TDDFT: a formulation

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1. TDDFT A FORMULATION

A. Motivation

The question to answer to develop a Linear response theory and, in our case more importantly a Time-dependent density functional theory (TDDFT) is the following:
How does a system react to an external perturbation?
Some quantities that can be obtain by answering this question are: *electrical conductivity* and *dielectric function*; these quantites are known as *reponse functions*. Consider a Hamiltonian:

B. Linear response formalism

$$H(t) = H_0 + V(t). \tag{1.1}$$

where the term H_0 is the unperturbed Hamiltonian and $V(t)$ is a time dependent perturbation that we switch on at some finite time t. We can now think of the perturbation as some c-number F_t coupled to an observable of the system $\hat{B}$

$$\hat{V}(t) = F_t \hat{B} \tag{1.2}$$

Now, suppose your unperturbed system is described by the density matrix:

$$\rho_0 = \frac{exp(-\beta \mathcal{H}_0)}{Tr[exp(-\beta \mathcal{H}_0)]} \tag{1.3}$$

We are averaging over the gran canonical ensamble

$$\mathcal{H}_0 = H_0 - \mu \hat{N} \tag{1.4}$$

After we switch on the perturbation, the density matrix will change

$$\rho_0^S \to \rho_t^S. \tag{1.5}$$

Let us now consider an observable of your system in consideration in the Schrödinger picture (superscript S); let's call it $\hat{A}^S$. From Quantum mechanics we know that the expectation value of this observable without the external perturbation is given by

$$\langle \hat{A}^S \rangle_0 = Tr\Big(\hat{\rho}_0^S \hat{A}^S\Big) \tag{1.6}$$

and, after we switch on the time dependent perturbation, the expectation value of $\hat{A}_S$ is

$$\langle \hat{A}^S \rangle_t = Tr\Big(\hat{\rho}_t^S \hat{A}^S\Big) \tag{1.7}$$

We use now the equation of motion of the density matrix in the Schödinger picture (you may know it as the Liouville-Von Neumann equation)

$$i\hbar \frac{\partial \rho_t^S}{\partial t} = \left[\hat{H}, \rho_t^S\right] \tag{1.8}$$

$$= \left[\hat{H}_0, \rho_t^S\right] + \left[\hat{V}_t, \rho_t^S\right] \tag{1.9}$$

To solve for $\hat{\rho}_t$ we need first to change to the interaction representation (superindex I):

$$\hat{\rho}_t^I(t) = e^{i\hbar\hat{\mathcal{H}}_0 t}\hat{\rho}_t^S e^{-i\hbar\hat{\mathcal{H}}_0 t} \tag{1.10}$$

and we know that the equation of motion for the density matrix in the interaction picture is given by

$$\frac{\partial \hat{\rho}_t^I(t)}{\partial t} = \frac{i}{\hbar}\left[\hat{\rho}_t^I(t), \hat{V}_t^I(t)\right]. \tag{1.11}$$

Before we can integrate Eq.(1.11), we need a boundary condition. This is given by our assumption that before the perturbation is switched on, our system is described by the unperturbed density matrix

$$\lim_{t\to-\infty} \hat{\rho}_t^I(t) = \hat{\rho}_0 \tag{1.12}$$

Now we can just integrate Eq.(1.11)

$$\hat{\rho}_t^I(t) = \hat{\rho}_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt' \left[\hat{V}_t^I(t'), \hat{\rho}_t^I(t')\right] \tag{1.13}$$

If one iterate equation (1.13) (this means, substite $\hat{\rho}_t^I(t)$ into itself), one find the solution with arbitrary precision

$$\hat{\rho}_t^{I,n}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_n \left[\hat{V}_{t_1}^I(t_1), \left[\hat{V}_{t_2}^I(t_2), \left[\cdots, [V_{t_n}^I(t_n), \hat{\rho}_0]\cdots\right]\right]\right] \tag{1.14}$$

If we assume that the time dependent perturbation is small, we can retain just the linear term in $\hat{V}_t$, we get then

$$\hat{\rho}_t^I(t) \approx \hat{\rho}_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt' \left[\hat{V}_{t'}^I(t'), \hat{\rho}_0\right] \tag{1.15}$$

and now we come back to the Schrödinger representation (just sandwich the operators on the left with $e^{-i\hat{\mathcal{H}}_0 t}$ and on the right with $e^{i\hat{\mathcal{H}}_0 t}$):

$$\hat{\rho}_t^S \approx \hat{\rho}_0 - \frac{i}{\hbar}\int_{-\infty}^{t} dt' e^{-i\hat{\mathcal{H}}_0 t}\left[\hat{V}_{t'}^I(t'), \hat{\rho}_0\right] e^{i\hat{\mathcal{H}}_0 t}. \tag{1.16}$$

