# Many-Body Wave Function in Linear-Response Time-Dependent Density Functional Theory (I)

6/5/12

- Second quantization

Consider the density operator for N-electron system,

$$\rho(\mathbf{x}) = \sum_{i=1}^{N} \delta(\mathbf{x} - \mathbf{r}_i) \tag{1}$$

In the second-quantization form, the operator is (2/24/10)

$$\hat{\rho}(\mathbf{x}) = \sum_{st\sigma} \hat{c}^{\dagger}_{s\sigma} \langle s\sigma | \delta(\mathbf{x} - \hat{\mathbf{r}}) | t\sigma \rangle \hat{c}_{t\sigma} \tag{2}$$

where $\hat{c}^{\dagger}_{s\sigma}$ & $\hat{c}_{s\sigma}$ are creation & anihilation operators for the generalized Kohn-Sham (GKS) orbital, $s\sigma$, and

$$\begin{aligned} \langle s\sigma | \delta(\mathbf{x} - \hat{\mathbf{r}}) | t\sigma \rangle &= \int d\mathbf{r}\, \phi^{*}_{s\sigma}(\mathbf{r})\, \delta(\mathbf{x} - \mathbf{r})\, \phi_{t\sigma}(\mathbf{r}) \\ &= \phi^{*}_{s\sigma}(\mathbf{x})\, \phi_{t\sigma}(\mathbf{x}) \end{aligned} \tag{3}$$

spin inner product vanishes otherwise

$$\therefore \hat{\rho}(\mathbf{r}) = \sum_{st\sigma} \hat{c}^{\dagger}_{s\sigma} \phi^{*}_{s\sigma}(\mathbf{r}) \phi_{t\sigma}(\mathbf{r}) \hat{c}_{t\sigma} \tag{4}$$

Now consider a state, which was in the ground-state GKS Slater determinant, $\Phi_0$, in the remote past, and has evolved, under an external potential $v(\mathbf{r},t)$, to $\Phi(t)$.

The density at time t is

$$\rho(\mathbf{r},t) = \langle \Phi(t) | \hat{\rho}(\mathbf{r}) | \Phi(t) \rangle \tag{5}$$

$$= \sum_{st\sigma} \phi^*_{t\sigma}(\mathbf{r}) \phi_{s\sigma}(\mathbf{r}) \langle \Phi(t) | \hat{C}^\dagger_{t\sigma} \hat{C}_{s\sigma} | \Phi(t) \rangle \tag{6}$$

Compare this with Eq.(23b) in 6/3/10

$$\delta\rho(\mathbf{r},t)^\forall \phi(\mathbf{r}) = \underbrace{\sum_{st\sigma} \int d\mathbf{r}' \phi_{s\sigma}(\mathbf{r}) \delta P_{st\sigma}(t) \phi^*_{t\sigma}(\mathbf{r}')}_{\text{nonlocal } \delta\rho \text{ operator}} \cdot \phi(\mathbf{r}') \tag{23b}$$

we identify

$$P_{st\sigma}(t) = \langle \Phi(t) | \hat{C}^\dagger_{t\sigma} \hat{C}_{s\sigma} | \Phi(t) \rangle \tag{7}$$

In general, the expectation value of any one-electron (non-spin-flip) operator

$$\hat{O} = \sum_{st\sigma} \hat{C}^\dagger_{s\sigma} \underbrace{\langle s\sigma | \hat{O} | t\sigma \rangle}_{\equiv O_{st\sigma}} \hat{C}_{t\sigma} = \sum_{st\sigma} \hat{C}^\dagger_{s\sigma} \hat{C}_{t\sigma} \underbrace{\int d\mathbf{r} \phi^*_{s\sigma}(\mathbf{r}) O(\mathbf{r}) \phi_{t\sigma}(\mathbf{r})}_{\equiv O_{st\sigma}} \tag{8}$$

has the expectation value at time t as

$$O(t) = \langle \Phi(t) | \hat{O} | \Phi(t) \rangle$$

$$= \sum_{st\sigma} O_{st\sigma} \underbrace{\langle \Phi(t) | \hat{C}^\dagger_{s\sigma} \hat{C}_{t\sigma} | \Phi(t) \rangle}_{P_{ts\sigma}(t)}$$

$$\therefore O(t) = \sum_{st\sigma} O_{st\sigma} P_{ts\sigma}(t) = \mathrm{tr}[OP(t)] \tag{9}$$

where

$$O_{st\sigma} = \langle s\sigma | \hat{O} | t\sigma \rangle = \int d\mathbf{r} \phi^*_{s\sigma}(\mathbf{r}) O(\mathbf{r}) \phi_{t\sigma}(\mathbf{r}) \tag{10}$$

