Casida equations

Density response

$$\delta n(x,\omega) = \int dx' \, \chi_s(x,x',\omega)\, \delta v_s(x',\omega) \tag{1}$$

The Kohn-Sham density response function has the form

$$\chi_s(x,x',\omega) = \lim_{\eta\to 0^+} \sum_{kl}' 2(\mu_l-\mu_k) \frac{\varphi_k(x)\varphi_l^*(x)\, \varphi_k^*(x')\varphi_l(x')}{\omega-(\epsilon_k-\epsilon_l)+i\eta}$$

If we define
$$\begin{cases} \omega_{kl} = \epsilon_k-\epsilon_l \\ \mu_{kl} = 2(\mu_l-\mu_k) \\ \Phi_{kl}(x) = \varphi_k^*(x)\varphi_l(x) \end{cases}$$

$\mu_l = 1$, occupied state
$\mu_l = 0$, unoccupied state

we can write

$$\chi_s(x,x',\omega) = \lim_{\eta\to 0^+} \sum_{kl} \mu_{kl} \frac{\Phi_{kl}^*(x)\,\Phi_{kl}(x')}{\omega-\omega_{kl}+i\eta} \tag{2}$$

Inserting (2) into (1) then gives

$$\delta n(x,\omega) = \sum_{kl}' \mu_{kl} P_{kl}(\omega)\, \Phi_{kl}^*(x) \tag{3}$$

where $P_{kl}(\omega) \stackrel{\text{def}}{=} \dfrac{\delta v_{s,kl}(\omega)}{\omega-\omega_{kl}+i\eta}$, $\delta v_{s,kl}(\omega) \stackrel{\text{def}}{=} \int dx\, \Phi_{kl}(x)\,\delta v_s(x,\omega)$ (4)

Our goal is to derive an equation for $P_{kl}(\omega)$

We start from the definition of the Hartree-xc kernel

$$\begin{aligned}\delta v_{Hxc}(x,\omega) &= \int dx'\, f_{Hxc}(x,x',\omega)\,\delta n(x',\omega) \\ &= \sum_{kl}' \mu_{kl} P_{kl}(\omega) \int dx'\, f_{Hxc}(x,x',\omega)\, \Phi_{kl}^*(x')\end{aligned} \tag{5}$$

where we used (3)

This means that

$$\delta v_{Hxc,ij}(\omega) \stackrel{\text{def}}{=} \int dx\, \Phi_{ij}(x)\,\delta v_{Hxc}(x,\omega) = \sum_{kl}' K_{ij,kl}(\omega) P_{kl}(\omega)\,\mu_{kl} \tag{6}$$

where we defined $K_{ij,kl}(\omega) \stackrel{\text{def}}{=} \int dx\,dx'\, \Phi_{ij}(x)\, f_{Hxc}(x,x',\omega)\, \Phi_{kl}^*(x')$

We also have that

$$\delta v_s(x,\omega) = \delta v(x,\omega) + \delta v_{Hxc}(\omega)$$

$$\Rightarrow \quad \delta v_{s,ij}(\omega) = \delta v_{ij}(\omega) + \delta v_{Hxc,ij}(\omega) \qquad (7)$$

where $\delta v_{ij}(\omega) \overset{\text{def}}{=} \int dx\, \Phi_{ij}(x)\, \delta v(x,\omega)$

Using (4) and (6) this can be written as

$$(\omega - \omega_{ij} + i\eta) P_{ij}(\omega) - \sum_{kl}' \mu_{kl} K_{ij,kl}(\omega) P_{kl}(\omega) = \delta v_{ij}(\omega) \qquad (8)$$

This is the equation for $P_{ij}(\omega)$ that we were looking for. In this equation we can let $\eta \to 0$ as $P_{ij}(\omega)$ does not have a pole at ω_{ij} (these are at the true excitation energies).