Since we now have an expression for the density matrix after the perturbation kicked in, we can calculate the expectation value in (1.7)

$$\langle \hat{A}^S \rangle_t = Tr\Big(\hat{\rho}_0 \hat{A}^S - \frac{i}{\hbar} \int_{-\infty}^{t} dt' e^{-i\hat{\mathcal{H}}_0 t} \Big[\hat{V}^I_{t'}(t'), \hat{\rho}_0 \Big] e^{i\hat{\mathcal{H}}_0 t} \Big) \tag{1.17}$$

$$= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' Tr\Big\{ e^{-i\hat{\mathcal{H}}_0 t} \Big[\hat{V}^I_{t'}(t'), \hat{\rho}_0 \Big] e^{i\hat{\mathcal{H}}_0 t} \hat{A}^S \Big\} \tag{1.18}$$

and we substitute the value of the potential $\hat{V}_t$ (Eq.(1.2))

$$\begin{aligned}
\langle \hat{A}^S \rangle_t &= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \underbrace{Tr\Big\{ e^{-i\hat{\mathcal{H}}_0 t} \Big[\hat{B}^I_{t'}(t'), \hat{\rho}_0 \Big] e^{i\hat{\mathcal{H}}_0 t} \hat{A}^S \Big\}}_{Tr\left\{ \hat{A}^S e^{-i\hat{\mathcal{H}}_0 t} \left[\hat{B}^I_{t'}(t'), \hat{\rho}_0 \right] e^{i\hat{\mathcal{H}}_0 t} \right\}} \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \underbrace{Tr\Big\{ \hat{A}^S e^{-i\hat{\mathcal{H}}_0 t} \Big[\hat{B}^I_{t'}(t'), \hat{\rho}_0 \Big] e^{i\hat{\mathcal{H}}_0 t} \Big\}}_{Tr\left\{ e^{i\hat{\mathcal{H}}_0 t} \hat{A}^S e^{-i\hat{\mathcal{H}}_0 t} \left[\hat{B}^I_{t'}(t'), \hat{\rho}_0 \right] \right\}} \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} Tr\Bigg\{ \underbrace{e^{i\hat{\mathcal{H}}_0 t} \hat{A}^S e^{-i\hat{\mathcal{H}}_0 t}}_{\hat{A}^I(t)} \Big[\hat{B}^I_{t'}(t'), \hat{\rho}_0 \Big] \Bigg\} \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} Tr\Big\{ \hat{A}^I(t) \Big[\hat{B}^I_{t'}(t'), \hat{\rho}_0 \Big] \Big\} \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \Big(Tr\Big\{ \hat{A}^I(t) \Big(\hat{B}^I_{t'}(t') \hat{\rho}_0 \Big) \Big\} - Tr\Big\{ \hat{A}^I(t) \Big(\hat{\rho}_0 \hat{B}^I_{t'}(t') \Big) \Big\} \Big) \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \Big(Tr\Big\{ \hat{\rho}_0 \hat{A}^I(t) \hat{B}^I_{t'}(t') \Big\} - Tr\Big\{ \hat{B}^I_{t'}(t') \hat{A}^I(t) \hat{\rho}_0 \Big\} \Big) \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \Big(Tr\Big\{ \hat{\rho}_0 \hat{A}^I(t) \hat{B}^I_{t'}(t') \Big\} - Tr\Big\{ \hat{\rho}_0 \hat{B}^I_{t'}(t') \hat{A}^I(t) \Big\} \Big) \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} Tr\Big\{ \hat{\rho}_0 \Big[\hat{A}^I(t), \hat{B}^I_{t'}(t') \Big] \Big\} \\
&= \langle \hat{A}^S \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \Big\langle \Big[\hat{A}^I(t), \hat{B}^I_{t'}(t') \Big] \Big\rangle_0
\end{aligned} \tag{1.19}$$

Where we have used mainly two properties of the trace: invariance under cyclic permutations and linearity. Now we have achieved, at least to some degree, to write down an expression for the change in the expectation value of a systems' observable $\hat{A}$ when a time dependent external scalar potential, coupled to an operator $\hat{B}$ acts at some time $t > t_0$ on the system. We can even say something more: we see that the expectation value on the integrand of 1.19 is taken with respect to the unperturbed density matrix! In this case, the Dirac representation of the operators $\hat{A}^I(t)$ and $\hat{B}^I(t')$ is the Heisenberg representation when the field is off! We can define the term inside of the integrand in 1.19 as the *double-time retarded Green's function*:

$$G^R(t, t') = -i\theta(t - t') \Big\langle \Big[\hat{A}(t), \hat{B}(t') \Big] \Big\rangle_0 \tag{1.20}$$

C. A specific case: $\hat{A}(t) = \hat{n}(\mathbf{r}, t)$ and $\hat{V}(t') = \int d^3r' v_1(\mathbf{r}', t')\hat{n}(\mathbf{r}')$

Suppose we want to measure the change on the systems' density ($\hat{A}(t) = \hat{n}(\mathbf{r}, t)$) after a time dependent perturbation acts on it. Then our operator in Eq.(1.2) becomes

$$\hat{V}(t') = F_{t'}\hat{B}(t') = \int d^3r' v_1(\mathbf{r}', t')\hat{n}(\mathbf{r}') \tag{1.21}$$

We assume here that to obtain the full response we have to perform an integration in space over $\mathbf{r}'$, but we will not write it explicitely for shortness in notation. We also make the inportant observation we are now working on the Heisenberg representation (unless we mention something else). Substitute both operators into equation (1.19).

$$\Delta\langle\hat{n}(\mathbf{r}, t)\rangle = \langle\hat{n}(\mathbf{r}, t)\rangle_t - \langle\hat{n}(\mathbf{r}, t)\rangle_0 = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' v_1(\mathbf{r}, t')\langle[\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')]\rangle_0 \tag{1.22}$$