## – Time evolution

$$i\frac{\partial}{\partial t}|\Phi(t)\rangle = \left[\hat{H} + \hat{V}(t)\right]|\Phi(t)\rangle \tag{11}$$

where

$$\hat{H} = \sum_{st\sigma} \hat{c}^{+}_{s\sigma}\langle s\sigma| -\frac{\nabla^2}{2} + v_{ion}(\mathbf{r})|t\sigma\rangle \hat{c}_{t\sigma}$$

$$+ \frac{1}{2}\sum_{st\sigma,uv\tau} \hat{c}^{+}_{s\sigma}\hat{c}^{+}_{u\tau}\,[s^*t|\frac{1}{r}|u^*v]\,\hat{c}_{v\tau}\hat{c}_{t\sigma} \tag{12}$$

$$\mathbf{r}'$$

$$\mathbf{r}$$

$$\hat{V}(t) = \sum_{st\sigma} \hat{c}^{+}_{s\sigma}\underbrace{\langle s\sigma|v|t\sigma\rangle}_{v_{st\sigma}}\hat{c}_{t\sigma} \tag{13}$$

and

$$\langle s\sigma|v|t\sigma\rangle = \int d\mathbf{r}\,\phi^*_{s\sigma}(\mathbf{r})\,v(\mathbf{r})\,\phi_{t\sigma}(\mathbf{r}) \equiv v_{st\sigma}(t) \tag{14}$$

— Perturbation

Let the many-electron eigenstates of $\hat{H}$ be $|\Phi_I\rangle$ with the corresponding eigenenergies $E_I$:

$$\hat{H}|\Phi_I\rangle = E_I|\Phi_I\rangle \tag{15}$$

Using $\{|\Phi_I\rangle\}$ as a basis set, we seek the perturbative solution of Eq.(11) as

$$|\Phi(t)\rangle = e^{-i\hat{H}t}\,\hat{S}(t,-\infty)\,|\Phi_0\rangle \tag{16}$$

The formal solution (2/11/10) is

$$\hat{S}(t,-\infty) = T\exp\left[-i\int_{-\infty}^{t} dt'\,\hat{V}_H(t')\right] \tag{17}$$

$$= 1 - i\int_{-\infty}^{t} dt'\,\hat{V}_H(t') + O(v^2) \tag{18}$$

where

$$\hat{V}_H(t) = e^{i\hat{H}t}\,\hat{V}(t)\,e^{-i\hat{H}t} \tag{19}$$

Substituting Eq.(18) in (16)

$$|\Phi(t)\rangle = \left[e^{-i\hat{H}t} - i\int_{-\infty}^{t} dt'\,e^{-i\hat{H}(t-t')}\,\hat{V}(t')\,e^{-i\hat{H}t'}\right]|\Phi_0\rangle$$

$$+ O(v^2) \tag{20}$$

– Density-matrix response

$$P_{st\sigma}(t) = \langle \Phi(t) | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi(t) \rangle$$

$$= \langle \Phi_0 | \left[ e^{i\hat{H}t} + i \int_{-\infty}^{t} dt' \, e^{i\hat{H}t'} \hat{V}(t') \, e^{i\hat{H}(t-t')} \right] \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma}$$

$$\times \left[ e^{-i\hat{H}t} - i \int_{-\infty}^{t} dt' \, e^{-i\hat{H}(t-t')} \hat{V}(t') \, e^{-i\hat{H}t'} \right] | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi_0 \rangle$$

$$- i \int_{-\infty}^{t} dt' \, \langle \Phi_0 | e^{iE_0 t} \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} \, e^{-i\hat{H}(t-t')} \hat{V}(t') \, e^{-iE_0 t'} | \Phi_0 \rangle$$

$$+ i \int_{-\infty}^{t} dt' \, \langle \Phi_0 | e^{iE_0 t'} \hat{V}(t') \, e^{i\hat{H}(t-t')} \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} \, e^{-iE_0 t} | \Phi_0 \rangle \qquad (21)$$

$$\therefore \delta P_{st\sigma}(t) \equiv \langle \Phi(t) | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi(t) \rangle - \langle \Phi_0 | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi_0 \rangle \qquad (22)$$

$$= -i \int_{-\infty}^{\infty} dt' \, \Theta(t-t') \Big\{ e^{iE_0(t-t')} \langle \Phi_0 | \hat{c}^{\dagger}_{t\sigma} c_{s\sigma} \underbrace{\,}_{\sum_I |\Phi_I\rangle\langle\Phi_I|} e^{-i\hat{H}(t-t')} V(t') | \Phi_0 \rangle$$

$$- e^{-iE_0(t-t')} \langle \Phi_0 | \hat{V}(t') \, e^{i\hat{H}(t-t')} \underbrace{\,}_{\sum_I |\Phi_I\rangle\langle\Phi_I|} \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi_0 \rangle \Big\}$$

$$= -i \int_{-\infty}^{\infty} dt' \, \Theta(t-t') \sum_I \Big\{ e^{-i(E_I - E_0)(t-t')} \langle \Phi_0 | \hat{c}^{\dagger}_{t\sigma} c_{s\sigma} | \Phi_I \rangle \langle \Phi_I | \hat{V}(t') | \Phi_0 \rangle$$

$$- e^{i(E_I - E_0)(t-t')} \langle \Phi_0 | \hat{V}(t') | \Phi_I \rangle \langle \Phi_I | \hat{c}^{\dagger}_{t\sigma} c_{s\sigma} | \Phi_0 \rangle \Big\}$$

