu^{KS} = \Omega^{\Delta SCF} \qquad (54)$$

Now, integrate Eq.(36) over occupation number

$$\langle \Omega^{LR\text{-}TDDFT,\,local} \rangle = \langle \omega_\nu^{KS} \rangle + \langle K_\nu \rangle + \langle \int d\mathbb{r}\, \rho_i(\mathbb{r})\, f_{xc}^{local}(\mathbb{r})\, \rho_a(\mathbb{r}) \rangle \qquad (55)$$

Substituting Eq.(54) to the first term in Eq.(55), and assuming the second and third terms of Eq.(55) are not sensitive to the occupation number (?), Eq.(55) becomes

$$\langle \Omega^{\text{LR-TDDFT, local}} \rangle = \Omega^{\Delta SCF} + K_\nu + \int d\mathbf{r}\, \rho_i(\mathbf{r}) f_{xc}^{local}(\mathbf{r}) \rho_a(\mathbf{r}) \qquad (56)$$

Substituting Eq. (21′) in (56),

$$\langle \Omega^{\text{LR-TDDFT, local}} \rangle = \tilde{\omega}_\nu^{KS} - J_\nu - \cancel{\int d\mathbf{r}\, \rho_i(\mathbf{r}) f_{xc}^{local}(\mathbf{r}) \rho_a(\mathbf{r})}$$
$$+ K_\nu + \cancel{\int d\mathbf{r}\, \rho_i(\mathbf{r}) f_{xc}^{local}(\mathbf{r}) \rho_a(\mathbf{r})}$$

$$\boxed{\begin{aligned} \therefore \langle \Omega^{\text{LR-TDDFT, local}} \rangle &\equiv \int_0^1 df_a\, \Omega^{\text{LR-TDDFT, local}} \\ &= \underbrace{\tilde{\omega}_\nu^{KS}}_{\substack{\text{SIC band}\\ \text{widening}}} - \underbrace{J_\nu}_{\substack{\text{e-h}\\ \text{binding}}} + \underbrace{K_\nu}_{\text{RPA}} \end{aligned}} \qquad (57)$$

where the SIC-KS excitation energy is

$$\tilde{\omega}_\nu^{KS} = \epsilon_a^{KS} + \underbrace{\frac{1}{2}\left[J_{aa} + \int d\mathbf{r}\, \rho_a(\mathbf{r}) f_{xc}^{local}(\mathbf{r}) \rho_a(\mathbf{r})\right]}_{U_a}$$
$$- \left\{ \epsilon_i^{KS} - \underbrace{\frac{1}{2}\left[J_{ii} + \int d\mathbf{r}\, \rho_i(\mathbf{r}) f_{xc}^{local}(\mathbf{r}) \rho_i(\mathbf{r})\right]}_{U_i} \right\} \qquad (58)$$

(A) Occupation-number integration of LR-TDDFT excitation energy with local xc functional has correct (1) SIC band widening & (2) electron-hole binding.

(B) For HOMO→LUMO excitation, reasonable approximation is

$$\int_0^1 df_a\, \Omega^{\text{LR-TDDFT, local}} \simeq \Omega^{\text{LR-TDDFT, local}}\left(f_{HOMO} = f_{LUMO} = \frac{1}{2}\right) \qquad (59)$$

Mid-point method