Before procceding, let us eliminate the time dependency on one of the operators in equation 1.22; we write explicitely both density operators in the Heisenberg picture:

$$\begin{aligned}
\Delta\langle\hat{n}(\mathbf{r}, t)\rangle &= -\frac{i}{\hbar}\int_{-\infty}^{t} dt' v_1(\mathbf{r}', t')\Big\langle \Big(e^{iH_0t}\hat{n}(\mathbf{r})e^{-iH_0t}e^{iH_0t'}\hat{n}(\mathbf{r}')e^{-iH_0t'} \\
&\quad -e^{iH_0t'}\hat{n}(\mathbf{r}')e^{-iH_0t'}e^{iH_0t}\hat{n}(\mathbf{r})e^{-iH_0t}\Big) \Big\rangle_0 \\
&= -\frac{i}{\hbar}\int_{-\infty}^{t} dt' v_1(\mathbf{r}', t')\Big\langle \Big(e^{iH_0(t-t')}\hat{n}(\mathbf{r})e^{-iH_0(t-t')}\hat{n}(\mathbf{r}') \\
&\quad -\hat{n}(\mathbf{r}')e^{iH_0(t-t')}\hat{n}(\mathbf{r})e^{-iH_0(t-t')}\Big) \Big\rangle_0
\end{aligned} \tag{1.23}$$

$$\boxed{\Delta\langle\hat{n}(\mathbf{r}, t)\rangle = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' v_1(\mathbf{r}', t')\langle[\hat{n}(\mathbf{r}, t - t'), \hat{n}(\mathbf{r}')]\rangle_0} \tag{1.24}$$

We define what is known as the density-density correlation function

$$\boxed{\chi(\mathbf{r}, \mathbf{r}', t - t') = -i\theta(t - t')\langle[\hat{n}(\mathbf{r}, (t - t')), \hat{n}(\mathbf{r}')]\rangle_0} \tag{1.25}$$

Also, since we are working on the Heisenberg picture, we know that the density matrix is a constant; even more, in 1.25 the expectation value is taken with respect to the unperturbed density matrix, so we can express 1.24 in terms of the ground state eigenstates Ψ_0 Then we have for the linear response function

$$\boxed{\Delta\langle\hat{n}(\mathbf{r}, t)\rangle = \hbar\int_{-\infty}^{\infty} dt' v_1(\mathbf{r}', t')\chi(\mathbf{r}, \mathbf{r}', t - t')} \tag{1.26}$$

with the density-density response function

$$\boxed{\chi(\mathbf{r},\mathbf{r}',t-t') = -i\theta(t-t')\,\langle\Psi_0|[\hat{n}(\mathbf{r},t-t'),\hat{n}(\mathbf{r}')]|\Psi_0\rangle} \tag{1.27}$$

Of course, we are interested in measuring frequencies (or energies) rather than some time dependent variables. For this, we have to Fourier transform all our quantities in 1.26 [1]

$$\begin{aligned}
\Delta\langle\hat{n}(\mathbf{r},t)\rangle &= \left(\frac{1}{2\pi}\right)^2 \frac{1}{\hbar}\int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega'\; v_1(\mathbf{r}',\omega')e^{-i\omega' t'} \int_{-\infty}^{\infty} d\omega\; e^{-i\omega\left(t-t'\right)}\chi(\mathbf{r},\mathbf{r}',\omega) \\
&= \left(\frac{1}{2\pi}\right)^2 \frac{1}{\hbar}\underbrace{\int_{-\infty}^{\infty} dt' e^{it'\left(\omega-\omega'\right)}}_{2\pi\delta(\omega-\omega')} \int_{-\infty}^{\infty} d\omega'\; v_1(\mathbf{r}',\omega') \int_{-\infty}^{\infty} d\omega\; \chi(\mathbf{r},\mathbf{r}',\omega)e^{-i\omega t} \\
&= \frac{1}{2\pi}\frac{1}{\hbar}\int_{-\infty}^{\infty} d\omega\; v_1(\mathbf{r}',\omega)\chi(\mathbf{r},\mathbf{r}',\omega)e^{-i\omega t}
\end{aligned} \tag{1.28}$$

To have this last equation in the so called *Lehmann representation*, we still need to find an explicit expression for the density-density reponse function $\chi(\mathbf{r},\mathbf{r}',\omega)$ in Eq.(1.28). To achieve this, consider first a general fourier transformation of a two times reponse function in frequency domain:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = -i\int_{-\infty}^{\infty} d\tau\theta(\tau)\langle\Psi_0|\Big[\hat{\alpha}(\tau),\hat{\beta}\Big]|\Psi_0\rangle e^{i\omega\tau} \tag{1.29}$$

where τ is just any time argument for the sake of argumentation. We consider also a complete set of eigenfunctions $\{\Psi_N\}$ of the unperturbed Hamiltonian $\hat{H}_0$. Here $N=0$ represents the ground state, $N=1$ the first excited state and so on and so forth. since its a complete set, it fullfils: $\sum_{i=0}^{N}|\Psi_i\rangle\langle\Psi_i| = 1$. Expand the commutator in 1.29 and insert the completeness relation between the operators