(23)

Substituting the GKS expansion of $\hat{V}(t)$ in Eq.(13) in Eq.(23),

$$\delta P_{st\sigma}(t) = -i\int_{-\infty}^{\infty} dt'\, \Theta(t-t') \sum_I$$

$$\times \left\{ e^{-i(E_I-E_0)(t-t')} \langle\Phi_0|\hat{c}^\dagger_{t\sigma}\hat{c}_{s\sigma}|\Phi_I\rangle \sum_{uv\tau} v_{uv\tau}(t') \langle\Phi_I|\hat{c}^\dagger_{u\tau}\hat{c}_{v\tau}|\Phi_0\rangle \right.$$

$$\left. - e^{i(E_I-E_0)(t-t')} \sum_{uv\tau} v_{uv\tau}(t') \langle\Phi_0|\hat{c}^\dagger_{u\tau}\hat{c}_{v\tau}|\Phi_I\rangle\langle\Phi_I|\hat{c}^\dagger_{t\sigma}\hat{c}_{s\sigma}|\Phi_0\rangle \right\} \qquad (24)$$

$$\therefore \chi_{st\sigma,uv\tau}(t-t') \equiv \frac{\delta P_{st\sigma}(t)}{\delta v_{uv\tau}(t')} \qquad (25)$$

$$= -i\,\Theta(t-t') \sum_I$$

$$\times \left\{ e^{-i(E_I-E_0)(t-t')} \langle\Phi_0|\hat{c}^\dagger_{t\sigma}\hat{c}_{s\sigma}|\Phi_I\rangle\langle\Phi_I|\hat{c}^\dagger_{u\tau}\hat{c}_{v\tau}|\Phi_0\rangle \right.$$

$$\left. - e^{i(E_I-E_0)(t-t')} \langle\Phi_0|\hat{c}^\dagger_{u\tau}\hat{c}_{v\tau}|\Phi_I\rangle\langle\Phi_I|\hat{c}^\dagger_{t\sigma}\hat{c}_{s\sigma}|\Phi_0\rangle \right\} \qquad (26)$$

Recall (2/25/10),

$$\Theta(t) = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega t}}{\omega + i0} \qquad (27)$$

Substituting Eq.(27) in (26),

$$\chi_{st\sigma,uv\tau}(t-t') = \cancel{(-i)}\int_{-\infty}^{\infty} \frac{d\omega}{-2\pi\cancel{i}} \sum_I \frac{1}{\omega+i0}$$

$$\times \left\{ e^{-i\underbrace{(\omega+E_I-E_0)}_{\equiv\,\omega'}(t-t')} \langle\Phi_0|\hat{c}^\dagger_{t\sigma}\hat{c}_{s\sigma}|\Phi_I\rangle\langle\Phi_I|\hat{c}^\dagger_{u\tau}\hat{c}_{v\tau}|\Phi_0\rangle \right.$$

$$\left. - e^{-i\underbrace{(\omega-E_I+E_0)}_{\equiv\,\omega'}(t-t')} \langle\Phi_0|\hat{c}^\dagger_{u\tau}\hat{c}_{v\tau}|\Phi_I\rangle\langle\Phi_I|\hat{c}^\dagger_{t\sigma}\hat{c}_{s\sigma}|\Phi_0\rangle \right\}$$

$$\therefore \chi_{s t\sigma, u v\tau}(t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \sum_{I}$$

$$\times \left\{ \frac{\langle \Phi_0 | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi_I \rangle \langle \Phi_I | \hat{c}^{\dagger}_{u\tau} \hat{c}_{v\tau} | \Phi_0 \rangle}{\omega - (E_I - E_0) + i0} - \frac{\langle \Phi_0 | \hat{c}^{\dagger}_{u\tau} \hat{c}_{v\tau} | \Phi_I \rangle \langle \Phi_I | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi_0 \rangle}{\omega + (E_I - E_0) + i0} \right\} \tag{28}$$

