Linear-Response Time-Dependent Density Functional Theory

6/15/11

– Kohn-Sham basis

Consider an orthonormal set of eigenstates, $\{\phi_{k\sigma}(\mathbf{r})\}$ (where k & σ are orbital & spin quantum numbers), which satisfy self-consistent Kohn-Sham equations,

$$h(\mathbf{r})\phi_{k\sigma}(\mathbf{r}) = \epsilon_{k\sigma}\phi_{k\sigma}(\mathbf{r}) \tag{1}$$

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

$$\rho(\mathbf{r}) = \sum_{k\sigma} f_{k\sigma}|\phi_{k\sigma}(\mathbf{r})|^2 \tag{3}$$

In Eq.(3), $f_{k\sigma} \in [0,1]$ is an occupation number. Here, we restrict ourselves to $f_{k\sigma} = 0$ or 1, and further to the ground state, Φ_0, which is a Slater determinant consisting of the lowest-energy Kohn-Sham orbitals,

$$\Phi_0 = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{1\uparrow}(\mathbf{r}_1) & \cdots & \phi_{1\uparrow}(\mathbf{r}_{N_{el}}) \\ \vdots & & \vdots \\ \phi_{N_{el}/2\downarrow}(\mathbf{r}_1) & \cdots & \phi_{N_{el}/2\downarrow}(\mathbf{r}_{N_{el}}) \end{vmatrix} \tag{4}$$

where N_{el} is the number of electrons and we have assumed a closed shell. Note that, rather than introducing spin coordinates, we simply impose orthogonality conditions,

$$\langle\phi_{k\sigma}|\phi_{k'\sigma'}\rangle \equiv \int d\mathbf{r}\, \phi^*_{k\sigma}(\mathbf{r})\phi_{k'\sigma'}(\mathbf{r}) = \delta_{kk'}\delta_{\sigma\sigma'} \tag{5}$$

— Time-dependent Kohn-Sham equation

The temporal evolution of a many-electron system is governed by

$$i\hbar \frac{\partial}{\partial t}\phi_{k\sigma}(\mathbf{r},t) = \left[h(\mathbf{r},t) + v_{ext}(\mathbf{r},t)\right]\phi_{k\sigma}(\mathbf{r},t) \qquad (6)$$

$$h(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2 + v_{ion}(\mathbf{r}) + \underbrace{\underbrace{\int d\mathbf{r}'\frac{e^2\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}}_{v_H(\mathbf{r},t)} + \underbrace{\frac{\delta A_{xc}}{\delta\rho(\mathbf{r},t)}}_{v_{xc}(\mathbf{r},t)}}_{v_{Hxc}(\mathbf{r},t)} \qquad (7)$$

$$\rho(\mathbf{r},t) = \sum_{k\sigma} f_{k\sigma}|\phi_{k\sigma}(\mathbf{r},t)|^2 \qquad (8)$$

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

$$\Phi(t) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{1\uparrow}(\mathbf{r}_1,t) & \cdots & \phi_{1\uparrow}(\mathbf{r}_{N_{el}},t) \\ \vdots & & \\ \phi_{N_{el}/2\downarrow}(\mathbf{r}_1,t) & \cdots & \phi_{N_{el}/2\downarrow}(\mathbf{r}_{N_{el}},t) \end{vmatrix} \qquad (9)$$

– Perturbation

Consider perturbation of $\Phi(t)$ on $v(\mathbb{r},t)$, where

$$h(\mathbb{r},t) = -\frac{\hbar^2}{2m}\nabla^2 + v_{ion}(\mathbb{r}) + \int d\mathbb{r}' \frac{e^2\rho(\mathbb{r}')}{|\mathbb{r}-\mathbb{r}'|} + \frac{\delta E_{xc}}{\delta\rho(\mathbb{r})}$$