$$\begin{aligned}
\chi(\omega) &= -\frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau\theta(\tau)\langle\Psi_0|\Big[\hat{\alpha}(\tau),\hat{\beta}\Big]|\Psi_0\rangle e^{i\omega\tau} \\
&= -\frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau\sum_{i=0}^{N}\theta(\tau)\Big(\langle\Psi_0|\hat{\alpha}(\tau)|\Psi_i\rangle\langle\Psi_i|\hat{\beta}|\Psi_0\rangle - \langle\Psi_0|\hat{\beta}|\Psi_i\rangle\langle\Psi_i|\hat{\alpha}(\tau)|\Psi_0\rangle\Big)e^{i\omega\tau} \\
&= -\frac{i}{\hbar}\sum_{i=0}^{N}\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau}\Big(\langle\Psi_0|e^{iH_0\tau}\hat{\alpha}e^{-iH_0\tau}|\Psi_i\rangle\langle\Psi_i|\hat{\beta}|\Psi_0\rangle - \langle\Psi_0|\hat{\beta}|\Psi_i\rangle\langle\Psi_i|e^{iH_0\tau}\hat{\alpha}e^{-iH_0\tau}|\Psi_0\rangle\Big) \\
&= -\frac{i}{\hbar}\sum_{i=0}^{N}\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau}\Big(e^{iE_0\tau}e^{-iE_i\tau}\langle\Psi_0|\hat{\alpha}|\Psi_i\rangle\langle\Psi_i|\hat{\beta}|\Psi_0\rangle - \langle\Psi_0|\hat{\beta}|\Psi_i\rangle\langle\Psi_i|\hat{\alpha}|\Psi_0\rangle e^{iE_i\tau}e^{-iE_0\tau}\Big) \\
&= -\frac{i}{\hbar}\sum_{i=0}^{N}\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau}\Big(e^{-i(E_i-E_0)\tau}\langle\Psi_0|\hat{\alpha}|\Psi_i\rangle\langle\Psi_i|\hat{\beta}|\Psi_0\rangle - \langle\Psi_0|\hat{\beta}|\Psi_i\rangle\langle\Psi_i|\hat{\alpha}|\Psi_0\rangle e^{-i(E_0-E_i)\tau}\Big)
\end{aligned} \tag{1.30}$$

[1] remember that the Fourier transform of a function $f(t)$ is defined as

$$f(t) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}f(\omega)e^{-i\omega t}$$

$$= -\frac{i}{\hbar}\sum_{i=0}^{N}\underbrace{\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i(\omega-(E_i-E_0))\tau}}_{\frac{-i}{(\omega-(E_i-E_0))+i\eta}}\Big(\langle\Psi_0|\hat{\alpha}|\Psi_i\rangle\langle\Psi_i|\hat{\beta}|\Psi_0\rangle\Big) - e^{i(\omega+(E_i-E_0))\tau}\Big(\langle\Psi_i|\hat{\beta}|\Psi_i\rangle\langle\Psi_i|\hat{\alpha}|\Psi_0\rangle\Big) \tag{1.31}$$

$$= -\frac{i}{\hbar}\sum_{i=0}^{N}\lim_{\eta\to 0+}\left(\frac{\langle\Psi_0|\hat{\alpha}|\Psi_i\rangle\langle\Psi_i|\hat{\beta}|\Psi_0\rangle}{\omega-(E_i-E_0)+i\eta} - \frac{\langle\Psi_i|\hat{\beta}|\Psi_i\rangle\langle\Psi_i|\hat{\alpha}|\Psi_0\rangle}{\omega+(E_i-E_0)+i\eta}\right) \tag{1.32}$$

where we have integrated in the complex plane the term underbraced. The last expression is called the *Lehmann representation*.

We now see that the Linear response function 1.28 has as an argument the density-density response function in the Lehmann representation 1.32

$$\boxed{\chi(\mathbf{r},\mathbf{r}',\omega) = -\frac{i}{\hbar}\sum_{i=0}^{N}\lim_{\eta\to 0+}\left(\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_i\rangle\langle\Psi_i|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega-(E_N-E_0)+i\eta} - \frac{\langle\Psi_i|\hat{n}(\mathbf{r}')|\Psi_i\rangle\langle\Psi_i|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega+(E_N-E_0)+i\eta}\right)} \tag{1.33}$$

D. Connection with TDDFT

Intuitively we can start to think about a possible relation between Time-dependent density functional theory and the Linear response theory.

Consider now some time-dependent potential of the form

$$v(\mathbf{r},t) = v_0(\mathbf{r}) + v_1(\mathbf{r},t)\theta(t-t_0) \tag{1.34}$$

i.e., the perturbation is switched on at a time t_0; before it, the system is in its ground state. Due to the Runge-Gross theorem, there exist a bijective relation between time dependent potentials and time dependent densities $n(\mathbf{r},t)$. We can write the time dependent density as a functional of the time dependent potential

$$n(\mathbf{r},t) = n[v](\mathbf{r},t) \tag{1.35}$$

Analogous to the time-independent case, the density $n(\mathbf{r},t)$ can be obtained from a non-interacting time-dependent Kohn-Sham system with an effective Kohn-Sham potential v_s

$$v_s[n](\mathbf{r},t) = v(\mathbf{r},t) + \int dt'\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n](\mathbf{r},t) \tag{1.36}$$

But we can also express the density as a functional of the Kohn-Sham potential v_s (bijective relation!)

$$n(\mathbf{r},t) = n[v_s](\mathbf{r},t) \tag{1.37}$$

On the other hand, we already know:

1. If the time-dependent perturbation is small (that we also assumed at the beggining of this section), how to obtain a linear response expression 1.26.