Noting the $I \neq 0$ term is identically zero, we can exclude $I=0$ from the sum. In the frequency space, then

$$\chi_{s t\sigma, u v\tau}(\omega) = \sum_{I \neq 0} \left\{ \frac{\langle \Phi_0 | \hat{c}^{\dagger}_{t\sigma} \hat{c}_{s\sigma} | \Phi_I \rangle \langle \Phi_I | \hat{c}^{\dagger}_{u\tau} \hat{c}_{v\tau} | \Phi_0 \rangle}{\omega - \omega_I + i0} - \frac{\langle \Phi_0 | \hat{c}^{\dagger}_{u\tau} \hat{c}_{v\tau} | \Phi_I \rangle \langle \Phi_I | \hat{c}^{\dagger}_{s\sigma} \hat{c}_{t\sigma} | \Phi_0 \rangle}{\omega + \omega_I + i0} \right\} \tag{29}$$

where

$$\omega_I = E_I - E_0 \tag{30}$$

— Dynamic dipole polarizability

Consider an electric field $\mathcal{E}(t)$; then the external potential is

$$V(\mathbf{r},t) = \mathcal{E}(t)\cdot\mathbf{r} = \sum_{\mu=x,y,z} \mathcal{E}_\mu(t)\, r_\mu \tag{31}$$

In the second quantized form,

$$\hat{V}(t) = \sum_{st\sigma} \hat{c}^\dagger_{s\sigma} \underbrace{\sum_{\mu=x,y,z} \mathcal{E}_\mu(t)\, r^\mu_{st\sigma}}_{= v_{st\sigma}(t)} c_{t\sigma} \tag{32}$$

where

$$r^\mu_{st\sigma} = \int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r})\, r_\mu\, \phi_{t\sigma}(\mathbf{r}) \tag{33}$$

We calculate the response of dipole moment

$$r_\mu(t) = \langle \Phi(t)|\hat{r}_\mu|\Phi(t)\rangle \quad (\mu = x,y,z) \tag{34}$$

$$= \sum_{st\sigma} r^\mu_{st\sigma} P_{ts\sigma}(t) \tag{35}$$

$$\therefore \delta r_\mu(t) = \sum_{st\sigma} r^\mu_{st\sigma} \sum_{uv\tau} \underbrace{\frac{\delta P_{ts\sigma}(t)}{\delta v_{uv\tau}(t')}}_{\chi_{ts\sigma,uv\tau}(t-t')} \cdot \sum_\nu \mathcal{E}_\nu(t')\, r^\nu_{uv\tau} \quad (\because \text{Eq. (32)}) \tag{36}$$

$$\therefore \alpha_{\mu\nu}(t-t') \equiv \underset{\text{electron}}{-} \frac{\delta r_\mu(t)}{\delta \mathcal{E}_\nu(t')} \tag{37}$$

$$= -\sum_{st\sigma,uv\tau} r^\mu_{st\sigma}\, \chi_{ts\sigma,uv\tau}(t-t')\, r^\nu_{uv\tau} \tag{38}$$

or in the frequency space,

$$\alpha_{\mu\nu}(\omega) = -\sum_{st\sigma,uv\tau} r^\mu_{ts\sigma}\, \chi_{st\sigma,uv\tau}(\omega)\, r^\nu_{uv\tau} \tag{39}$$

Substituting Eq. (29) in (39),

$$\alpha_{\mu\nu}(\omega) = -\sum_{st\sigma, uv\tau} \sum_{I\neq 0} r^{\mu}_{ts\sigma} \left\{ \frac{\langle \Phi_0 | \hat{C}^{+}_{t\sigma} \hat{C}_{s\sigma} | \Phi_I \rangle \langle \Phi_I | \hat{C}^{+}_{u\tau} \hat{C}_{v\tau} | \Phi_0 \rangle}{\omega - \omega_I + i0} - \frac{\langle \Phi_0 | \hat{C}^{+}_{u\tau} \hat{C}_{v\tau} | \Phi_I \rangle \langle \Phi_I | \hat{C}^{+}_{t\sigma} \hat{C}_{s\sigma} | \Phi_0 \rangle}{\omega + \omega_I + i0} \right\} r^{\nu}_{uv\tau} \tag{40}$$

Note that

$$\sum_{st\sigma} \hat{C}^{+}_{t\sigma} r^{\mu}_{ts\sigma} C_{s\sigma} = \hat{r}^{\mu} \tag{41}$$

Substituting Eq. (41) in (40),

$$\alpha_{\mu\nu}(\omega) = -\sum_{I\neq 0} \left\{ \frac{\langle \Phi_0 | \hat{r}_{\mu} | \Phi_I \rangle \langle \Phi_I | \hat{r}_{\nu} | \Phi_0 \rangle}{\omega - \omega_I + i0} - \frac{\langle \Phi_0 | \hat{r}_{\nu} | \Phi_I \rangle \langle \Phi_I | \hat{r}^{\mu} | \Phi_0 \rangle}{\omega + \omega_I + i0} \right\} \tag{42}$$