From Eq. 3 we see that the only relevant matrix elements $P_{ij}(\omega)$ are those for which $\mu_{ij} = 2(\mu_j - \mu_i) \neq 0$, so for i occupied and j unoccupied or vice versa.
So let us only those matrix elements and thereby reduce the dimensionality (in a finite basis) of Eq. 8.
Let us label occupied states by i, j, k, l and unoccupied states by a, b, c, d.
Then Eq. (3) can be written as

$$\delta n(x,\omega) = \sum_{ia} \mu_{ia} P_{ia}(\omega) \Phi_{ia}(x) + \mu_{ai} P_{ai}(\omega) \Phi_{ai}(x)$$

$$= \sum_{ia} 2 P_{ai}(\omega) \Phi_{ai}(x) - 2 P_{ia}(\omega) \Phi_{ia}(x)$$

$$= \sum_{ia} X_{ia}(\omega) \Phi_{ia}(\omega) + Y_{ia}(\omega) \Phi^*_{ia}(\omega)$$

where we defined

$$X_{ia}(\omega) = -2 P_{ia}(\omega) \quad , \quad Y_{ia}(\omega) = 2 P_{ai}(\omega) \qquad (9)$$

From Eq. 8 we then have ($\eta \to 0$)

$$(\omega + i\eta - \omega_{ia}) P_{ia}(\omega) - \sum_{jb} \left[\mu_{jb} K_{ia,jb} P_{jb} + \mu_{bj} K_{ia,bj} P_{bj}\right] = \delta v_{ia}(\omega)$$

$$(\omega + i\eta - \omega_{ai}) P_{ai}(\omega) - \sum_{jb} \left[\mu_{jb} K_{ai,jb} P_{jb} + \mu_{bj} K_{ai,bj} P_{bj}\right] = \delta v_{ai}(\omega)$$

With the definitions (9) we can write this as

$$(\omega + i\eta + \omega_{ai})(-X_{ia}(\omega)) - \sum_{jb} \left[(-2) K_{ia,jb} (-X_{jb}) + 2 K_{ia,bj} Y_{jb}\right] = 2\,\delta v_{ia}$$

$$(\omega + i\eta - \omega_{ai})\, Y_{ia}(\omega) - \sum_{jb} \left[(-2) K_{ai,jb} (-X_{jb}) + 2 K_{ai,bj} Y_{jb}\right] = 2\,\delta v_{ia}^*$$

We multiply by -1 and rewrite this a bit as

$$(\omega + i\eta + \omega_{ai}) X_{ia} + \sum_{jb} 2K_{ia,jb} X_{jb} + \sum_{jb} 2K_{ia,bj} Y_{jb} = -2\,\delta v_{ia}$$

$$\sum_{jb} 2K_{ai,jb} X_{jb} + (-\omega - i\eta + \omega_{ai}) Y_{ia} + \sum_{jb} 2K_{ai,bj} Y_{jb} = -2\,\delta v_{ia}^*$$

This can be written in block form as

$$\left[\begin{pmatrix} A & B \\ C & D \end{pmatrix} - (\omega + i\eta)\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\right]\begin{pmatrix} X \\ Y \end{pmatrix} = -2\begin{pmatrix} \delta v \\ \delta v^* \end{pmatrix} \qquad (10)$$

$$\begin{cases} A_{ia,jb} = \delta_{ij}\delta_{ab}\,\omega_{ai} + 2K_{ia,jb}(\omega) \\ B_{ia,jb} = 2K_{ia,bj} \\ C_{ia,jb} = 2K_{ai,jb} \\ D_{ia,jb} = \delta_{ij}\delta_{ab}\,\omega_{ai} + 2K_{ai,bj}(\omega) \end{cases}$$

If the orbitals are real then $B = C$ and $A = D$.

In that case Eq. 10 can be written as:

$$\left[\begin{pmatrix} A & B \\ B & A \end{pmatrix} - (\omega + i\eta)\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\right]\begin{pmatrix} X \\ Y \end{pmatrix} = -2\begin{pmatrix} \delta v \\ \delta v^* \end{pmatrix} \qquad (11)$$

These are the so-called Casida equations of TDDFT.

Let us now consider a simple limiting case of two orbitals $\varphi_1(x)$ and $\varphi_2(x)$ which we take to be real.
Then (with $(i,a) = (1,2)$)

$$\delta n(x,\omega) = \Phi_{12}(x)\left[X_{12}(\omega) + Y_{12}(\omega)\right] = \varphi_1(x)\varphi_2(x)\left[X_{12}(\omega) + Y_{12}(\omega)\right] \tag{12}$$

From Eq. (11) we then have with,

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} = \begin{pmatrix} \omega_{21} + 2K_{12,12}(\omega) & 2K_{12,12}(\omega) \\ 2K_{12,12}(\omega) & \omega_{21} + 2K_{12,12}(\omega) \end{pmatrix}$$

that

$$\underbrace{\begin{bmatrix} \omega + i\eta + \omega_{21} + 2K_{12,12}(\omega) & 2K_{12,12}(\omega) \\ 2K_{12,12}(\omega) & -(\omega+i\eta) + \omega_{21} + 2K_{12,12}(\omega) \end{bmatrix}}_{\text{call this matrix } M(\omega)} \begin{pmatrix} X_{12}(\omega) \\ Y_{12}(\omega) \end{pmatrix} = -2 \begin{pmatrix} \delta v_{12}(\omega) \\ \delta v_{12}^*(\omega) \end{pmatrix}$$

