Linear-Response Time-Dependent Density Functional Theory: Hybrid Functionals (I)

6/3/12

– Generalized Kohn-Sham basis

Consider an orthonormal set of orbitals $\{\phi_{s\sigma}(\mathbf{r})\}$, where s & σ are orbital & spin indices. Rather than introducing spin coordinates, we simply impose orthonormality constraints,

$$\langle \phi_{s\sigma} | \phi_{t\tau} \rangle \equiv \int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r})\, \phi_{t\tau}(\mathbf{r}) = \delta_{st}\, \delta_{\sigma\tau} \tag{1}$$

Consider an N-electron system approximated with a single Slater determinant in a closed shell.

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{1\uparrow}(\mathbf{r}_1) & \cdots & \phi_{1\uparrow}(\mathbf{r}_N) \\ \phi_{1\downarrow}(\mathbf{r}_1) & \cdots & \phi_{1\downarrow}(\mathbf{r}_N) \\ \vdots & & \vdots \\ \phi_{N/2\uparrow}(\mathbf{r}_1) & \cdots & \phi_{N/2\uparrow}(\mathbf{r}_N) \\ \phi_{N/2\downarrow}(\mathbf{r}_1) & \cdots & \phi_{N/2\downarrow}(\mathbf{r}_N) \end{vmatrix} \tag{2}$$

Initially, the electrons occupy the ground state Φ_0, where the lowest-energy N/2 orbitals are occupied. Here, the orbitals are numbered in ascending order of energy, according to the single-electron Hamiltonian of choice. We also consider spin-resctricted orbitals, so that a pair of spin up & down orbitals share the same spatial wave function.

The orbitals are solutions of an effective single-electron eigenvalue problem,

$$h(\mathbf{r})\,\phi_{s\sigma}(\mathbf{r}) = \epsilon_{s\sigma}\,\phi_{s\sigma}(\mathbf{r}), \tag{3}$$

and the electron density is given by

$$\rho(\mathbf{r}) = \sum_{s\sigma} f_{s\sigma}\,\rho_{s\sigma}(\mathbf{r}) = \sum_{s\sigma} f_{s\sigma}\,\rho_{s\sigma}(\mathbf{r}), \tag{4}$$

where the occupation number is $f_{s\sigma} \in [0,1]$; in the ground state Φ_0, $f_{s\sigma} = 1$ $(s \leq N/2)$ or 0 (else).

The effective single-electron Hamiltonian $h(\mathbf{r})$ is one of the following:

(Kohn-Sham equation)

$$h(\mathbf{r}) = -\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \underbrace{\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{v_H(\mathbf{r})} + \underbrace{\frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}}_{v_{xc}[\rho](\mathbf{r})}, \tag{5}$$

where $v_{ion}(\mathbf{r})$ is the ionic potential.

(Canonical Hartree-Fock (HF) equation)

$$
\begin{aligned}
h(\mathbf{r}) \forall \phi(\mathbf{r}) = & \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) \right] \phi(\mathbf{r}) \\
& + \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma}(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}') \phi(\mathbf{r}) \\
& - \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma}(\mathbf{r}') \phi(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}) \qquad \text{swap} \qquad (6)
\end{aligned}
$$

where

$$
\sum_{i\sigma}^{occ} = \sum_{i=1}^{N/2} \sum_{\sigma=\downarrow}^{\uparrow} = \sum_{i\sigma} f_{i\sigma} \qquad (7)
$$

We also introduce a short-hand operator notation,

$$
h(\mathbf{r}) = -\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \sum_{i\sigma}^{occ} \left[J_{i\sigma}(\mathbf{r}) - K_{i\sigma}(\mathbf{r}) \right] \qquad (8)
$$

$$
= -\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + v_H(\mathbf{r}) - \sum_{i\sigma}^{occ} K_{i\sigma}(\mathbf{r}) \qquad (9)
$$

where the (local) Coulomb & (nonlocal) exchange operators are defined as

$$
J_{i\sigma}(\mathbf{r}) \forall \phi(\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma}(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}') \phi(\mathbf{r}) \qquad (10)
$$

$$
K_{i\sigma}(\mathbf{r}) \forall \phi(\mathbf{r}) = \int d\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma}(\mathbf{r}') \phi(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}) \qquad (11)
$$

(Range-separated hybrid exact-exchange functional)

Here, the electron repulsion operator is split into the short- & long-range parts,

$$\frac{1}{r} = \underbrace{\frac{1-\mathrm{erf}(\mu r)}{r}}_{\text{short-range}} + \underbrace{\frac{\mathrm{erf}(\mu r)}{r}}_{\text{long-range}}, \tag{12}$$

which respectively are used to determine the short- & long-range parts of the exchange-correlation (xc) potential. Here, μ is a range-separation parameter.

$$\begin{aligned} \hat{h}(\mathbf{r})\phi(\mathbf{r}) &= \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + v_H(\mathbf{r})\right]\phi(\mathbf{r}) \\ &\quad - \sum_{i\sigma}^{occ}\int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\phi^*_{i\sigma}(\mathbf{r}')\phi(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}) \\ &\quad + \underbrace{\frac{\delta(E_{xc}-E_x^{lr})}{\delta\rho(\mathbf{r})}}_{(v_{xc}-v_x^{lr})[\rho](\mathbf{r})}\phi(\mathbf{r}) \end{aligned} \tag{13}$$

where E_x^{lr} is the long-range contribution to the exchange functional used in the Kohn-Sham (KS) scheme, e.g., the generalized gradient approximation (GGA).

Time-dependent generalized Kohn-Sham equation

Consider a time-dependent external single-electron potential $v(\mathbf{r},t)$. The time evolution of the generalized Kohn-Sham (GKS) system is governed by

$$i\frac{\partial}{\partial t}\phi_{s\sigma}(\mathbf{r},t) = \left[h(\mathbf{r},t) + v(\mathbf{r},t) \right] \phi_{s\sigma}(\mathbf{r},t) \tag{14}$$

$$h(\mathbf{r},t)\,{}^{\forall}\phi(\mathbf{r}) = \Big[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}$$
$$- \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \phi_{i\sigma}^{*}(\mathbf{r}',t)\phi(\mathbf{r}')\phi_{i\sigma}(\mathbf{r},t)$$
$$+ \frac{\delta(A_{xc} - A_{x}^{lr})}{\delta\rho(\mathbf{r},t)} \tag{15}$$

$$\rho(\mathbf{r},t) = \sum_{s\sigma} f_{s\sigma} |\phi_{s\sigma}(\mathbf{r},t)|^2 = \sum_{i\sigma}^{occ} |\phi_{i\sigma}(\mathbf{r},t)|^2 \tag{16}$$

We assume that the system was in the ground-state determinant, Φ_0, at remote past, $t=-\infty$, after which $v(\mathbf{r},t)$ was turned on. The system at time t is a single Slater determinant,

$$\Phi(t) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{1\uparrow}(\mathbf{r}_1 t) & \cdots & \phi_{1\uparrow}(\mathbf{r}_N t) \\ \phi_{1\downarrow}(\mathbf{r}_1 t) & \cdots & \phi_{1\downarrow}(\mathbf{r}_N t) \\ \vdots & & \vdots \\ \phi_{N/2\uparrow}(\mathbf{r}_1 t) & \cdots & \phi_{N/2\uparrow}(\mathbf{r}_N t) \\ \phi_{N/2\downarrow}(\mathbf{r}_1 t) & \cdots & \phi_{N/2\downarrow}(\mathbf{r}_N t) \end{vmatrix} \tag{17}$$

(GKS orbital representation)

We use the complete set of the ground-state GKS orbitals to represent the operation of $v(\mathbf{r},t)$ on $\forall$ wavefunction $\Phi(\mathbf{r})$:

$$v(\mathbf{r},t)\,\Phi(\mathbf{r})$$

$$= \sum_{s\sigma} |s\sigma\rangle\langle s\sigma|\, v \sum_{t\tau} |t\tau\rangle\langle t\tau|\Phi\rangle$$

$$= \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r})\, v_{st\sigma}(t)\, C_{t\sigma} \qquad (18)$$

where

$$v_{st\sigma}(t) = \int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r})\, v(\mathbf{r},t)\, \phi_{t\sigma}(\mathbf{r}) \qquad (19)$$

$$\Phi(\mathbf{r}) = \sum_{s\sigma} C_{s\sigma}\, \phi_{s\sigma}(\mathbf{r}) \qquad (20)$$

and we have assumed that $v(\mathbf{r},t)$ does not flip spin so that its matrix elements between unlike spins are 0.