2. If the observable that we want to measure, is the density, we know that form of the density-density reponse function 1.22

Therefore we can use the Kohn-Sham potential to write:

$$\Delta n_1(\mathbf{r},t) = \int dt' \int d^3r' \chi_s(\mathbf{r},t,\mathbf{r}',t') v_{s_1}(\mathbf{r}',t'). \tag{1.38}$$

This leads (at least in principle) to the same linear response as Eq.(1.28). Note the differences though: now we haven't said anything about particle density operators or so. They quantities are functionals (i.e. functions of functions), therefore we have

$$\chi_s(\mathbf{r},t,\mathbf{r}',t') = \left.\frac{\delta n[v_s](\mathbf{r},t)}{\delta v_s(\mathbf{r}',t')}\right|_{v_s[n_0](\mathbf{r})} \tag{1.39}$$

and for the linearized effective potential

$$v_{s_1}[n](\mathbf{r},t) = \underbrace{v_1(\mathbf{r},t)}_{\text{the perturbation}} + \underbrace{\int d^3r' \frac{\Delta n_1(\mathbf{r}',t')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Linearized Hartree potential}} + \underbrace{v_{xc1}(\mathbf{r},t)}_{\text{linearized xc potential}} \tag{1.40}$$

Equation 1.40 is the linear-response equation for TDDFT. The linearized xc potential can be obtained by applying a functional Taylor expansion [2]

$$v_{xc1}[n](\mathbf{r},t) = \int dt' \int d^3r' \underbrace{\left.\frac{\delta v_{xc}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\right|_{n_0(\mathbf{r})}}_{f_{xc}(\mathbf{r},t,\mathbf{r}',t')} \Delta n_1(\mathbf{r},t) \tag{1.41}$$

where, in our case, $\Delta n_1(\mathbf{r}',t')$ is just the linear response in 1.38! We had also defined the xc kernel f_{xc}. Now we can substitute 1.40 into 1.38

[2] Remember that if we have a functional $f[g(x)]$, then its functional Taylor expansion around a point x_0 is $f[g(x)] = f[g_0] + \int dx \frac{\delta f[g_0]}{\delta g(x)} \Delta g(x) + \cdots$

$$\begin{aligned}
\Delta n_1(\mathbf{r},t) &= \int dt' \int d^3r' \chi_s(\mathbf{r},t,\mathbf{r}',t')\Big(v_1(\mathbf{r}',t') + \int d^3r'' \frac{\Delta n_1(\mathbf{r}'',t')}{|\mathbf{r}'-\mathbf{r}''|} + v_{xc1}(\mathbf{r}'',t'')\Big) \\
&= \int dt' \int d^3r' \chi_s(\mathbf{r},t,\mathbf{r}',t')\left(v_1(\mathbf{r}',t') + \underbrace{\int d^3r'' \frac{\Delta n_1(\mathbf{r}'',t')}{|\mathbf{r}'-\mathbf{r}''|}}_{\int dt'' \int d^3\mathbf{r}'' \frac{\delta(t'-t'')\Delta n_1(\mathbf{r}'',t'')}{|\mathbf{r}'-\mathbf{r}''|}} + \int dt'' \int d^3r'' f_{xc}(\mathbf{r}',t',\mathbf{r}'',t'')\Delta n_1(\mathbf{r}'',t'')\right) \\
&= \int dt' \int d^3r' \chi_s(\mathbf{r},t,\mathbf{r}',t')\Big(v_1(\mathbf{r}',t') + \int dt'' \int d^3\mathbf{r}'' \frac{\delta(t'-t'')\Delta n_1(\mathbf{r}'',t'')}{|\mathbf{r}'-\mathbf{r}''|} \\
&+ \int dt'' \int d^3r'' f_{xc}(\mathbf{r}',t',\mathbf{r}'',t'')\Delta n_1(\mathbf{r}'',t'')\Big)
\end{aligned}$$

$$\boxed{\begin{aligned}
\Delta n_1(\mathbf{r},t) = \int dt' \int d^3r' \chi_s(\mathbf{r},t,\mathbf{r}',t') \cdot (v_1(\mathbf{r}',t') + \\
\int dt'' \int d^3\mathbf{r}'' \Big\{ \frac{\delta(t'-t'')}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc}(\mathbf{r}',t',\mathbf{r}'',t'') \Big\} \Delta n_1(\mathbf{r}'',t'')\Big)
\end{aligned}} \tag{1.42}$$

Some things can be said about Eq.(1.42). First, to obtain the linear response, we need to calculate it self-consistently, because both sides depend on $\Delta n_1(\mathbf{r},t)$. Second: the terms on the right hand side are non interacting (Kohn-Sham system).

This equation leads to the same reponse function as if we would take interacting density-density reponse function and the full (non linearized) external potential (1.34) that we can write as

$$\Delta n_1(\mathbf{r},t) = \int dt' \int d^3r' \chi(\mathbf{r},t,\mathbf{r}',t') v_1(\mathbf{r}',t') \tag{1.43}$$

and now simply substitute 1.43 into 1.42

$$\boxed{\begin{aligned}
\int dt' \int d^3r' \chi(\mathbf{r},t,\mathbf{r}',t') v_1(\mathbf{r}',t) = \int dt' \int d^3r' \chi_s(\mathbf{r},t,\mathbf{r}',t') \cdot \\
\Big(v_1(\mathbf{r}',t') + \int dt'' \int d^3\mathbf{r}'' \Big\{ \frac{\delta(t'-t'')}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc}(\mathbf{r}',t',\mathbf{r}'',t'') \Big\} \\
\int dt''' \int d^3r''' \chi(\mathbf{r}'',t'',\mathbf{r}''',t''') v_1(\mathbf{r}''',t''')\Big)
\end{aligned}} \tag{1.44}$$

This equation is general, that means, applies for any potential considered in 1.34. Therefore we can leave appart for a moment the potential terms (of course if the xc kernel and the Hartree potential are independent of the perturbation) (Is that why we can do the following steps???)