We can then calculate $(X_{12}(\omega), Y_{12}(\omega))$

If we use that for a matrix $\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad-bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$

we find that

$$\begin{pmatrix} X_{12}(\omega) \\ Y_{12}(\omega) \end{pmatrix} = \frac{-2}{\omega_{21}^2 + 4\omega_{21}K_{12,12}(\omega) - (\omega+i\eta)^2} \begin{bmatrix} -(\omega+i\eta) + \omega_{21} + 2K_{12,12} & -2K_{12,12} \\ -2K_{12,12} & \omega + i\eta + \omega_{21} + 2K_{12,12} \end{bmatrix} \begin{pmatrix} \delta v_{12} \\ \delta v_{12}^* \end{pmatrix} \tag{13}$$

Let us now apply a perturbation of the form

$$\delta v(x,t) = \delta(t) f(x) \qquad \text{(delta "kick")}$$

Such that $\delta v(x,\omega) = f(x)$ is frequency independent

Then $\delta v_{12}(\omega) = \int dx\, \varphi_1(x)\varphi_2(x) f(x) = \lambda$ (some number)

Then we find

$$\begin{pmatrix} X_{12}(\omega) \\ Y_{12}(\omega) \end{pmatrix} = \frac{-2\lambda}{\omega_{21}^2 + 4\omega_{21} K_{12,12}(\omega) - (\omega+i\eta)^2} \begin{pmatrix} -(\omega+i\eta)+\omega_{21} \\ (\omega+i\eta)+\omega_{21} \end{pmatrix} \quad (14)$$

If we define $\Omega(\omega) = \sqrt{\omega_{21}^2 + 4\omega_{21} K_{12,12}(\omega)}$, then we have that

$$X_{12}(\omega) + Y_{12}(\omega) = \frac{2\lambda\omega_{21}}{\Omega(\omega)^2 - (\omega+i\eta)^2}$$

$$= \frac{\lambda\omega_{21}}{\Omega(\omega)} \left\{ \frac{1}{\omega - \Omega(\omega) + i\eta} - \frac{1}{\omega + \Omega(\omega) + i\eta} \right\}$$

For the induced density we therefore find

$$\delta n(x,\omega) = \frac{\lambda\omega_{21}}{\Omega(\omega)} \varphi_1(x)\varphi_2(x) \left\{ \frac{1}{\omega - \Omega(\omega) + i\eta} - \frac{1}{\omega + \Omega(\omega) + i\eta} \right\} \quad (15)$$

If we have an approximation for $f_{Hxc}(x,x',\omega)$ that is frequency independent, then $\Omega(\omega) = \bar{\Omega}$ does not depend on ω. In that case we can Fourier transform to obtain $\delta n(x,t)$ in time.

$$\delta n(x,t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} \delta n(x,\omega)$$

$$= \frac{\lambda\omega_{21}}{\bar{\Omega}} \varphi_1(x)\varphi_2(x) \int \frac{d\omega}{2\pi} \left\{ \frac{1}{\omega - \bar{\Omega} + i\eta} - \frac{1}{\omega + \bar{\Omega} + i\eta} \right\} e^{-i\omega t}$$

$$= \frac{\lambda\omega_{21}}{\bar{\Omega}} \varphi_1(x)\varphi_2(x) \cdot \theta(t) \left[i e^{-i\bar{\Omega}t} - i e^{i\bar{\Omega}t} \right\}$$

$$= \frac{2\lambda\omega_{21}}{\bar{\Omega}} \varphi_1(x)\varphi_2(x)\, \theta(t) \sin(\bar{\Omega}t) \quad (16)$$

The density oscillates at frequency $\bar{\Omega} = \sqrt{\omega_{21}^2 + 4\omega_{21} K_{12,12}}$

If the f_{Hxc} is frequency dependent then $\delta n(x,\omega)$ can have additional poles.

These happen for all ω that satisfy

$$0 = \omega_{21}^2 + 4\omega_{21} K_{12,12}(\omega) - \omega^2$$

and in that case the explicit form of (15) is more complicated.