Density response

Consider perturbation of $v(\mathbf{r},t)$ on $\Phi(t)$ such that

$$\phi_{s\sigma}(\mathbf{r},t) = \phi_{s\sigma}(\mathbf{r}) + \delta\phi_{s\sigma}(\mathbf{r},t) \tag{21}$$

The density response, up to the 1st order in v, is

$$\rho(\mathbf{r},t) = \sum_{i\sigma}^{occ} [\phi_{i\sigma}^*(\mathbf{r}) + \delta\phi_{i\sigma}^*(\mathbf{r},t)][\phi_{i\sigma}(\mathbf{r}) + \delta\phi_{i\sigma}(\mathbf{r},t)]$$

$$= \underbrace{\sum_{i\sigma}^{occ} |\phi_{i\sigma}(\mathbf{r})|^2}_{\rho(\mathbf{r})} + \underbrace{\sum_{i\sigma}^{occ} [\phi_{i\sigma}^*(\mathbf{r})\,\delta\phi_{i\sigma}(\mathbf{r},t) + \delta\phi_{i\sigma}^*(\mathbf{r},t)\,\phi_{i\sigma}(\mathbf{r})]}_{\equiv\, \delta\rho(\mathbf{r},t)} \tag{22}$$

Like any other functions, the operation of $\delta\rho(\mathbf{r},t)$ on $\forall$ wavefunction $\phi(\mathbf{r})$ is represented by the complete set of the ground-state GKS orbitals

$$\delta\rho(\mathbf{r},t)\,{}^{\forall}\phi(\mathbf{r})$$

$$= \sum_{s\sigma} |s\sigma\rangle\langle s\sigma|\,\delta\rho \sum_{t\tau} |t\tau\rangle\langle t\tau|\phi\rangle$$

(∵ $\delta\rho(\mathbf{r})$ doesn't flip spins)

$$= \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r})\,\delta P_{st\sigma}(t)\, C_{t\sigma} \tag{23a}$$

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

where

$$\delta P_{st\sigma}(t) = \int d\mathbf{r}\, \phi_{s\sigma}^*(\mathbf{r})\,\delta\rho(\mathbf{r},t)\,\phi_{t\sigma}(\mathbf{r}) \tag{24}$$

- Perturbed self-consistent Hamiltonian

$$
\begin{aligned}
h(\mathbf{r},t)\,{}^{\forall}\phi(\mathbf{r}) &= \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + v(\mathbf{r},t)\right]\phi(\mathbf{r}) \\
&+ \int d\mathbf{r}'\,\frac{\rho(\mathbf{r}') + \delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\,\phi(\mathbf{r}) \\
&- \sum_{i\sigma}^{occ}\int d\mathbf{r}'\,\frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\left[\phi^*_{i\sigma}(\mathbf{r}') + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\right]\phi(\mathbf{r}')\left[\phi_{i\sigma}(\mathbf{r}) + \delta\phi_{i\sigma}(\mathbf{r},t)\right] \\
&+ \left\{\left.\frac{\delta(A_{xc}-A_x^{lr})}{\delta\rho(\mathbf{r},t)}\right|_{v=0} + \iint d\mathbf{r}'dt'\,\frac{\delta^2(A_{xc}-A_x^{lr})}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')}\,\delta\rho(\mathbf{r}',t')\right\}\phi(\mathbf{r})
\end{aligned}
$$

$$
\begin{aligned}
&= \left.\begin{aligned}
&\left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \int d\mathbf{r}'\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi(\mathbf{r}) \\
&- \sum_{i\sigma}^{occ}\int d\mathbf{r}'\,\frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\,\phi^*_{i\sigma}(\mathbf{r}')\,\phi(\mathbf{r}')\,\phi_{i\sigma}(\mathbf{r}) \\
&+ \left.\frac{\delta(A_{xc}-A_x^{lr})}{\delta\rho(\mathbf{r},t)}\right|_{v=0}\phi(\mathbf{r})
\end{aligned}\right\}\ h(\mathbf{r}) \\
&+ \left[v(\mathbf{r},t) + \int d\mathbf{r}'\,\frac{\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi(\mathbf{r}) \\
&- \sum_{i\sigma}^{occ}\int d\mathbf{r}'\,\frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\left[\phi^*_{i\sigma}(\mathbf{r}')\,\delta\phi_{i\sigma}(\mathbf{r},t) + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\,\phi_{i\sigma}(\mathbf{r})\right] \times \phi(\mathbf{r}') \\
&+ \iint d\mathbf{r}'dt'\,\frac{\delta^2(A_{xc}-A_{xc}^{lr})}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')}\,\delta\rho(\mathbf{r}',t')\,\phi(\mathbf{r})
\end{aligned}
$$

δv_{Hxc}

– Perturbed self-consistent Hamiltonian

$$
\begin{aligned}
h(\mathbf{r},t)\,{}^{\forall}\phi(\mathbf{r}) = {} & \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + v(\mathbf{r},t)\right]\phi(\mathbf{r}) \\
& + \int d\mathbf{r}' \frac{\rho(\mathbf{r}') + \delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\phi(\mathbf{r}) \\
& - \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\left[\phi^*_{i\sigma}(\mathbf{r}') + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\right]\phi(\mathbf{r}')\left[\phi_{i\sigma}(\mathbf{r}) + \delta\phi_{i\sigma}(\mathbf{r},t)\right] \\
& + \left\{ \left.\frac{\delta(A_{xc} - A_x^{lr})}{\delta\rho(\mathbf{r},t)}\right|_{v=0} + \iint d\mathbf{r}'dt' \frac{\delta^2(A_{xc} - A_x^{lr})}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')}\delta\rho(\mathbf{r}',t') \right\}\phi(\mathbf{r})
\end{aligned}
$$

$$
\begin{aligned}
= {} & \left.\begin{aligned}
& \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi(\mathbf{r}) \\
& - \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\phi^*_{i\sigma}(\mathbf{r}')\phi(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}) \\
& + \left.\frac{\delta(A_{xc} - A_x^{lr})}{\delta\rho(\mathbf{r},t)}\right|_{v=0}\phi(\mathbf{r})
\end{aligned}\right\} h(\mathbf{r}) \\
& + \left[v(\mathbf{r},t) + \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi(\mathbf{r}) \\
& - \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\left[\phi^*_{i\sigma}(\mathbf{r}')\delta\phi_{i\sigma}(\mathbf{r},t) + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\phi_{i\sigma}(\mathbf{r})\right] \times \phi(\mathbf{r}') \\
& + \iint d\mathbf{r}'dt' \frac{\delta^2(A_{xc} - A_{xc}^{lr})}{\delta\rho(\mathbf{r},t)\,\delta\rho(\mathbf{r}',t')}\delta\rho(\mathbf{r}',t')\,\phi(\mathbf{r})
\end{aligned}
$$