We get the next formula (just mupltiply the terms in parenthesis)

$$\chi(\mathbf{r},t,\mathbf{r}',t') = \chi_s(\mathbf{r},t,\mathbf{r}',t') + \int dt'' \int d^3\mathbf{r}'' \int dt''' \int d^3r'''\chi_s(\mathbf{r},t,\mathbf{r}',t')\left\{\frac{\delta(t'-t'')}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc}(\mathbf{r}',t',\mathbf{r}'',t'')\right\}\chi(\mathbf{r}''',t''',\mathbf{r}',t')) \tag{1.45}$$

If you analyse the shape of this last equation, you can clearly see that it is a Dyson type equation. Recall for instance, the NEGF type of equation for a single particle:

$$\underbrace{\hat{G}^+(t-t_0)}_{\text{what we want}} = \underbrace{\hat{G}_0^+(t-t_0)}_{\text{non interacting}} + \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \underbrace{\hat{G}_0^+(t-t')}_{\text{non interacting}} \overbrace{\hat{\Sigma}^+(t'-t'')}^{\text{some quantity relating interacting and non interacting}} \underbrace{\hat{G}^+(t''-t_0)}_{\text{interacting}}$$

In section 1.C we said that the response function depends just on the time differences $t-t'$. And due to Eq.(1.45), the kernel f_{xc} should also depend only on the time differences (yes?) Then we can take the Fourier transformation of the xc kernel

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega) = \int d(t-t')e^{i\omega(t-t')}\frac{\delta v_{xc}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\bigg|_{n_i(\mathbf{r})} \tag{1.46}$$

And transform the full linear Kohn-Sham response function

$$\boxed{\Delta n_1(\mathbf{r},\omega) = \int d^3r'\chi_s(\mathbf{r},\mathbf{r}',\omega)\left[v_1(\mathbf{r}',\omega) + \int d^3x\left\{\frac{1}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc}(\mathbf{r}',\mathbf{r}'',\omega)\right\}\Delta n_1(\mathbf{r}'',\omega)\right] \qquad (1.47)}$$

Look at the similarities with equation 1.28, in fact, of course, they lead to the same exact value for the response. In the present case, the Lehmann representation of the density-density correlation function of the noninteracting case, is given by Eq.(1.33), but instead a many body Hamiltonian with eigenfunctions Ψ_i, we use the auxiliary Kohn-Sham non interacting Hamiltonian with its eigenvalues and eigenfunctions:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_{j,k}^{\infty}(f_k - f_j)\frac{\varphi_j^0(\mathbf{r})\varphi_k^{0*}(\mathbf{r})\varphi_j^{0*}(\mathbf{r})\varphi_k^0(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta} \tag{1.48}$$

where $f_{j/k}$ are the occupation numbers of the Kohn-Sham ground state. We see that the density-density response function has now poles at the excited states of the KS non interacting system.

E. The Casida equation

In practice, to obtain excitation energies that correspond to the real spectrum of the system into consideration, the poles in the Kohn-Sham linear response equations have to be modified. This is the objective of the Casida equations: the correction of the excitation energies arising from the Kohn-Sham auxiliary system 1.48. In other words, obtain an expresion for the real excitation energies Ω_n of the linear response function.

To derive a general type of equation, first we need to include spin in equations in section 1.D. This is done in a straight forward (not trivial!) manner by noticing that now, the eigenvectors are non-spin degenerate, i.e. there are Kohn-Sham orbitals for spin up, and Kohn-Sham orbitals for spin down.
The linear spin-dependent density response is

$$\Delta n_{1\sigma}(\mathbf{r},\omega) = \sum_{\sigma'} \int d^3r' \chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega) v_{s1,\sigma'}(\mathbf{r}',\omega) \tag{1.49}$$

where the spin-dependent linearized effective potential is

$$v_{s_1,\sigma}(\mathbf{r},\omega) = v_{1,\sigma}(\mathbf{r},t) + \sum_{\sigma'} \int d^3r' \left\{ \frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega) \right\} \Delta n_1(\mathbf{r}',t) \tag{1.50}$$

and the Kohn-Sham response function

$$\chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega) = \delta_{\sigma\sigma'} \sum_{j,k}^{\infty} (f_{k,\sigma} - f_{j,\sigma}) \frac{\varphi^0_{j,\sigma}(\mathbf{r})\varphi^{0*}_{k,\sigma}(\mathbf{r})\varphi^{0*}_{j,\sigma}(\mathbf{r}')\varphi^0_{k,\sigma}(\mathbf{r}')}{\omega - (\epsilon_{j,\sigma} - \epsilon_{k,\sigma}) + i\eta}$$

$$\boxed{\chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega) = \delta_{\sigma\sigma'} \sum_{j,k}^{\infty} \gamma_{jk\sigma} \frac{\Phi^*_{jk\sigma}(\mathbf{r})\Phi_{jk\sigma}(\mathbf{r}')}{\omega - \omega_{jk\sigma} + i\eta}} \tag{1.51}$$

where in the last equality we have renamed the following variables:

$$\gamma_{jk\sigma} = f_{k\sigma} - f_{j\sigma} \tag{1.52}$$

$$\Phi_{jk\sigma}(\mathbf{r}) = \varphi^*_{j,\sigma}(\mathbf{r})\varphi_{k,\sigma}(\mathbf{r}) \tag{1.53}$$

$$\omega_{jk\sigma} = \epsilon_{j\sigma} - \epsilon_{k\sigma} \tag{1.54}$$

Now we can start the derivation of the Casida equation.