$$+ v_{ext}(\mathbb{r},t) + \underbrace{\underbrace{\int d\mathbb{r}' \frac{e^2\delta\rho(\mathbb{r}',t)}{|\mathbb{r}-\mathbb{r}'|}}_{\delta v_H(\mathbb{r},t)} + \underbrace{\int d\mathbb{r}'\int dt' \frac{\delta^2 A_{xc}}{\delta\rho(\mathbb{r},t)\delta\rho(\mathbb{r}',t')}\,\delta\rho(\mathbb{r}',t')}_{\delta v_{xc}(\mathbb{r},t)}}_{\delta v_{Hxc}(\mathbb{r},t)} \quad (10)$$

$$= h(\mathbb{r}) + \underbrace{v_{ext}(\mathbb{r},t) + \delta v_{Hxc}(\mathbb{r},t)}_{v(\mathbb{r},t)} \quad (11)$$

— Linear response

We seek the solution of

$$i\hbar\frac{\partial}{\partial t}\phi_{k\sigma}(\mathbf{r},t) = [\hat{h}(\mathbf{r}) + \hat{v}(\mathbf{r},t)]\,\phi_{k\sigma}(\mathbf{r},t) \tag{12}$$

in the form

$$\phi_{k\sigma}(\mathbf{r},t) = e^{-i\hat{h}t/\hbar}\,\hat{S}(t,-\infty)\,\phi_{k\sigma}(\mathbf{r}). \tag{13}$$

The formal solution (2/11/10) is

$$\hat{S}(t,-\infty) = T\exp\left(-\frac{i}{\hbar}\int_{-\infty}^{t} dt'\,\hat{v}_h(t')\right) \tag{14a}$$

$$= 1 - \frac{i}{\hbar}\int_{-\infty}^{t} dt'\,\hat{v}_h(t') + O(v^2) \tag{14b}$$

where

$$\hat{v}_h(t) = e^{i\hat{h}t/\hbar}\,\hat{v}(t)\,e^{-i\hat{h}t/\hbar} \tag{15}$$

Substituting Eq. (14b) in (13)

$$\phi_{k\sigma}(\mathbf{r},t) = \left[e^{-i\hat{h}t/\hbar} - \frac{i}{\hbar}\int_{-\infty}^{t} dt'\,e^{-i\hat{h}(t-t')/\hbar}\,\hat{v}(t')\,e^{-i\hat{h}t'/\hbar}\right]\phi_{k\sigma}(\mathbf{r}) + O(v^2) \tag{16}$$

– Density response

$$\delta\rho(\mathbf{r},t) \equiv \rho(\mathbf{r},t) - \rho(\mathbf{r}) \tag{17}$$

where

$$\rho(\mathbf{r}) = \sum_{k\sigma} f_{k\sigma} |\phi_{k\sigma}(\mathbf{r})|^2 \tag{18}$$

Substituting Eq. (16) in (17),

$$\delta\rho(\mathbf{r},t) = \sum_{k\sigma} f_{k\sigma} \left(e^{i\hat{h}t/\hbar} + \frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{i\hat{h}(t-t')/\hbar}\, \hat{v}(t')\, e^{i\hat{h}t'/\hbar} \right) \phi^*_{k\sigma}(\mathbf{r})$$

$$\times \left(e^{-i\hat{h}t/\hbar} - \frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{-i\hat{h}(t-t')/\hbar}\, \hat{v}(t')\, e^{-i\hat{h}t'/\hbar} \right) \phi_{k\sigma}(\mathbf{r})$$

$$- \sum_{k\sigma} f_{k\sigma} |\phi_{k\sigma}(\mathbf{r})|^2$$

$$= \sum_{k\sigma} f_{k\sigma} \left(e^{i\epsilon_{k\sigma}t/\hbar} \phi^*_{k\sigma}(\mathbf{r}) + \frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{i\hat{h}(t-t')/\hbar}\, \hat{v}(t')\, e^{i\epsilon_{k\sigma}t'/\hbar} \phi^*_{k\sigma}(\mathbf{r}) \right)$$