δv_{Hxc}

$$h(\mathbf{r},t)\,\forall\,\phi(\mathbf{r}) = \Big[h(\mathbf{r}) + \underbrace{v(\mathbf{r},t) + \delta v_{Hxc}(\mathbf{r},t)}_{v_{sc}(\mathbf{r},t)}\Big]\phi(\mathbf{r}) \qquad (25)$$

where

$$h(\mathbf{r})\phi(\mathbf{r}) = \Bigg[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \underbrace{\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{v_H(\mathbf{r})} + \underbrace{\frac{\delta(A_{xc}-A_x^{lr})}{\delta\rho(\mathbf{r},t)}}_{(v_{xc}-v_x^{lr})[\rho(\mathbf{r})](\mathbf{r})}\Bigg|_{v=0}\Bigg]\phi(\mathbf{r})$$

$$-\sum_{i\sigma}^{occ}\int d\mathbf{r}'\frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\phi^*_{i\sigma}(\mathbf{r}')\phi(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}) \qquad (26)$$

$$\delta v_{Hxc}(\mathbf{r},t)\phi(\mathbf{r}) = \Bigg[\underbrace{\int d\mathbf{r}'\frac{\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}}_{\delta v_H(\mathbf{r},t)} + \iint d\mathbf{r}'dt'\underbrace{\frac{\delta^2(A_{xc}-A_x^{lr})}{\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t')}}_{f_{xc}(\mathbf{r},\mathbf{r}';t-t')}\delta\rho(\mathbf{r}',t')\Bigg]\phi(\mathbf{r})$$

(ground-state property)

$$-\sum_{i\sigma}^{occ}\int d\mathbf{r}'\frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\left[\phi^*_{i\sigma}(\mathbf{r}')\delta\phi_{i\sigma}(\mathbf{r},t) + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\phi_{i\sigma}(\mathbf{r})\right]\phi(\mathbf{r}')$$

(27)

Time-dependent perturbation: linear response

We seek the solution of

$$i\frac{\partial}{\partial t}\phi_{s\sigma}(\mathbb{r},t) = [h(\mathbb{r}) + v_{sc}(\mathbb{r},t)]\phi_{s\sigma}(\mathbb{r},t) \tag{28}$$

in the form

$$\phi_{s\sigma}(\mathbb{r},t) = e^{-iht}\, S(t,-\infty)\, \phi_{s\sigma}(\mathbb{r}) \tag{29}$$

The formal solution (2/11/10) is

$$S(t,-\infty) = T\exp\left[-i\int_{-\infty}^{t} dt'\, v_{sc,h}(t')\right] \tag{30}$$

$$= 1 - i\int_{-\infty}^{t} dt'\, v_{sc,h}(t') + O(v^2) \tag{31}$$

where

$$v_{sc,h}(t) = e^{iht}\, v_{sc}(t)\, e^{-iht} \tag{32}$$

Substituting Eq.(31) in (29)

$$\phi_{s\sigma}(\mathbb{r},t) = \left[e^{-iht} - i\int_{-\infty}^{t} dt'\, e^{-ih(t-t')}\, v_{sc}(t')\, e^{-iht'}\right]\phi_{s\sigma}(\mathbb{r}) + O(v^2) \tag{33}$$

(Density response)

$$\rho(\mathbf{r},t) = \sum_{s\sigma} f_{s\sigma}\left[e^{iht} + i\int_{-\infty}^{t} dt'\, e^{ih(t-t')} v_{sc}(t')\, e^{iht'}\right]\phi^*_{s\sigma}(\mathbf{r})$$

$$\times\left[e^{-iht} - i\int_{-\infty}^{t} dt'\, e^{-ih(t-t')} v_{sc}(t')\, e^{-iht'}\right]\phi_{s\sigma}(\mathbf{r})$$

$$= \sum_{s\sigma} f_{s\sigma}\left[e^{i\epsilon_{s\sigma}t} + i\int_{-\infty}^{t} dt'\, e^{ih(t-t')} v_{sc}(t')\, e^{i\epsilon_{s\sigma}t'}\right]\phi^*_{s\sigma}(\mathbf{r})$$

$$\times\left[e^{-i\epsilon_{s\sigma}t} - i\int_{-\infty}^{t} dt'\, e^{-ih(t-t')} v_{sc}(t')\, e^{-i\epsilon_{s\sigma}t'}\right]\phi_{s\sigma}(\mathbf{r})$$

$$= \underbrace{\sum_{s\sigma} f_{s\sigma}|\phi_{s\sigma}(\mathbf{r})|^2}_{\rho(\mathbf{r})}$$

$$+ \sum_{s\sigma} f_{s\sigma}\left[-i\,\phi^*_{s\sigma}(\mathbf{r})\int_{-\infty}^{t} dt'\, e^{-ih(t-t')} v_{sc}(t')\, e^{i\epsilon_{s\sigma}(t-t')}\phi_{s\sigma}(\mathbf{r})\right.$$

$$\left. + i\,\phi_{s\sigma}(\mathbf{r})\int_{-\infty}^{t} dt'\, e^{ih(t-t')} v_{sc}(t')\, e^{-i\epsilon_{s\sigma}(t-t')}\phi^*_{s\sigma}(\mathbf{r})\right] \quad (34)$$

$$\therefore\ \delta\rho(\mathbf{r},t) \equiv \rho(\mathbf{r},t) - \rho(\mathbf{r})$$

$$= -i\sum_{s\sigma} f_{s\sigma}\left[\phi^*_{s\sigma}(\mathbf{r})\int_{-\infty}^{t} dt'\, e^{-i(h-\epsilon_{s\sigma})(t-t')} v_{sc}(t')\,\phi_{s\sigma}(\mathbf{r})\right.$$

$$\left. - \phi_{s\sigma}(\mathbf{r})\int_{-\infty}^{t} dt'\, e^{i(h-\epsilon_{s\sigma})(t-t')} v_{sc}(t')\,\phi^*_{s\sigma}(\mathbf{r})\right]$$

$$= \int_{-\infty}^{\infty} dt'(-i)\,\theta(t-t')\sum_{s\sigma} f_{s\sigma}\left[\phi^*_{s\sigma}(\mathbf{r})\, e^{-i(h-\epsilon_{s\sigma})(t-t')}\, v_{sc}(t')\,\phi_{s\sigma}(\mathbf{r})\right.$$

$$\left. - \phi_{s\sigma}(\mathbf{r})\, e^{i(h-\epsilon_{s\sigma})(t-t')}\, v_{sc}(t')\,\phi^*_{s\sigma}(\mathbf{r})\right] \quad (35)$$

Note that

$$v_{sc}(\mathbb{r},t')\,\phi_{s\sigma}(\mathbb{r})$$

$$= v_{sc}(t')\,|s\sigma\rangle$$

$$= \sum_t |t\sigma\rangle\langle t\sigma|v_{sc}|s\sigma\rangle$$

$$= \sum_t \phi_{t\sigma}(\mathbb{r}) \underbrace{\int d\mathbb{r}'\,\phi^*_{t\sigma}(\mathbb{r}')\,v_{sc}(\mathbb{r}',t')\,\phi_{s\sigma}(\mathbb{r}')}_{\equiv\, v^{sc}_{ts\sigma}(t')} \qquad (36)$$

Using the completeness relation, Eq. (36), in (35),

$$\delta\rho(\mathbb{r},t) = \int_{-\infty}^{\infty} dt'\,(-i)\,\Theta(t-t')\sum_{s\sigma} f_{s\sigma}$$

$$\times\Big[\phi^*_{s\sigma}(\mathbb{r})\,e^{-i(h-\epsilon_{s\sigma})(t-t')}\sum_t \phi_{t\sigma}(\mathbb{r})\,v^{sc}_{ts\sigma}(t')$$

$$\qquad\qquad h \to \epsilon_{t\sigma}$$

$$-\,\phi_{s\sigma}(\mathbb{r})\,e^{i(h-\epsilon_{s\sigma})(t-t')}\sum_t \phi^*_{t\sigma}(\mathbb{r})\,v^{sc\,*}_{ts\sigma}(t')\Big] \qquad (37)$$

$$\qquad\qquad h \to \epsilon_{t\sigma}$$

Note that

$$v^{sc*}_{ts\sigma}(t) = \int d\mathbb{r}\,\phi_{t\sigma}(\mathbb{r})\,v_{sc}(\mathbb{r},t)\,\phi^*_{s\sigma}(\mathbb{r}) = v^{sc}_{st\sigma}(t) \qquad (38)$$