1. Consider Eq.(1.49) but without the external perturbation term $v_{1,\sigma}(\mathbf{r},t)$

$$\Delta n_{1\sigma}(\mathbf{r},\Omega) = \int d^3r' \chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\Omega) \left(\cancel{v_{1,\sigma}(\mathbf{r},t)} + \sum_{\sigma'\sigma''} \int d^3r'' \left\{ \frac{1}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc,\sigma'\sigma''}(\mathbf{r}',\mathbf{r}'',\Omega) \right\} \Delta n_{1,\sigma'}(\mathbf{r}'',\Omega) \right)$$
$$\Delta n_{1\sigma}(\mathbf{r},\Omega) = \int d^3r' \chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\Omega) \sum_{\sigma'\sigma''} \int d^3r'' \underbrace{\left\{ \frac{1}{|\mathbf{r}'-\mathbf{r}''|} + f_{xc,\sigma'\sigma''}(\mathbf{r}',\mathbf{r}'',\Omega) \right\}}_{f_{Hxc,\sigma'\sigma''}} \Delta n_{1,\sigma'}(\mathbf{r}'',\Omega) \tag{1.55}$$

(remember, in principle, now were are looking for the real excitation energies Ω). where we have also defined the Hartre-exchange-correlation term as $f_{Hxc,\sigma'\sigma''}$.

2. One could argue that the without the perturbation, there is no sense in doing all the calculations for the linear response theory, but the way we now attack the problem is the following: A system can sustain a finite response at its excitation energies without any external stimulation[2]. You can think that at some very early time there was a delta potential that made the system undergo to one of its excited states at some frequency ω

3. The next step is to multiply equation 1.55 times $f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\omega)$ and integrate over $\mathbf{r}$.

$$\underbrace{\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\Delta n_{1\sigma}(\mathbf{r},\Omega)}_{g_{\alpha\sigma}(\mathbf{x},\Omega)} = \int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\int d^3r'\chi_{s,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\Omega)\sum_{\sigma'\sigma''} \underbrace{\int d^3r'' f_{Hxc,\sigma'\sigma''}(\mathbf{r}',\mathbf{r}'',\Omega)\Delta n_{1,\sigma'}(\mathbf{r}'',\Omega)}_{g_{\sigma'\sigma''}(\mathbf{r}',\Omega)} \tag{1.56}$$

4. Now we can substitute Eq.(1.51) into equation 1.56

$$g_{\alpha\sigma}(\mathbf{x},\Omega) = \sum_{\sigma'\sigma''}\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\int d^3r'\delta_{\sigma\sigma'}\sum_{j,k}^{\infty}\gamma_{jk\sigma}\frac{\Phi^*_{jk\sigma}(\mathbf{r})\Phi_{jk\sigma}(\mathbf{r}')}{\Omega-\omega_{jk\sigma}+i\eta}g_{\sigma'\sigma''}(\mathbf{r}',\Omega)$$

$$g_{\alpha\sigma}(\mathbf{x},\Omega) = \sum_{\sigma'\sigma''}\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\int d^3r'\underbrace{\delta_{\sigma\sigma'}}_{\sigma=\sigma'}\sum_{j,k}^{\infty}\gamma_{jk\sigma}\Phi^*_{jk\sigma}(\mathbf{r})\frac{\Phi_{jk\sigma}(\mathbf{r}')}{\Omega-\omega_{jk\sigma}+i\eta}g_{\sigma'\sigma''}(\mathbf{r}',\Omega)$$

$$g_{\alpha\sigma}(\mathbf{x},\Omega) = \sum_{\sigma'}\sum_{j,k}^{\infty}\frac{\gamma_{jk\sigma}}{\Omega-\omega_{jk\sigma}+i\eta}\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\Phi^*_{jk\sigma}(\mathbf{r})\int d^3r'\Phi_{jk\sigma}(\mathbf{r}')g_{\sigma\sigma'}(\mathbf{r}',\Omega)$$

and we define some new quantity $H_{jk\sigma}(\Omega)$

$$g_{\alpha\sigma}(\mathbf{x},\Omega) = \sum_{j,k}^{\infty}\frac{\gamma_{jk\sigma}}{\Omega-\omega_{jk\sigma}+i\eta}\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\Phi^*_{jk\sigma}(\mathbf{r})\underbrace{\sum_{\sigma'}\int d^3r'\Phi_{jk\sigma}(\mathbf{r}')g_{\sigma\sigma'}(\mathbf{r}',\Omega)}_{H_{jk\sigma}(\Omega)}$$

$$g_{\alpha\sigma}(\mathbf{x},\Omega) = \sum_{j,k}^{\infty}\frac{\gamma_{jk\sigma}}{\Omega-\omega_{jk\sigma}+i\eta}\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\Phi^*_{jk\sigma}(\mathbf{r})H_{jk\sigma}(\Omega) \tag{1.57}$$

and multiply 1.57 both sides of the equation on the left by $\sum_{\sigma}\int d^3x\Phi_{j'k'\alpha}(\mathbf{x})$

$$\underbrace{\sum_{\sigma}\int d^3x\Phi_{j'k'\alpha}(\mathbf{x})g_{\alpha\sigma}(\mathbf{x},\Omega)}_{H_{j'k'\alpha}(\Omega)} = \sum_{\sigma}\int d^3x\Phi_{j'k'\alpha}(\mathbf{x})\sum_{j,k}^{\infty}\frac{\gamma_{jk\sigma}}{\Omega-\omega_{jk\sigma}+i\eta}\int d^3r f_{Hxc,\alpha\sigma}(\mathbf{x},\mathbf{r},\Omega)\Phi^*_{jk\sigma}(\mathbf{r})H_{jk\sigma}(\Omega) \tag{1.58}$$

$$H_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \frac{\gamma_{j'k'\sigma'}}{\Omega - \omega_{j'k'\sigma'} + i\eta} \underbrace{\int d^3x \int d^3r \Phi_{jk\sigma}(\mathbf{x}) f_{Hxc,\sigma\sigma'}(\mathbf{x},\mathbf{r},\Omega)\Phi^*_{j'k'\sigma'}(\mathbf{r})}_{K_{jk\sigma,j'k'\sigma'}(\Omega)} H_{j'k'\sigma'}(\Omega) \tag{1.59}$$