The mean polarizability is

$$\bar{\alpha}(\omega) = \frac{1}{3} \operatorname{tr} \alpha(\omega) \tag{43}$$

$$= -\sum_{\mu=x,y,z} \sum_{I\neq 0} \frac{1}{3} \left\{ \frac{\langle \Phi_0 | \hat{r}_{\mu} | \Phi_I \rangle \langle \Phi_I | \hat{r}_{\mu} | \Phi_0 \rangle}{\omega - \omega_I + i0} - \frac{\langle \Phi_0 | \hat{r}_{\mu} | \Phi_I \rangle \langle \Phi_I | \hat{r}_{\mu} | \Phi_0 \rangle}{\omega + \omega_I + i0} \right\} \tag{44}$$

$$\therefore \operatorname{Re} \bar{\alpha}(\omega) = -\sum_{\mu=x,y,z} \sum_{I\neq 0} \frac{1}{3} |\langle \Phi_0 | \hat{r}_{\mu} | \Phi_I \rangle|^2 \underbrace{\left( \frac{1}{\omega - \omega_I} - \frac{1}{\omega + \omega_I} \right)}_{\frac{\cancel{\omega} + \omega_I - \cancel{\omega} + \omega_I}{(\omega - \omega_I)(\omega + \omega_I)}}$$

$$= \sum_{I\neq 0} \frac{\sum_{\mu} \frac{2}{3} \omega_I |\langle \Phi_0 | \hat{r}_{\mu} | \Phi_I \rangle|^2}{\omega_I^2 - \omega^2} = \sum_{I\neq 0} \frac{f_I}{\omega_I^2 - \omega^2} \tag{45}$$

# Many-Body Wave Function in Linear-Response Time-Dependent Density Functional Theory (II)

6/7/12

— Real perturbation

Consider a real potential & real generalized Kohn-Sham (GKS) orbitals, then

$$v_{st\sigma}(t) = \int d\mathbf{r}\, \phi^{\cancel{*}}_{s\sigma}(\mathbf{r})\, v(\mathbf{r},t)\, \phi_{t\sigma}(\mathbf{r}) = v^{*}_{st\sigma}(t) \tag{1}$$

and the linear-response of the density matrix [Eq.(21) of 6/5/12] becomes

$$\left\{ \begin{bmatrix} \mathbb{A}(\omega) & \mathbb{B}(\omega) \\ \mathbb{B}^{*}(\omega) & \mathbb{A}^{*}(\omega) \end{bmatrix} - \omega \begin{bmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{bmatrix} \right\} \begin{bmatrix} \delta\mathbb{P}(\omega) \\ \delta\mathbb{P}^{*}(\omega) \end{bmatrix} = - \begin{bmatrix} v(\omega) \\ v(\omega) \end{bmatrix} \tag{2}$$

where

$$A_{ai\sigma,bj\tau}(\omega) = \delta_{ab}\delta_{ij}\delta_{\sigma\tau}\, \overset{\epsilon_{b\tau}-\epsilon_{j\tau}}{\omega_{jb\tau}} + K_{ai\sigma,bj\tau}(\omega) \tag{3}$$

$$B_{ai\sigma,bj\tau}(\omega) = K_{ai\sigma,jb\tau}(\omega) \tag{4}$$

$$K_{st\sigma,uv\tau}(\omega) = [\phi^{*}_{s\sigma}\phi_{t\sigma}| \frac{1}{r} + f_{xc}(\omega) - f^{lr}_{x} | \phi^{*}_{v\tau}\phi_{u\tau}]$$
$$- \delta_{\sigma\tau}\, [\phi^{*}_{s\sigma}\phi_{u\tau}| \frac{\mathrm{erf}(\mu r)}{r} | \phi^{*}_{v\tau}\phi_{t\sigma}] \tag{5}$$

For real GKS orbitals & adiabatic fxc, all the matrix elements are real, and Eq. (2) becomes

$$\begin{cases} \mathbb{A}(\omega)\,\delta\mathbb{P}(\omega) + \mathbb{B}(\omega)\,\delta\mathbb{P}^*(\omega) - \omega\,\delta\mathbb{P}(\omega) = -\mathcal{V}(\omega) & (6) \\ \mathbb{B}(\omega)\,\delta\mathbb{P}(\omega) + \mathbb{A}(\omega)\,\delta\mathbb{P}^*(\omega) + \omega\,\delta\mathbb{P}^*(\omega) = -\mathcal{V}(\omega) & (7) \end{cases}$$

Eq. (6) + (7)

$$(\mathbb{A}+\mathbb{B})(\delta\mathbb{P}+\delta\mathbb{P}^*) - \omega(\delta\mathbb{P}-\delta\mathbb{P}^*) = -2\mathcal{V} \qquad (8)$$

Eq. (6) − (7)

$$(\mathbb{A}-\mathbb{B})(\delta\mathbb{P}-\delta\mathbb{P}^*) - \omega(\delta\mathbb{P}+\delta\mathbb{P}^*) = 0 \qquad (9)$$

From Eq. (9),

$$\delta\mathbb{P}-\delta\mathbb{P}^* = \omega(\mathbb{A}-\mathbb{B})^{-1}(\delta\mathbb{P}+\delta\mathbb{P}^*) \qquad (10)$$