$$\times \left(e^{-i\epsilon_{k\sigma}t/\hbar} \phi_{k\sigma}(\mathbf{r}) - \frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{-i\hat{h}(t-t')/\hbar}\, \hat{v}(t')\, e^{-i\epsilon_{k\sigma}t'/\hbar} \phi_{k\sigma}(\mathbf{r}) \right)$$

$$- \sum_{k\sigma} f_{k\sigma} |\phi_{k\sigma}(\mathbf{r})|^2$$

$$\delta\rho(\mathbf{r},t) = \sum_{k\sigma} f_{k\sigma}\Big[\left(-\frac{i}{\hbar}\right)\phi^*_{k\sigma}(\mathbf{r})\int_{-\infty}^{t} dt' e^{-i\hat{h}(t-t')/\hbar}\,\hat{v}(t')\,e^{i\epsilon_{k\sigma}(t-t')/\hbar}\,\phi_{k\sigma}(\mathbf{r})$$

$$+\frac{i}{\hbar}\phi_{k\sigma}(\mathbf{r})\int_{-\infty}^{t} dt' e^{i\hat{h}(t-t')/\hbar}\,\hat{v}(t')\,e^{-i\epsilon_{k\sigma}(t-t')/\hbar}\,\phi^*_{k\sigma}(\mathbf{r})$$

$$= -\frac{i}{\hbar}\sum_{k\sigma} f_{k\sigma}\Big[\phi^*_{k\sigma}(\mathbf{r})\int_{-\infty}^{t} dt' \, e^{-i(\hat{h}-\epsilon_{k\sigma})(t-t')/\hbar}\,\hat{v}(t')\,\phi_{k\sigma}(\mathbf{r})$$

$$-\phi_{k\sigma}(\mathbf{r})\int_{-\infty}^{t} dt' \, e^{i(\hat{h}-\epsilon_{k\sigma})(t-t')/\hbar}\,\hat{v}(t')\,\phi_{k\sigma}(\mathbf{r})\Big]$$

$$= \int_{-\infty}^{\infty} dt' \left(-\frac{i}{\hbar}\right)\Theta(t-t')\sum_{k\sigma} f_{k\sigma}$$

$$\times\Big[\phi^*_{k\sigma}(\mathbf{r})\, e^{-i(\hat{h}-\epsilon_{k\sigma})(t-t')/\hbar}\,\hat{v}(t')\,\phi_{k\sigma}(\mathbf{r})$$

$$-\phi_{k\sigma}(\mathbf{r})\, e^{i(\hat{h}-\epsilon_{k\sigma})(t-t')/\hbar}\,\hat{v}(t')\,\phi^*_{k\sigma}(\mathbf{r})\Big] \qquad (19)$$

Note that

$$v(\mathbf{r},t')\,\phi_{k\sigma}(\mathbf{r})$$

$$= \hat{v}\,|k\sigma\rangle$$

$$= \sum_j |j\sigma\rangle\langle j\sigma|\hat{v}|k\sigma\rangle$$

$$= \sum_j \phi_{j\sigma}(\mathbf{r})\int d\mathbf{r}'\,\phi^*_{j\sigma}(\mathbf{r}')\,v(\mathbf{r}',t')\,\phi_{k\sigma}(\mathbf{r}') \qquad (20)$$

Using the completeness relation, Eq. (20), in Eq. (19),

$$\delta\rho(\mathbf{r},t) = \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' \left(-\frac{i}{\hbar}\right)\Theta(t-t') \sum_j \sum_{k\sigma} f_{k\sigma}$$

$$\times \Big[\phi^*_{k\sigma}(\mathbf{r})\, e^{-i(\underbrace{\hat{h}}_{\to\,\epsilon_{j\sigma}}-\epsilon_{k\sigma})(t-t')/\hbar}\, \phi_{j\sigma}(\mathbf{r})\, \phi^*_{j\sigma}(\mathbf{r}')\, \phi_{k\sigma}(\mathbf{r}')$$