Using Eq. (38) in (37),

$$\delta\rho(\mathbb{r},t) = \int_{-\infty}^{\infty} dt'(-i)\,\Theta(t-t')\sum_{st\sigma} f_{s\sigma}$$

$$\times\Big[\phi^*_{s\sigma}(\mathbb{r})\,e^{-i\omega_{st\sigma}(t-t')}\,v^{sc}_{ts\sigma}(t')\,\phi_{t\sigma}(\mathbb{r})$$

$$\underbrace{-\,\phi_{s\sigma}(\mathbb{r})\,e^{i\omega_{st\sigma}(t-t')}\,v^{sc}_{st\sigma}(t')\,\phi^*_{t\sigma}(\mathbb{r})}_{s\leftrightarrow t}\Big]$$

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

$$\times\Big[f_{s\sigma}\,\phi^*_{s\sigma}(\mathbb{r})\,e^{-i\omega_{st\sigma}(t-t')}\,\phi_{t\sigma}(\mathbb{r})\,v^{sc}_{ts\sigma}(t')$$

$$-\,f_{t\sigma}\,\phi^*_{s\sigma}(\mathbb{r})\,e^{-i\omega_{st\sigma}(t-t')}\,\phi_{t\sigma}(\mathbb{r})\,v^{sc}_{ts\sigma}(t')\Big]$$

$$= \int_{-\infty}^{\infty} dt'(-i)\,\Theta(t-t')\sum_{st\sigma}(f_{s\sigma}-f_{t\sigma})\,\phi^*_{s\sigma}(\mathbb{r})\,e^{-i\omega_{st\sigma}(t-t')}\,\phi_{t\sigma}(\mathbb{r})\,v^{sc}_{ts\sigma}(t'), \tag{39}$$

where the electron-hole excitation energy is

$$\omega_{st\sigma} \equiv \epsilon_{t\sigma} - \epsilon_{s\sigma} \tag{40}$$

Comparison of Eq. (39) with the definition of density-matrix response, Eq. (23), identifies

$$\delta P_{ts\sigma}(t) = \int_{-\infty}^{\infty} dt' (-i)\Theta(t-t')(f_{s\sigma}-f_{t\sigma})\, e^{-i\omega_{st\sigma}(t-t')}\, v^{sc}_{ts\sigma}(t') \tag{41}$$

— Fourier transform

Let's define

$$\delta P_{st\sigma}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \delta P_{st\sigma}(\omega)\, e^{-i\omega t} \tag{42}$$

$$v^{sc}_{st\sigma}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, v^{sc}_{st\sigma}(\omega)\, e^{-i\omega t} \tag{43}$$

Recall (2/25/10),

$$\Theta(t) = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega t}}{\omega + i0} \tag{44}$$

Substituting Eq. (44) in (41),

$$\delta P_{ts\sigma}(t) = \int_{-\infty}^{\infty} dt' \cancel{(-i)} \int_{-\infty}^{\infty} \frac{d\omega}{\cancel{-}2\pi \cancel{i}} \frac{e^{-i\omega(t-t')}}{\omega + i0} (f_{s\sigma}-f_{t\sigma})\, e^{-i\omega_{st\sigma}(t-t')}\, v^{sc}_{ts\sigma}(t')$$

$$= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{f_{s\sigma}-f_{t\sigma}}{\omega + i0}\, e^{-i(\omega+\omega_{st\sigma})t} \underbrace{\int_{-\infty}^{\infty} dt'\, e^{i(\omega+\omega_{st\sigma})t'}\, v^{sc}_{ts\sigma}(t')}_{v^{sc}_{ts\sigma}(\omega+\omega_{st\sigma})}$$

$$\omega + \omega_{st\sigma} \equiv \omega'$$

$$= \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{f_{s\sigma}-f_{t\sigma}}{\omega' - \omega_{st\sigma} + i0}\, v^{sc}_{ts\sigma}(\omega')\, e^{-i\omega' t} \tag{45}$$

$$\therefore\ \delta P_{ts\sigma}(\omega) = \frac{f_{s\sigma}-f_{t\sigma}}{\omega - \omega_{st\sigma} + i0}\, v^{sc}_{ts\sigma}(\omega) \tag{46}$$

Or $s \leftrightarrow t$

$$\delta P_{st\sigma}(\omega) = \frac{f_{t\sigma} - f_{s\sigma}}{\omega - \omega_{ts\sigma} + i0} \, v^{sc}_{st\sigma}(\omega) \tag{46'}$$

Now let's define the GKS response function as

$$\chi^{GK}_{st\sigma,uv\tau}(t-t') \equiv \frac{\delta P_{st\sigma}(t)}{\delta v^{sc}_{uv\tau}(t')} \tag{47}$$

and its Fourier transform

$$\chi^{GK}_{st\sigma,uv\tau}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \chi^{GK}_{st\sigma,uv\tau}(\omega) e^{-i\omega t} \tag{48}$$

From Eq. (46'),

$$\chi^{GK}_{st\sigma,uv\tau}(\omega) = \delta_{su}\delta_{tv}\delta_{\sigma\tau} \frac{f_{t\sigma} - f_{s\sigma}}{\omega - \omega_{ts\sigma} + i0} \tag{49}$$

Coupling matrix

From Eqs. (25) & (27),

$v_{sc}(\mathbf{r},t)\ ^{\forall}\phi(\mathbf{r})$

$$= \left[v(\mathbf{r},t) + \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + \iint d\mathbf{r}'dt'\, f_{xc}(\mathbf{r},\mathbf{r}';t-t')\,\delta\rho(\mathbf{r}',t') \right]\phi(\mathbf{r})$$

$$- \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \left[\phi^*_{i\sigma}(\mathbf{r}')\,\delta\phi_{i\sigma}(\mathbf{r},t) + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\,\phi_{i\sigma}(\mathbf{r})\right]\phi(\mathbf{r}')$$

$$= \left[\overset{ⓐ}{v(\mathbf{r},t)} + \overset{ⓑ}{\int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}} + \overset{ⓒ}{\iint d\mathbf{r}'dt'\, \underset{\hookrightarrow f_{xc}-f_x^{lr}}{\tilde{f}_{xc}}(\mathbf{r},\mathbf{r}';t-t')\,\delta\rho(\mathbf{r}',t')} \right]\phi(\mathbf{r})$$

$$- \overset{ⓓ}{\int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}} \underbrace{\left\{ \sum_{i\sigma}^{occ}\left[\phi^*_{i\sigma}(\mathbf{r}')\,\delta\phi_{i\sigma}(\mathbf{r},t) + \delta\phi^*_{i\sigma}(\mathbf{r}',t)\,\phi_{i\sigma}(\mathbf{r})\right]\right\}}_{\equiv\, \delta\rho(\mathbf{r}',\mathbf{r};t)} \phi(\mathbf{r}') \tag{50}$$

We now expand Eq. (50) with the complete GKS orbital set as

$$\sum_{s\sigma} |s\sigma\rangle\langle s\sigma| v_{sc}(t) \sum_{t\cancel{\sigma}} |t\cancel{\sigma}_{\sigma}\rangle\langle t\cancel{\sigma}_{\sigma}|\phi\rangle \tag{51}$$

$$= \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r})\ \langle s\sigma| v_{sc}(t) |t\sigma\rangle\ C_{t\sigma} \tag{52}$$

term-by-term (ⓐ-ⓓ)

$$ⓐ = \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r}) \underbrace{\int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r})\, v(\mathbf{r},t)\, \phi_{t\sigma}(\mathbf{r})}_{v_{st\sigma}(t)} \int d\mathbf{r}'\, \phi^*_{t\sigma}(\mathbf{r}')\, \phi(\mathbf{r}')$$

$$= \int d\mathbf{r}' \underbrace{\sum_{st\sigma} \phi_{s\sigma}(\mathbf{r})\, v_{st\sigma}(t)\, \phi^*_{t\sigma}(\mathbf{r}')} \cdot \phi(\mathbf{r}') \tag{53}$$

Namely, if we expand

$$v_{sc}(\mathbf{r},t)\,{}^{\forall}\phi(\mathbf{r}) = \int d\mathbf{r}' \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r})\, v^{sc}_{st\sigma}(t)\, \phi^*_{t\sigma}(\mathbf{r}') \cdot \phi(\mathbf{r}') \tag{54}$$