Substituting Eq. (10) in Eq. (8),

$$(\mathbb{A}+\mathbb{B})(\delta\mathbb{P}+\delta\mathbb{P}^*) - \omega^2(\mathbb{A}-\mathbb{B})^{-1}(\delta\mathbb{P}+\delta\mathbb{P}^*) = -2\mathcal{V}$$

$$\therefore \left\{\omega^2[\mathbb{A}(\omega)-\mathbb{B}(\omega)]^{-1} - [\mathbb{A}(\omega)+\mathbb{B}(\omega)]\right\}\underbrace{[\delta\mathbb{P}(\omega)+\delta\mathbb{P}^*(\omega)]}_{2[\mathrm{Re}\mathbb{P}](\omega)} = 2\mathcal{V}(\omega) \qquad (11)$$

Eq. (11) describes the real-part of the density-matrix response to a real external potential.

$(\mathbb{A}-\mathbb{B}) \times$ Eq. (11)

$$[\omega^2 \mathbb{1} - (\mathbb{A}-\mathbb{B})(\mathbb{A}+\mathbb{B})] \, \mathrm{Re}\mathbb{P} = (\mathbb{A}-\mathbb{B}) \mathcal{V} \tag{12}$$

$(\mathbb{A}-\mathbb{B})^{-1/2} \times$ Eq. (12)

$$[\omega^2 (\mathbb{A}-\mathbb{B})^{-1/2} - (\mathbb{A}-\mathbb{B})^{1/2} (\mathbb{A}+\mathbb{B})] \underbrace{\;}_{(\mathbb{A}-\mathbb{B})^{1/2}(\mathbb{A}-\mathbb{B})^{-1/2}} \mathrm{Re}\mathbb{P} = (\mathbb{A}-\mathbb{B})^{1/2} \mathcal{V}$$

$$\therefore \; [\omega^2 \mathbb{1} - \underbrace{(\mathbb{A}-\mathbb{B})^{1/2} (\mathbb{A}+\mathbb{B}) (\mathbb{A}-\mathbb{B})^{1/2}}_{\Omega(\omega)}] (\mathbb{A}-\mathbb{B})^{-1/2} \, \mathrm{Re}\mathbb{P} = (\mathbb{A}-\mathbb{B})^{1/2} \mathcal{V} \tag{13}$$

$[\omega^2 \mathbb{1} - \Omega(\omega)]^{-1} \times$ Eq. (13)

$$(\mathbb{A}-\mathbb{B})^{-1/2} \, \mathrm{Re}\mathbb{P} = [\omega^2 \mathbb{1} - \Omega(\omega)]^{-1} (\mathbb{A}-\mathbb{B})^{1/2} \mathcal{V} \tag{14}$$

$(\mathbb{A}-\mathbb{B})^{1/2} \times$ Eq. (14)

$$\underbrace{(\mathrm{Re}\mathbb{P})(\omega)}_{= \frac{\mathbb{P}(\omega) + \mathbb{P}^*(\omega)}{2}} = [\mathbb{A}(\omega) - \mathbb{B}(\omega)]^{1/2} [\omega^2 \mathbb{1} - \Omega(\omega)]^{-1} [\mathbb{A}(\omega) - \mathbb{B}(\omega)]^{1/2} \mathcal{V}(\omega) \tag{15}$$

where

$$\Omega(\omega) = [\mathbb{A}(\omega) - \mathbb{B}(\omega)]^{1/2} [\mathbb{A}(\omega) + \mathbb{B}(\omega)] [\mathbb{A}(\omega) - \mathbb{B}(\omega)]^{1/2} \tag{16}$$

Since the Coulomb-like integral is symmetric w.r.t. the integration variables $\mathbf{r}$ & $\mathbf{r}'$, for real GKS orbitals & adiabatic $f_{xc}$, $\mathbb{A}$ & $\mathbb{B}$ are real symmetric. If $\mathbb{A}-\mathbb{B}$ is positive definite ($\forall$ its real eigenvalues are positive), $(\mathbb{A}-\mathbb{B})^{1/2}$ exists and $\Omega(\omega)$ is a well-defined real symmetrix matrix that has real eigenvalues.

– Eigenvalue problem

$$\Omega(\omega_I)\, \mathbb{F}_I = \omega_I^2\, \mathbb{F}_I \tag{17}$$

If, in addition to $\mathbb{A}-\mathbb{B}$, $\mathbb{A}+\mathbb{B}$ is positive definite, then all eigenvalues $\omega_I^2$ are positive, hence $\omega_I$ are real. For these eigenfrequencies, $\omega_I$, nonzero $(\mathrm{Re}\mathbb{P})(\omega_I)$ can exist without $v$ in Eq. (15), i.e., $\omega_I$ is an excitation energy.

Comparing Eq. (17) with Eq. (13), where $v = 0$,

$$\mathbb{F}_I = [\mathbb{A}(\omega_I) - \mathbb{B}(\omega_I)]^{-1/2}(\delta\mathbb{P}_I + \delta\mathbb{P}_I^*) \tag{18}$$

(within the normalization constant).