$$- \phi_{k\sigma}(\mathbf{r})\, e^{i(\underbrace{\hat{h}}_{\to\,\epsilon_{j\sigma}}-\epsilon_{k\sigma})(t-t')/\hbar}\, \phi^*_{j\sigma}(\mathbf{r})\, \phi_{j\sigma}(\mathbf{r}')\, \phi^*_{k\sigma}(\mathbf{r}') \Big]\, v(\mathbf{r}',t')$$

$$= \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' \left(-\frac{i}{\hbar}\right)\Theta(t-t') \sum_j \sum_{k\sigma} f_{k\sigma}$$

$$\times \Big[\phi^*_{k\sigma}(\mathbf{r})\, \phi_{j\sigma}(\mathbf{r})\, e^{-i\omega_{jk\sigma}(t-t')}\, \phi^*_{j\sigma}(\mathbf{r}')\, \phi_{k\sigma}(\mathbf{r}')$$

$$- \phi_{k\sigma}(\mathbf{r})\, \phi^*_{j\sigma}(\mathbf{r})\, e^{i\omega_{jk\sigma}(t-t')}\, \phi_{j\sigma}(\mathbf{r}')\, \phi^*_{k\sigma}(\mathbf{r}') \Big]\, v(\mathbf{r}',t') \qquad (21)$$

where

$$\omega_{jk\sigma} \equiv \frac{\epsilon_{j\sigma} - \epsilon_{k\sigma}}{\hbar} \qquad (22)$$

$$\therefore \frac{\delta\rho(\mathbf{r},t)}{\delta v(\mathbf{r}',t')} \equiv \chi_{KS}(\mathbf{r},\mathbf{r}';t-t') \qquad (23)$$

$$= \left(-\frac{i}{\hbar}\right)\Theta(t-t') \sum_{jk\sigma} f_{k\sigma}$$

$$\times \Big[\phi^*_{k\sigma}(\mathbf{r})\, \phi_{j\sigma}(\mathbf{r})\, e^{-\omega_{jk\sigma}(t-t')}\, \phi^*_{j\sigma}(\mathbf{r}')\, \phi_{k\sigma}(\mathbf{r}')$$

$$- \phi_{k\sigma}(\mathbf{r})\, \phi^*_{j\sigma}(\mathbf{r})\, e^{i\omega_{jk\sigma}(t-t')}\, \phi_{j\sigma}(\mathbf{r}')\, \phi^*_{k\sigma}(\mathbf{r}') \Big] \qquad (24)$$

The density-density response function is defined as

$$\chi(\mathbf{r},\mathbf{r}';t-t') \equiv \frac{\delta\rho(\mathbf{r},t)}{\delta v_{ext}(\mathbf{r}',t')} \tag{25}$$

Using the chain rule,

$$\chi(\mathbf{r},\mathbf{r}'';t-t'') = \frac{\delta\rho(\mathbf{r},t)}{\delta v_{ext}(\mathbf{r}'',t'')}$$

$$= \int d\mathbf{r}'\int_{-\infty}^{\infty}dt'\, \underbrace{\frac{\delta\rho(\mathbf{r},t)}{\delta v(\mathbf{r}',t')}}_{\chi_{KS}(\mathbf{r},\mathbf{r}';t-t')} \cdot \frac{\delta v(\mathbf{r}',t')}{\delta v_{ext}(\mathbf{r}'',t'')} \tag{26}$$

From Eqs. (10) and (11),

$$\frac{\delta v(\mathbf{r}',t')}{\delta v_{ext}(\mathbf{r}'',t'')} = \delta(\mathbf{r}'-\mathbf{r}'')\delta(t'-t'') + \int d\mathbf{r}'''\frac{e^2}{|\mathbf{r}'-\mathbf{r}'''|}\underbrace{\frac{\delta\rho(\mathbf{r}''',t')}{\delta v_{ext}(\mathbf{r}'',t'')}}_{\chi(\mathbf{r}''',\mathbf{r}'';t'-t'')}$$