Then the first term of $v^{sc}_{st\sigma}(t)$ is

$$v^{sc}_{st\sigma}(t)_{ⓐ} = v_{st\sigma}(t) \tag{55}$$

$$ⓑ = \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r}) \int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r}) \int d\mathbf{r}' \frac{\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} \phi_{t\sigma}(\mathbf{r}) \int d\mathbf{r}''\, \phi^*_{t\sigma}(\mathbf{r}'')\, \phi(\mathbf{r}'') \tag{56}$$

$$\therefore\ v^{sc}_{st\sigma}(t)_{ⓑ} = \iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{r}) \frac{\delta\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} \phi_{t\sigma}(\mathbf{r})$$

Using the expansion, Eq. (23b),

$$v^{sc}_{st\sigma}(t)_{ⓑ} = \sum_{uv\tau} \iint d\mathbf{r}\, d\mathbf{r}' \frac{\phi^*_{s\sigma}(\mathbf{r})\, \phi_{u\tau}(\mathbf{r}')\, \delta P_{uv\tau}(t)\, \phi^*_{v\tau}(\mathbf{r}')\, \phi_{t\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \sum_{uv\tau} \iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{r})\, \phi_{t\sigma}(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{v\tau}(\mathbf{r}')\, \phi_{u\tau}(\mathbf{r}')\, \delta P_{uv\tau}(t)$$

$$= \sum_{uv\tau} \left[\phi^*_{s\sigma} \phi_{t\sigma} \middle| \frac{1}{r} \middle| \phi^*_{v\tau} \phi_{u\tau} \right] \delta P_{uv\tau}(t)$$

$$\therefore\ v^{sc}_{st\sigma}(t)_{ⓑ} = \sum_{uv\tau} [\phi^*_{s\sigma}\phi_{t\sigma}|\tfrac{1}{r}|\phi^*_{v\tau}\phi_{u\tau}]\ \delta P_{uv\tau}(t) \tag{57}$$

where the Coulomb-like integral is defined as

$$[f|h(r)|g] \equiv \iint d\mathbf{r}\,d\mathbf{r}'\ f(\mathbf{r})\ h(|\mathbf{r}-\mathbf{r}'|)\ g(\mathbf{r}') \tag{58}$$

$$ⓒ = \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r}) \int d\mathbf{r}\,\phi^*_{s\sigma}(\mathbf{r}) \iint d\mathbf{r}'dt'\ f_{xc}(\mathbf{r},\mathbf{r}';t-t')\ \delta\rho(\mathbf{r}',t')$$

$$\times \sum_{t\sigma} \phi_{t\sigma}(\mathbf{r}) \int d\mathbf{r}''\phi^*_{t\sigma}(\mathbf{r}'')\ \phi(\mathbf{r}'')$$

$$\therefore\ v^{sc}_{st\sigma}(t)_{ⓒ} = \int d\mathbf{r}\,\phi^*_{s\sigma}(\mathbf{r}) \iint d\mathbf{r}'dt'\ \tilde{f}_{xc}(\mathbf{r},\mathbf{r}';t-t')\ \delta\rho(\mathbf{r}',t')\ \phi_{t\sigma}(\mathbf{r}) \tag{59}$$

Using the expansion, Eq. (23b),

$$v^{sc}_{st\sigma}(t)_{ⓒ} = \int d\mathbf{r}\,\phi^*_{s\sigma}(\mathbf{r}) \iint d\mathbf{r}'dt'\ \tilde{f}_{xc}(\mathbf{r},\mathbf{r}';t-t') \sum_{uv\tau} \phi_{u\tau}(\mathbf{r}')\ \delta P_{uv\tau}(t')\ \phi^*_{v\tau}(\mathbf{r}')$$

$$\times\ \phi_{t\sigma}(\mathbf{r}) \tag{60}$$

convolution

Or, in the Fourier space,

$$v^{sc}_{st\sigma}(\omega)_{ⓒ} = \sum_{uv\tau} \iint d\mathbf{r}\,d\mathbf{r}'\ \phi^*_{s\sigma}(\mathbf{r})\,\phi_{t\sigma}(\mathbf{r})\ \tilde{f}_{xc}(\mathbf{r},\mathbf{r}';\omega)\ \phi^*_{v\tau}(\mathbf{r}')\,\phi_{u\tau}(\mathbf{r}')\ \delta P_{uv\tau}(\omega) \tag{61}$$

$$\therefore\ v^{sc}_{st\sigma}(\omega)_{ⓒ} = \sum_{uv\tau} [\phi^*_{s\sigma}\phi_{t\sigma}|\tilde{f}_{xc}(\omega)|\phi^*_{v\tau}\phi_{u\tau}]\ \delta P_{uv\tau}(\omega) \tag{62}$$

where

$$[\phi^*_{s\sigma}\phi_{t\sigma}|f_{xc}(\omega)|\phi^*_{v\tau}\phi_{u\tau}] = \iint d\mathbf{r}\,d\mathbf{r}'\ \phi^*_{s\sigma}(\mathbf{r})\,\phi_{t\sigma}(\mathbf{r})\ \tilde{f}_{xc}(\mathbf{r},\mathbf{r}';\omega)\ \phi^*_{v\tau}(\mathbf{r}')\,\phi_{u\tau}(\mathbf{r}') \tag{63}$$

$$
\text{ⓓ} = -\int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \delta\rho(\mathbf{r}',\mathbf{r};t)\,\phi(\mathbf{r}')
$$

$$
= -\sum_{s\sigma} \phi_{s\sigma}(\mathbf{r}) \iint d\mathbf{x}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{x}) \frac{\mathrm{erf}(\mu|\mathbf{x}-\mathbf{r}'|)}{|\mathbf{x}-\mathbf{r}'|} \delta\rho(\mathbf{r}',\mathbf{x};t)
$$

$$
\times \sum_{t\sigma} \phi_{t\sigma}(\mathbf{r}') \int d\mathbf{r}''\, \phi^*_{t\sigma}(\mathbf{r}'')\,\phi(\mathbf{r}'')
$$

$$
= -\int d\mathbf{r}'' \underbrace{\left\{ \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r}) \Bigg[\underbrace{\iint d\mathbf{x}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{x}) \frac{\mathrm{erf}(\mu|\mathbf{x}-\mathbf{r}'|)}{|\mathbf{x}-\mathbf{r}'|} \delta\rho(\mathbf{r}',\mathbf{x};t)\,\phi_{t\sigma}(\mathbf{r}')}_{v^{sc}_{st\sigma}(t)_{ⓓ}} \Bigg] \phi^*_{t\sigma}(\mathbf{r}'') \right\}}_{\text{nonlocal } v^{sc}(\mathbf{r},\mathbf{r}'';t)_{ⓓ} \text{ operator}} \phi(\mathbf{r}'') \qquad (64)
$$

$$
\therefore v^{sc}_{st\sigma}(t)_{ⓓ} = -\iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{r}) \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \delta\rho(\mathbf{r}',\mathbf{r};t)\,\phi_{t\sigma}(\mathbf{r}') \qquad (65)
$$