- Dynamic dipole polarizability

Consider an electric field $\mathcal{E}(t)$, such that

$$v_{st\sigma}(t) = \sum_{\mu=x,y,z} \mathcal{E}_\mu(t)\, r^\mu_{st\sigma} \tag{19}$$

where

$$\mathbf{r}_{st\sigma} = \int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r})\, \mathbf{r}\, \phi_{t\sigma}(\mathbf{r}) \tag{20}$$

The real-part of the dipole response is

$$-\delta r_\mu(\omega) = -\sum_{st\sigma} r^\mu_{ts\sigma} \operatorname{Re} \delta P_{st\sigma}(\omega) \tag{21}$$

Using Eq. (15)

$$-\delta r_\mu(\omega) = -\sum_{st\sigma} r^\mu_{ts\sigma} \sum_{uv\tau} \left[(\mathbb{A}-\mathbb{B})^{1/2}(\omega^2\mathbb{1}-\Omega)^{-1}(\mathbb{A}-\mathbb{B})^{1/2}\right]_{st\sigma,uv\tau} \times \sum_\nu \mathcal{E}_\nu(t)\, r^\nu_{uv\tau} \tag{22}$$

$$\therefore \alpha_{\mu\nu}(\omega) \equiv -\frac{\delta r_\mu(\omega)}{\delta \mathcal{E}_\nu(\omega)} \tag{23}$$

$$= -\sum_{st\sigma,uv\tau} r^\mu_{ts\sigma}\left[(\mathbb{A}-\mathbb{B})^{1/2}(\omega^2\mathbb{1}-\Omega)^{-1}(\mathbb{A}-\mathbb{B})^{1/2}\right]_{st\sigma,uv\tau} r^\nu_{uv\tau} \tag{24}$$

Note that $\delta P_{st\sigma}(t)$ is nonzero for $f_{s\sigma}-f_{t\sigma}>0$ (i.e. $\delta P_{ia\sigma}$) and $f_{s\sigma}-f_{t\sigma}<0$ (i.e. $\delta P_{ai}$), where $\delta P_{ia}(t) = \delta P^*_{ai}(t)$. Restricting the st sum in Eq. (24) only to ai,

$$\alpha_{\mu\nu}(\omega) = -2\sum_{ai\sigma,bj\tau} r^\mu_{ia\sigma}\left[(\mathbb{A}-\mathbb{B})^{1/2}(\omega^2\mathbb{1}-\Omega)^{-1}(\mathbb{A}-\mathbb{B})^{1/2}\right]_{ai\sigma,bj\tau} r^\nu_{bj\tau} \tag{25}$$

Noting that

$$\mathbb{r}_{ia\sigma} = \int d\mathbb{r}\, \phi^*_{i\sigma}(\mathbb{r})\, \mathbb{r}\, \phi_{a\sigma}(\mathbb{r}) = \Big[ \underbrace{\int d\mathbb{r}\, \phi^*_{a\sigma}(\mathbb{r})\, \mathbb{r}\, \phi_{i\sigma}(\mathbb{r})}_{\mathbb{r}_{ai\sigma}} \Big]^* = \mathbb{r}^\dagger_{ai\sigma} \qquad (26)$$

Eq. (25) becomes

$$\alpha_{\mu\nu}(\omega) = -2 \sum_{ai\sigma, bj\tau} (\mathbb{r}^\dagger)^\mu_{ai\sigma} \left[ (\mathbb{A}-\mathbb{B})^{1/2} (\omega^2 \mathbb{1} - \Omega)^{-1} (\mathbb{A}-\mathbb{B})^{1/2} \right]_{ai\sigma, bj\tau} \mathbb{r}^\nu_{bj\tau} \qquad (27)$$

$$= -2\, \mathbb{r}^\dagger_\mu (\mathbb{A}-\mathbb{B})^{1/2} (\omega^2 \mathbb{1} - \Omega)^{-1} (\mathbb{A}-\mathbb{B})^{1/2}\, \mathbb{r}_\nu \qquad (28)$$

(Spectral representation)

Expanding Eq. (28) with the complete set of eigenvectors in Eq. (17), Eq. (28) becomes

$$\alpha_{\mu\nu}(\omega) = -2 \sum_{I \neq 0} \mathbb{r}^\dagger_\mu (\mathbb{A}-\mathbb{B})^{1/2} \frac{\mathbb{F}_I\, \overset{\text{row vector}}{\mathbb{F}^\dagger_I}}{\omega^2 - \omega_I^2} (\mathbb{A}-\mathbb{B})^{1/2}\, \mathbb{r}_\nu \qquad (29)$$

(Sum-over-states representation)