$$+\int d\mathbf{r}'''\int dt'''\underbrace{\frac{\delta^2 A_{xc}}{\delta\rho(\mathbf{r}',t')\delta\rho(\mathbf{r}''',t''')}}_{f_{xc}(\mathbf{r}',\mathbf{r}''';t'-t''')}\underbrace{\frac{\delta\rho(\mathbf{r}''',t''')}{\delta v_{ext}(\mathbf{r}'',t'')}}_{\chi(\mathbf{r}''',\mathbf{r}'';t'''-t'')}$$

$$= \delta(\mathbf{r}'-\mathbf{r}'')\delta(t'-t'')$$

$$+\int d\mathbf{r}'''\int_{-\infty}^{\infty}dt'''\left[\frac{e^2}{|\mathbf{r}'-\mathbf{r}'''|}\delta(t'-t''') + f_{xc}(\mathbf{r}',\mathbf{r}''';t'-t''')\right]$$

$$\times\, \chi(\mathbf{r}''',\mathbf{r}'';t'''-t'') \tag{27}$$

where

$$f_{xc}(\mathbf{r},\mathbf{r}';t-t') \equiv \frac{\delta^2 A_{xc}}{\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t')} \tag{28}$$

Substituting Eq. (27) in (26)

$$\chi(\mathbf{r},\mathbf{r}'';t-t'') = \chi_{KS}(\mathbf{r},\mathbf{r}'';t-t'')$$

$$+\int d\mathbf{r}'\int_{-\infty}^{\infty}dt'\,\chi_{KS}(\mathbf{r},\mathbf{r}';t-t')\int d\mathbf{r}'''\int_{-\infty}^{\infty}dt'''\left[\frac{e^2}{|\mathbf{r}'-\mathbf{r}'''|}\delta(t'-t''')+f_{xc}(\mathbf{r}',\mathbf{r}''';t'-t''')\right]$$

$$\times\,\chi(\mathbf{r}''',\mathbf{r}'';t'''-t'') \qquad (29)$$

– Fourier transform

Let's define

$$\chi(\mathbf{r},\mathbf{r}';t-t') = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\chi(\mathbf{r},\mathbf{r}';\omega)\,e^{-i\omega(t-t')} \tag{30}$$

$$\chi_{KS}(\mathbf{r},\mathbf{r}';t-t') = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\chi_{KS}(\mathbf{r},\mathbf{r}';\omega)\,e^{-i\omega(t-t')} \tag{31}$$

Recall (2/25/10 note)

$$\theta(t) = -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,\frac{e^{-i\omega t}}{\omega+i0} \tag{32}$$

Substituting Eq. (32) in (24)

$$\chi_{KS}(\mathbf{r},\mathbf{r}';t-t') = \frac{\cancel{i}}{\hbar}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi \cancel{i}}\,\frac{e^{-i\omega(t-t')}}{\omega+i0}\sum_{jk\sigma} f_{k\sigma}$$

$$\times\Big[\phi^*_{k\sigma}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r})\,e^{-i\omega_{jk\sigma}(t-t')}\,\phi^*_{j\sigma}(\mathbf{r}')\,\phi_{k\sigma}(\mathbf{r}')$$

$$-\,\phi_{k\sigma}(\mathbf{r})\,\phi^*_{j\sigma}(\mathbf{r})\,e^{i\omega_{jk\sigma}(t-t')}\,\phi_{j\sigma}(\mathbf{r}')\,\phi^*_{k\sigma}(\mathbf{r}')\Big]$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\sum_{jk\sigma} f_{k\sigma}$$

$$\times\Big[\phi^*_{k\sigma}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r})\,\frac{e^{-i\overbrace{(\omega+\omega_{jk\sigma})}^{\omega'}(t-t')}}{\underbrace{\omega}_{\omega'-\omega_{jk\sigma}}+i0}\,\phi^*_{j\sigma}(\mathbf{r}')\,\phi_{k\sigma}(\mathbf{r}')$$