Now, recall the definition of $\delta\rho(\mathbf{r}',\mathbf{r};t)$ in Eq. (50):

$$
\delta\rho(\mathbf{r}',\mathbf{r};t) = \sum_{i\sigma}^{occ} \Big[\phi^*_{i\sigma}(\mathbf{r}') \underset{\uparrow \atop \sum_s |s\sigma\rangle\langle s\sigma|}{\delta\phi_{i\sigma}(\mathbf{r},t)} + \underset{\uparrow \atop \sum_s |s\sigma\rangle\langle s\sigma|}{\delta\phi^*_{i\sigma}(\mathbf{r}',t)}\, \phi_{i\sigma}(\mathbf{r}) \Big] \qquad (66)
$$

$$
= \sum_{i\sigma}^{occ} \sum_s \Big[\phi^*_{i\sigma}(\mathbf{r}')\,\phi_{s\sigma}(\mathbf{r}) \underbrace{\int d\mathbf{r}''\, \phi^*_{s\sigma}(\mathbf{r}'')\,\delta\phi_{i\sigma}(\mathbf{r}'',t)}_{\equiv\, \delta\phi_{si\sigma}(t)}
$$

$$
+ \phi^*_{s\sigma}(\mathbf{r}') \underbrace{\int d\mathbf{r}''\, \phi_{s\sigma}(\mathbf{r}'')\,\delta\phi^*_{i\sigma}(\mathbf{r}'',t)}_{\delta\phi^*_{si\sigma}(t)}\, \phi_{i\sigma}(\mathbf{r}) \Big] \qquad (67)
$$

$$
= \sum_{i}^{occ}\sum_s\sum_\sigma \Big[\phi^*_{i\sigma}(\mathbf{r}')\,\delta\phi_{si\sigma}(t)\,\phi_{s\sigma}(\mathbf{r}) + \phi^*_{s\sigma}(\mathbf{r}')\,\delta\phi^*_{si\sigma}\,\phi_{i\sigma}(\mathbf{r}) \Big] \qquad (68)
$$

The GKS expansion of density matrix in Eq. (68) can be written as

$$
\delta\rho(\mathbf{r}',\mathbf{r};t) = \sum_{uv\tau} \phi_{u\tau}(\mathbf{r})\,\delta P_{uv\tau}(t)\,\phi^*_{v\tau}(\mathbf{r}') \qquad (69)
$$

Substituting Eq. (69) in (65),

$$v^{sc}_{st\sigma}(t)_{ⓓ} = -\sum_{uv\tau}\iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{r})\, \phi_{u\tau}(\mathbf{r}) \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{v\tau}(\mathbf{r}')\, \phi_{t\sigma}(\mathbf{r}')$$

$$\times\, \delta P_{uv\tau}(t) \qquad (70)$$

Recall that the $\mathbf{r}$ & $\mathbf{r}'$ integrations implicitly include spin-coordinate inner products $\langle\sigma|\tau\rangle$ & $\langle\tau|\sigma\rangle$, which are nonzero only when $\sigma = \tau$.

$$\therefore\ v^{sc}_{st\sigma}(t)_{ⓓ} = -\sum_{uv\tau} \delta_{\sigma\tau} \left[\phi^*_{s\sigma}\phi_{u\tau} \middle| \frac{\mathrm{erf}(\mu r)}{r} \middle| \phi^*_{v\tau}\phi_{t\sigma}\right] \delta P_{uv}(t) \qquad (71)$$

exchange

In summary,

$$v^{sc}_{st\sigma}(\omega) = v_{st\sigma}(\omega) + \sum_{uv\tau}\left[\phi^*_{s\sigma}\phi_{t\sigma} \middle| \frac{1}{r} + \overset{f_{xc}-f_x^{lr}}{\tilde{f}_{xc}(\omega)} \middle| \phi^*_{v\tau}\phi_{u\tau}\right] \delta P_{uv\tau}(\omega)$$

$$- \sum_{uv\tau} \delta_{\sigma\tau} \left[\phi^*_{s\sigma}\phi_{u\tau} \middle| \frac{\mathrm{erf}(\mu r)}{r} \middle| \phi^*_{v\tau}\phi_{t\sigma}\right] \delta P_{uv\tau}(\omega)$$

$$(72)$$

Here, we define the coupling matrix as

$$K_{st\sigma,\,uv\tau}(\omega) \equiv \frac{\delta v^{Hxc}_{st\sigma}(\omega)}{\delta P_{uv\tau}(\omega)} \tag{73}$$

$$= \left[\phi^*_{s\sigma}\phi_{t\sigma} \left| \frac{1}{r} + f_{xc}(\omega) - f^{l}_{xc} \right| \phi^*_{v\tau}\phi_{u\tau}\right]$$

from 2nd quantization

$$-\delta_{\sigma\tau}\left[\phi^*_{s\sigma}\phi_{u\tau} \left| \frac{\text{erf}(\mu r)}{r} \right| \phi^*_{v\tau}\phi_{t\sigma}\right] \tag{74}$$

exchange

Then Eq. (72) becomes

$$v^{sc}_{st\sigma}(\omega) = v_{st\sigma}(\omega) + \sum_{uv\tau} K_{st\sigma,\,uv\tau}(\omega)\,\delta P_{uv\tau}(\omega) \tag{75}$$

Substituting Eq. (75) in (46),

$$\delta P_{st\sigma}(\omega) = \frac{f_{t\sigma} - f_{s\sigma}}{\omega - \omega_{ts\sigma} + i0}\left[v_{st\sigma}(\omega) + \sum_{uv\tau} K_{st\sigma,\,uv\tau}(\omega)\,\delta P_{uv\tau}(\omega)\right] \tag{76}$$

Note that the density-matrix response is nonzero only when $f_{t\sigma} - f_{s\sigma} \neq 0$, for which case we can rewrite Eq. (76) as

$$\frac{\omega - \omega_{ts\sigma}}{f_{t\sigma} - f_{s\sigma}}\,\delta P_{st\sigma}(\omega) - \sum_{uv\tau} K_{st\sigma,\,uv\tau}(\omega)\,\delta P_{uv\tau}(\omega) = v_{st\sigma}(\omega)$$

or

$$\sum_{uv\tau}^{f_{v\tau} - f_{u\tau} \neq 0}\left[\delta_{su}\delta_{tv}\delta_{\sigma\tau}\frac{\omega - \omega_{vu\tau}}{f_{v\tau} - f_{u\tau}} - K_{st\sigma,\,uv\tau}(\omega)\right]\delta P_{uv\tau}(\omega) = v_{st\sigma}(\omega) \tag{77}$$

Linear-Response Time-Dependent Density Functional Theory: Hybrid Functionals (II)

6/5/12

— Density-matrix response equation

Consider an external single-electron potential $v(\mathbf{r},t)$ that operates on $^{\forall}$wavefunction $\phi(\mathbf{r})$ as

$$v(\mathbf{r},t)\,{}^{\forall}\phi(\mathbf{r}) = \int d\mathbf{r}' \left[\sum_{st\sigma} \phi_{s\sigma}(\mathbf{r})\, v_{st\sigma}(t)\, \phi^*_{t\sigma}(\mathbf{r}')\right] \phi(\mathbf{r}') \qquad (1)$$

where $\{\phi_{s\sigma}(\mathbf{r})\}$ is the complete set of generalized Kohn-Sham (GKS) orbitals, and

$$v_{st\sigma}(t) = \int d\mathbf{r}\, \phi^*_{s\sigma}(\mathbf{r})\, v(\mathbf{r},t)\, \phi_{t\sigma}(\mathbf{r}) \qquad (2)$$

We assume that the system was in the ground-state single Slater determinant at remote past and has followed time-dependent GKS equations.

We consider the linear response of the density matrix,

$$\delta\rho(\mathbf{r},\mathbf{r}';t) = \delta \sum_{i\sigma}^{occ} \phi^*_{i\sigma}(\mathbf{r},t)\, \phi_{i\sigma}(\mathbf{r}',t), \qquad (3)$$

to $v(\mathbf{r},t)$, with its GKS expansion

$$\delta\rho(\mathbf{r},\mathbf{r}';t) = \sum_{st\sigma} \phi_{s\sigma}(\mathbf{r}')\, \delta P_{st\sigma}(t)\, \phi^*_{t\sigma}(\mathbf{r}) \qquad (4)$$

Note that

$\iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{u\tau}(\mathbf{r}') \times$ Eq. (4) $\times\, \phi_{v\tau}(\mathbf{r})$

$$\iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{u\tau}(\mathbf{r}')\, \delta\rho(\mathbf{r},\mathbf{r}';t)\, \phi_{v\tau}(\mathbf{r}) = \sum_{st\sigma} \delta P_{st\sigma}(t) \underbrace{\int d\mathbf{r}\, \phi^*_{t\sigma}(\mathbf{r})\, \phi_{v\tau}(\mathbf{r})}_{\delta_{tv}\delta_{\sigma\tau}} \underbrace{\int d\mathbf{r}'\, \phi^*_{u\tau}(\mathbf{r}')\, \phi_{s\sigma}(\mathbf{r}')}_{\delta_{su}\delta_{\sigma\tau}}$$