From Eq. (42) in 6/5/12, the sum-over-states (SOS) representation of the polarizability is

$$\alpha_{\mu\nu}(\omega) = -\sum_{I\neq 0}\left\{\frac{\langle\Phi_0|\hat{r}_\mu|\Phi_I\rangle\langle\Phi_I|\hat{r}_\nu|\Phi_0\rangle}{\omega-\omega_I+i0} - \frac{\langle\Phi_0|\hat{r}_\nu|\Phi_I\rangle\langle\Phi_I|\hat{r}_\mu|\Phi_0\rangle}{\omega+\omega_I+i0}\right\} \quad (30)$$

For the real part of a diagonal response,

$$\mathrm{Re}\,\alpha_{\mu\mu}(\omega) = -\sum_{I\neq 0}\langle\Phi_0|\hat{r}_\mu|\Phi_I\rangle\langle\Phi_I|\hat{r}_\mu|\Phi_0\rangle\underbrace{\left(\frac{1}{\omega-\omega_I}-\frac{1}{\omega+\omega_I}\right)}_{\frac{\cancel{\omega}+\omega_I-\cancel{\omega}+\omega_I}{(\omega-\omega_I)(\omega+\omega_I)}=\frac{2\omega_I}{\omega^2-\omega_I^2}}$$

$$= -2\sum_{I\neq 0}\frac{\omega_I\langle\Phi_0|\hat{r}_\mu|\Phi_I\rangle\langle\Phi_I|\hat{r}_\nu|\Phi_0\rangle}{\omega^2-\omega_I^2} \quad (31)$$

Equating Eqs. (29) & (31), we identify

$$\underbrace{\mathbb{r}_\mu^\dagger(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I\cdot\mathbb{F}_I^\dagger(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{r}_\mu}_{\text{TDDFT}} = \underbrace{\omega_I\langle\Phi_0|\hat{r}_\mu|\Phi_I\rangle\langle\Phi_I|\hat{r}_\mu|\Phi_0\rangle}_{\text{SOS}} \quad (32)$$

or

$$\mathbb{r}_\mu^\dagger(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I = \omega_I^{1/2}\langle\Phi_I|\hat{r}_\mu|\Phi_0\rangle \quad (33)$$

$$\therefore \sum_{ai\sigma} r^\mu_{ai\sigma}\left[(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I\right]_{ai\sigma} = \omega_I^{1/2}\sum_{ai\sigma} r^\mu_{ai\sigma}\langle\Phi_I|\hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}|\Phi_0\rangle$$

$$\therefore \left[(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I\right]_{ai\sigma} = \omega_I^{1/2}\langle\Phi_I|\hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}|\Phi_0\rangle \quad (34)$$

Substituting the singly-excited state,

$$|\Phi_I\rangle = \sum_{ai\sigma} A_{ai\sigma}\, \hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}|\Phi_0\rangle \tag{35}$$

in Eq. (34),

$$[(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I]_{ai\sigma} = \omega_I^{1/2}\sum_{bj\tau} A_{bj\tau}\underbrace{\langle\Phi_0|\hat{c}^\dagger_{j\tau}\hat{c}_{b\tau}\hat{c}^\dagger_{a\sigma}c_{i\sigma}|\Phi_0\rangle}_{\text{only nonzero if } i=j,\ a=b,\ \sigma=\tau}$$

$$\langle\Phi_0|\hat{c}^\dagger_{i\sigma}\hat{c}_{a\sigma}\hat{c}^\dagger_{a\sigma}c_{i\sigma}|\Phi_0\rangle$$
$$= \langle\Phi_0|\hat{c}^\dagger_{i\sigma}(1-\hat{c}^\dagger_{a\sigma}\cancel{\hat{c}_{a\sigma}})c_{i\sigma}|\Phi_0\rangle$$
$$= \langle\Phi_0|1-\hat{c}_{i\sigma}\cancel{\hat{c}^\dagger_{i\sigma}}|\Phi_0\rangle$$
$$= 1$$

$$\therefore\ A_{ai\sigma} = [(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I]_{ai\sigma}/\omega_I^{1/2} \tag{36}$$

Therefore, the singly-excited state that reproduces the TDDFT linear response, Eq. (28), is

$$|\Phi_I\rangle = \sum_{ai\sigma}\frac{[(\mathbb{A}-\mathbb{B})^{1/2}\mathbb{F}_I]_{ai\sigma}}{\sqrt{\omega_I}}\hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}|\Phi_0\rangle \tag{37}$$

Note from Eq. (18)

$$\mathbb{F}_I = (\mathbb{A}-\mathbb{B})^{-1/2}(\delta\mathbb{P}_I+\delta\mathbb{P}_I^*) \tag{38}$$

Substituting Eq. (38) in (37),

$$\boxed{|\Phi_I\rangle = \sum_{ai\sigma}\frac{(\delta\mathbb{P}_I+\delta\mathbb{P}_I^*)_{ai\sigma}}{\sqrt{\omega_I}}\hat{c}^\dagger_{a\sigma}\hat{c}_{i\sigma}|\Phi_0\rangle} \tag{39}$$