$$-\,\phi_{k\sigma}(\mathbf{r})\,\phi^*_{j\sigma}(\mathbf{r})\,\frac{e^{-i\overbrace{(\omega-\omega_{jk\sigma})}^{\omega'}(t-t')}}{\underbrace{\omega}_{\omega'+\omega_{jk\sigma}}+i0}\,\phi_{j\sigma}(\mathbf{r}')\,\phi^*_{k\sigma}(\mathbf{r}')\Big]$$

$$\chi_{KS}(\mathbf{r},\mathbf{r}';t-t') = \frac{1}{\hbar}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\sum_{jk\sigma} f_{k\sigma}$$
$$\times\left[\frac{\phi^*_{k\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r}')\phi_{k\sigma}(\mathbf{r}')}{\omega-\omega_{jk\sigma}+i0} - \frac{\phi_{k\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}')\phi^*_{k\sigma}(\mathbf{r}')}{\omega+\omega_{jk\sigma}+i0}\right] \tag{33}$$

Comparing Eqs. (31) and (33), we obtain

$$\chi_{KS}(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{\hbar}\sum_{jk\sigma} f_{k\sigma}\left[\frac{\phi^*_{k\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r}')\phi_{k\sigma}(\mathbf{r}')}{\omega-\omega_{jk\sigma}+i0} - \frac{\phi_{k\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}')\phi^*_{k\sigma}(\mathbf{r}')}{\omega+\omega_{jk\sigma}+i0}\right] \tag{34}$$

Or, interchanging the indices $j\leftrightarrow k$ in the second term,

$$\chi_{KS}(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{\hbar}\sum_{jk\sigma}(f_{k\sigma}-f_{j\sigma})\frac{\phi^*_{k\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r}')\phi_{k\sigma}(\mathbf{r}')}{\omega-\omega_{jk\sigma}+i0} \tag{35}$$

Note that

$$f_{k\sigma}(1-f_{j\sigma}) - f_{j\sigma}(1-f_{k\sigma})$$
$$= f_{k\sigma} - \cancel{f_{k\sigma}f_{j\sigma}} - f_{j\sigma} + \cancel{f_{j\sigma}f_{k\sigma}}$$

Thus,

$$\chi_{KS}(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{\hbar}\sum_{jk\sigma}\left[f_{k\sigma}(1-f_{j\sigma}) - f_{j\sigma}(1-f_{k\sigma})\right]$$
$$\times\frac{\phi^*_{k\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r}')\phi_{k\sigma}(\mathbf{r}')}{\omega-\omega_{jk\sigma}+i0} \tag{36}$$

Interchanging the indices back $j\leftrightarrow k$ in the second term, excitation

occupied hole $\rightarrow$ unoccupied electron

$$\chi_{KS}(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{\hbar}\sum_{jk\sigma} f_{k\sigma}(1-f_{j\sigma}) \times \left[\frac{\phi^*_{k\sigma}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r})\,\phi^*_{j\sigma}(\mathbf{r}')\,\phi_{k\sigma}(\mathbf{r}')}{\omega - \omega_{jk\sigma} + i0} - \frac{\phi_{k\sigma}(\mathbf{r})\,\phi^*_{j\sigma}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r}')\,\phi^*_{k\sigma}(\mathbf{r}')}{\omega + \omega_{jk\sigma} + i0} \right] \tag{37}$$

Note that

$$\delta(t-t') = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \tag{38}$$

Using Eq. (38) and convolution in Eq. (29),

$$\chi(\mathbf{r},\mathbf{r}'';\omega) = \chi_{KS}(\mathbf{r},\mathbf{r}'';\omega) + \int d\mathbf{r}'\,\chi_{KS}(\mathbf{r},\mathbf{r}';\omega)\int d\mathbf{r}'''\left[\frac{e^2}{|\mathbf{r}'-\mathbf{r}'''|} + f_{xc}(\mathbf{r}',\mathbf{r}''';\omega)\right]\chi(\mathbf{r}''',\mathbf{r}'';\omega) \tag{39}$$