$= \delta P \quad (t)$

$$\therefore \; \delta P_{s\sigma\tau}(t) = \iint d\mathbf{r}\, d\mathbf{r}'\, \phi^*_{s\sigma}(\mathbf{r}')\, \delta\rho(\mathbf{r}, \mathbf{r}'; t)\, \phi_{t\sigma}(\mathbf{r}) \tag{5}$$

In the frequency space, the density-matrix elements satisfy the following equation:

$$\sum_{uv\tau}^{f_{v\tau}-f_{u\tau}>0} \left[\delta_{su}\delta_{tv}\delta_{\sigma\tau} \frac{\omega - \omega_{vu\tau}}{f_{v\tau}-f_{u\tau}} - K_{st\sigma, uv\tau}(\omega) \right] \delta P_{uv\tau}(\omega) = v_{st\sigma}(\omega) \tag{6}$$

where $f_{s\sigma} \in [0, 1]$ is the occupation number,

$$\omega_{\underrightarrow{st}\sigma} = \epsilon_{t\sigma} - \epsilon_{s\sigma} \tag{7}$$

is the noninteracting excitation energy, and the coupling matrix elements are defined as

$$K_{st\sigma, uv\tau}(\omega) = \left[\phi^*_{s\sigma}\phi_{t\sigma} \middle| \frac{1}{r} + (f_{xc} - f_{x}^{lr})(\omega) \middle| \phi^*_{v\tau}\phi_{u\tau}\right]$$

2nd quantization

$$- \delta_{\sigma\tau}\left[\phi^*_{s\sigma}\phi_{u\tau} \middle| \frac{\mathrm{erf}(\mu r)}{r} \middle| \phi^*_{v\tau}\phi_{t\sigma}\right] \tag{8}$$

exchange

Here, the Coulomb-like integral is defined as

$$[f | h(r) | g] = \iint d\mathbf{r}\, d\mathbf{r}'\, f(\mathbf{r})\, h(\mathbf{r} - \mathbf{r}')\, g(\mathbf{r}') \tag{9}$$

Particle-hole separation

We label the GKS orbitals in ascending order of GKS energy $\epsilon_{s\sigma}$, and consider an N-electron closed-shell ground-state Slater determinant as the unperturbed state, where both spin up & down states are occupied for $1 \le s \le N/2$. We use indices, $i, j, \ldots \in [1, N/2]$ for occupied orbitals, and $a, b, \ldots > N/2$ for virtual orbitals.

Note that the density-matrix response $\delta P_{st\sigma}$ is nonzero only when $f_{t\sigma} - f_{s\sigma} \neq 0$.

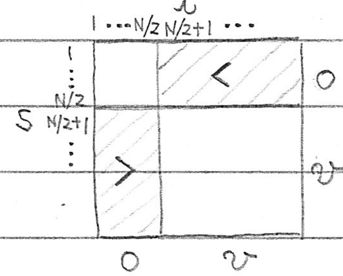

Fig.(1)

Also, note that $\delta P_{st\sigma}$ is Hermitian:

$$\delta P^*_{st\sigma}(t) = \left\{ \iint d\mathbf{r}\, d\mathbf{r}' \, \phi^*_{s\sigma}(\mathbf{r}') \, \delta\left[\sum_{i\sigma}^{occ} \phi^*_{i\sigma}(\mathbf{r}, t) \, \phi_{i\sigma}(\mathbf{r}', t) \right] \phi_{t\sigma}(\mathbf{r}) \right\}^*$$

$$= \iint d\mathbf{r}\, d\mathbf{r}' \, \phi^*_{t\sigma}(\mathbf{r}) \, \delta\left[\sum_{i\sigma}^{occ} \phi^*_{i\sigma}(\mathbf{r}', t) \, \phi_{i\sigma}(\mathbf{r}, t) \right] \phi_{s\sigma}(\mathbf{r}')$$

$$\overset{\mathbf{r} \leftrightarrow \mathbf{r}'}{=} \iint d\mathbf{r}\, d\mathbf{r}' \, \phi^*_{t\sigma}(\mathbf{r}') \, \delta\left[\sum_{i\sigma}^{occ} \phi^*_{i\sigma}(\mathbf{r}, t) \, \phi_{i\sigma}(\mathbf{r}', t) \right] \phi_{s\sigma}(\mathbf{r})$$

$$= \delta P_{ts\sigma}(t) \qquad (10)$$

Fourier transform of $\delta P^*_{ai\sigma}(t)$

not $[\delta P_{ai\sigma}(\omega)]^*$

Therefore,

$$\delta P_{\underset{<}{ia\sigma}}(\omega) = \delta P^*_{\underset{>}{ai\sigma}}(\omega) \tag{11}$$

We now label the row of Eq. (6) as $st = ai$ and the column $uv = bj$ (i.e. only consider the > block in Fig.(1))

$$\sum_{bj\tau}\left[\delta_{ab}\delta_{ij}\delta_{\sigma\tau}\underbrace{\frac{\omega-\omega_{jb\tau}}{f_{j\tau}-f_{b\tau}}}_{\substack{=1-0\\=1}} - K_{ai\sigma,bj\tau}(\omega)\right]\overset{\to\,>\text{ block}}{\delta P_{bj\tau}(\omega)}$$

$$-\sum_{bj\tau} K_{\underset{>}{ai\sigma},\underset{<}{jb\tau}}(\omega)\,\underbrace{\overset{\to\,<\text{ block}}{\delta P_{jb\tau}(\omega)}}_{\delta P^*_{bj\tau}(\omega)} = v_{ai\sigma}(\omega) \tag{11}$$

The equation for the < block is

$$\sum_{jb\tau}\left[\delta_{ij}\delta_{ab}\delta_{\sigma\tau}\underbrace{\frac{\omega-\omega_{bj\tau}}{f_{b\tau}-f_{j\tau}}}_{\substack{=0-1\\=-1}} - K_{ia\sigma,jb\tau}(\omega)\right]\underbrace{\overset{\to\,<\text{ block}}{\delta P_{jb\tau}(\omega)}}_{\delta P^*_{bj\tau}(\omega)}$$

$$-\sum_{jb\tau} K_{\underset{<}{ia\sigma},\underset{>}{bj\tau}}(\omega)\,\overset{\to\,>\text{ block}}{\delta P_{bj\tau}(\omega)} = \underbrace{v_{ia\sigma}(\omega)}_{v^*_{ai\sigma}(\omega)} \tag{12}$$

$$-\omega+\omega_{bj\tau} = -\omega-\omega_{jb\tau}$$

Note, for adiabatic (ω-independent) xc functional,

$$
\begin{aligned}
K_{ia\sigma,jb\tau}(\cancel{\omega}) &= [\phi^*_{i\sigma}\phi_{a\sigma} | \frac{1}{r} + (f_{xc} - f_x^{lr})(\cancel{\omega}) | \phi^*_{b\tau}\phi_{j\tau}] \\
&\quad - \delta_{\sigma\tau}[\phi^*_{i\sigma}\phi_{j\tau} | \frac{\mathrm{erf}(\mu r)}{r} | \phi^*_{b\tau}\phi_{a\sigma}] \\
&= \Big\{ \underbrace{[\phi^*_{a\sigma}\phi_{i\sigma} | \frac{1}{r} + f_{xc} - f_x^{l} | \phi^*_{j\tau}\phi_{b\tau}] - \delta_{\sigma\tau}[\phi^*_{j\tau}\phi_{i\sigma} | \frac{\mathrm{erf}(\mu r)}{r} | \phi^*_{a\sigma}\phi_{b\tau}]}_{K_{ai\sigma,bj\tau}(\cancel{\omega})} \Big\}^* \\
&= K^*_{ai\sigma,bj\tau}(\cancel{\omega}) \qquad (13)
\end{aligned}
$$

Using this symmetry in Eq.(12), we can simplify Eqs.(11)-(12) as

$$
\left\{
\begin{aligned}
&\sum_{bj\tau}\left[\delta_{ab}\delta_{ij}\delta_{\sigma\tau}(-\omega + \omega_{jb\tau}) + K_{ai\sigma,bj\tau}(\omega)\right]\delta P_{bj\tau}(\omega) \\
&\qquad + \sum_{bj\tau} K_{ai\sigma,jb\tau}(\omega)\,\delta P^*_{bj\tau}(\omega) = -v_{ai\sigma}(\omega) \qquad (14) \\
&\sum_{bj\tau}\left[\delta_{ab}\delta_{ij}\delta_{\sigma\tau}(\omega + \omega_{jb\tau}) + K^*_{ai\sigma,bj\tau}(\omega)\right]\delta P^*_{bj\tau}(\omega) + \sum_{bj\tau} K^*_{ai\sigma,jb\tau}(\omega) \\
&\qquad + \sum_{bj\tau} K^*_{ai\sigma,jb\tau}(\omega)\,\delta P_{bj\tau}(\omega) = -v^*_{ai\sigma}(\omega) \qquad (15)
\end{aligned}
\right.
$$

Let's define $NN_v \times NN_v$ matrices (N & N_v are the number of occupied & virtual orbitals):

$$\begin{cases} A_{ai\sigma,bj\tau}(\omega) = \delta_{ab}\delta_{ij}\delta_{\sigma\tau}\,\omega_{jb\tau} + K_{ai\sigma,bj\tau}(\omega) & (16) \\ B_{ai\sigma,bj\tau}(\omega) = K_{ai\sigma,jb\tau}(\omega) & (17) \end{cases}$$

We also define NN_v-element vectors, $\delta\mathbb{P}$ & $\mathcal{V}$. Then, Eqs. (14) & (15) become:

$$\begin{cases} \mathbb{A}(\omega)\,\delta\mathbb{P}(\omega) + \mathbb{B}(\omega)\,\delta\mathbb{P}^*(\omega) - \omega\,\delta\mathbb{P}(\omega) = -\mathcal{V}(\omega) & (18) \\ \mathbb{B}^*(\omega)\,\delta\mathbb{P}(\omega) + \mathbb{A}^*(\omega)\,\delta\mathbb{P}^*(\omega) + \omega^*\,\delta\mathbb{P}(\omega) = -\mathcal{V}^*(\omega) & (19) \end{cases}$$

Eqs. (18) & (19) can be combined as

$$\left\{ \begin{bmatrix} \mathbb{A}(\omega) & \mathbb{B}(\omega) \\ \mathbb{B}^*(\omega) & \mathbb{A}^*(\omega) \end{bmatrix} - \omega \begin{bmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{bmatrix} \right\} \begin{bmatrix} \delta\mathbb{P}(\omega) \\ \delta\mathbb{P}^*(\omega) \end{bmatrix} = - \begin{bmatrix} \mathcal{V}(\omega) \\ \mathcal{V}^*(\omega) \end{bmatrix} \quad (20)$$

$\delta\mathbb{P}(\omega)$ & $\delta\mathbb{P}^*(\omega)$ are commonly denoted as $\mathbb{X}$ & $\mathbb{Y}$:

$$\left\{ \begin{bmatrix} \mathbb{A}(\omega) & \mathbb{B}(\omega) \\ \mathbb{B}^*(\omega) & \mathbb{A}^*(\omega) \end{bmatrix} - \omega \begin{bmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{bmatrix} \right\} \begin{bmatrix} \mathbb{X}(\omega) \\ \mathbb{Y}(\omega) \end{bmatrix} = - \begin{bmatrix} \mathcal{V}(\omega) \\ \mathcal{V}^*(\omega) \end{bmatrix} \quad (21)$$

- Excitation energies

The excitation energies ω are signified by nonzero density fluctuations, $\mathbb{X}$ & $\mathbb{Y}$, for zero external potential:

$$\begin{bmatrix} \mathbb{A}(\omega) & \mathbb{B}(\omega) \\ \mathbb{B}^*(\omega) & \mathbb{A}^*(\omega) \end{bmatrix} \begin{bmatrix} \mathbb{X} \\ \mathbb{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{bmatrix} \begin{bmatrix} \mathbb{X} \\ \mathbb{Y} \end{bmatrix} \tag{22}$$

Now let's consider real orbitals, for which

$$\begin{cases} \mathbb{A}\mathbb{X} + \mathbb{B}\mathbb{Y} = \omega \mathbb{X} & (23) \\ \mathbb{B}\mathbb{X} + \mathbb{A}\mathbb{Y} = -\omega \mathbb{Y} & (24) \end{cases}$$

(23) + (24)

$$(\mathbb{A}+\mathbb{B})(\mathbb{X}+\mathbb{Y}) = \omega(\mathbb{X}-\mathbb{Y}) \tag{25}$$

(23) − (24)

$$(\mathbb{A}-\mathbb{B})(\mathbb{X}-\mathbb{Y}) = \omega(\mathbb{X}+\mathbb{Y}) \tag{26}$$

$(\mathbb{A}-\mathbb{B}) \times$ (25)

$$(\mathbb{A}-\mathbb{B})(\mathbb{A}+\mathbb{B})(\mathbb{X}+\mathbb{Y}) = \omega(\mathbb{A}-\mathbb{B})(\mathbb{X}-\mathbb{Y}) \tag{27}$$

Using Eq. (26) in (27),

$$(\mathbb{A}-\mathbb{B})(\mathbb{A}+\mathbb{B})(\mathbb{X}+\mathbb{Y}) = \omega^2(\mathbb{X}+\mathbb{Y}) \tag{28}$$

Here,

$$(\mathbb{A}-\mathbb{B})_{ai\sigma,bj\tau} = \delta_{ab}\delta_{ij}\delta_{\sigma\tau}\,\omega_{jb\tau} + K_{aj\sigma,bj\tau}(\omega) - K_{aj\sigma,jb\tau}(\omega) \quad (29)$$

For the Hartree & xc terms with real orbitals, exchanging $\phi_{b\tau}(\mathbf{r}')\phi_{j\tau}(\mathbf{r}')$ in the definition of the interaction matrix in Eq. (8).

$$\therefore\ (\mathbb{A}-\mathbb{B})^{Hxc}_{ai\sigma,bj\tau} = \delta_{ab}\delta_{ij}\delta_{\sigma\tau}\,\underbrace{\omega_{jb\tau}}_{\epsilon_{b\tau}-\epsilon_{j\tau}>0} \quad (30)$$

is positive definite. For the long-range exact-exchange correction, however,

$$(\mathbb{A}-\mathbb{B})^{eex}_{ai\sigma,bj\tau} = -\delta_{\sigma\tau}\left\{\left[\phi^*_{a\sigma}\phi_{b\tau}\middle|\frac{erf(\mu r)}{r}\middle|\phi^*_{j\tau}\phi_{i\sigma}\right] - \left[\phi^*_{a\sigma}\phi_{j\tau}\middle|\frac{erf(\mu r)}{r}\middle|\phi^*_{b\tau}\phi_{i\sigma}\right]\right\} \quad (31)$$

may have negative eigenvalues (e.g. triplet instability).

If $\mathbb{A}-\mathbb{B}$ is positive definite,

$(\mathbb{A}-\mathbb{B})^{-1/2} \times (28)$

$$(\mathbb{A}-\mathbb{B})^{1/2}\underbrace{(\mathbb{A}+\mathbb{B})}_{(\mathbb{A}-\mathbb{B})^{1/2}(\mathbb{A}-\mathbb{B})^{-1/2}}(\mathbb{X}+\mathbb{Y}) = \omega^2(\mathbb{A}-\mathbb{B})^{-1/2}(\mathbb{X}+\mathbb{Y}) \quad (32)$$

$$\therefore\ (\mathbb{A}-\mathbb{B})^{1/2}(\mathbb{A}+\mathbb{B})(\mathbb{A}-\mathbb{B})^{1/2}\,\mathbb{T} = \omega^2\,\mathbb{T} \quad (33)$$

which is a Hermitian eigenvalue problem, where