In the last equation, we make the change of variables $\alpha \to \sigma;\ \sigma \to \sigma'$ and also $j \leftrightarrow j';\ k \leftrightarrow k'$ to get

$$H_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \frac{\gamma_{j'k'\sigma'}}{\Omega - \omega_{j'k'\sigma'} + i\eta} K_{jk\sigma,j'k'\sigma'}(\Omega) H_{j'k'\sigma'}(\Omega) \tag{1.60}$$

$$H_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \underbrace{\frac{H_{j'k'\sigma'}(\Omega)}{\Omega - \omega_{j'k'\sigma'} + i\eta}}_{\beta_{j'k'\sigma'}(\Omega)} \gamma_{j'k'\sigma'} K_{jk\sigma,j'k'\sigma'}(\Omega)$$

$$H_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \beta_{j'k'\sigma'}(\Omega)\gamma_{j'k'\sigma'} K_{jk\sigma,j'k'\sigma'}(\Omega) \tag{1.61}$$

(a) We then notice the definition of the term $\beta_{j'k'\sigma'}(\Omega)$ and notice that the left hand side of equation 1.61 can be re-written in terms of the function $\beta_{jk\sigma}(\Omega)$.

$$\beta_{jk\sigma}(\Omega)(\Omega - \omega_{jk\sigma} + i\eta) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \beta_{j'k'\sigma'}(\Omega)\gamma_{j'k'\sigma'} K_{jk\sigma,j'k'\sigma'}(\Omega)$$

$$\Omega\beta_{jk\sigma}(\Omega) - (\omega_{jk\sigma} - i\eta)\beta_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \beta_{j'k'\sigma'}(\Omega)\gamma_{j'k'\sigma'} K_{jk\sigma,j'k'\sigma'}(\Omega) \tag{1.62}$$

$$\Omega\beta_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \left\{ \delta_{jj'}\delta_{kk'}\delta_{\sigma\sigma'}(\omega_{j'k'\sigma'} - i\eta)\beta_{j'k'\sigma'}(\Omega) + \beta_{j'k'\sigma'}(\Omega)\gamma_{j'k'\sigma'} K_{jk\sigma,j'k'\sigma'}(\Omega) \right\} \tag{1.63}$$

We added the delta functions on the first term on the right hand side to ensure consistency between equation 1.62 and equation 1.63

$$\boxed{\Omega\beta_{jk\sigma}(\Omega) = \sum_{\sigma'} \sum_{j',k'}^{\infty} \left\{ \delta_{jj'}\delta_{kk'}\delta_{\sigma\sigma'}(\omega_{j'k'\sigma'} - i\eta) + \gamma_{j'k'\sigma'} K_{jk\sigma,j'k'\sigma'}(\Omega) \right\} \beta_{j'k'\sigma'}(\Omega) \tag{1.64}}$$

5. Equation 1.64 is called the Casida equation in a non-matrix type form. Again, this equation yields to the real excitation energies Ω of the system into consideration. Let us analyse two cases

(a) Case 1: $\gamma_{j'k'\sigma'} = 0$

This means, that the occupation numbers of the Kohn-Sham orbitals are the same, i.e.

$$f_{k'\sigma'} = f_{j'\sigma'} \tag{1.65}$$

But that would be that the density-density response function for the Kohn-Sham system is 0! (see Eq.(1.51))

(b) Case 2: $\gamma_{j'k'\sigma'} \neq 0$

This is telling us that in order to have any response in the system, only transitions between occupied and unnocupied Kohn-Sham orbitals are allowed. (That intuitively makes sense). So, we have that either $f_{j\sigma} = 1$ and $f_{k\sigma} = 0$ or the other way around $f_{j\sigma} = 0$ and $f_{k\sigma} = 1$

We then rename the **occupied states** indexes by i, i' and the **unocuppied states** with a, a', and we can separate the sums of Eq.(1.64) accordingly. Then we have

i. when f_j is occupied and f_k is unocuppied

$$\Omega\beta_{ia\sigma}(\Omega) = \sum_{\sigma'}\sum_{j',k'}^{\infty}\Big\{\delta_{ij'}\delta_{ak'}\delta_{\sigma\sigma'}(\omega_{j'k'\sigma'} - i\eta) + \gamma_{j'k'\sigma'}K_{ia\sigma,j'k'\sigma'}(\Omega)\Big\}\beta_{j'k'\sigma'}(\Omega) \tag{1.66}$$

$$\Omega\beta_{ia\sigma}(\Omega) = \sum_{\sigma'}\sum_{j',k'}^{\infty}\Big\{\delta_{ij'}\delta_{ak'}\delta_{\sigma\sigma'}(\omega_{j'k'\sigma'} - i\eta)\beta_{j'k'\sigma'}(\Omega) + \gamma_{j'k'\sigma'}K_{ia\sigma,j'k'\sigma'}(\Omega)\beta_{j'k'\sigma'}(\Omega)\Big\} \tag{1.67}$$

For the sum we have two options in the γ term

$$\gamma_{j'k'\sigma'} = \begin{cases} f_{k'} - f_{j'} = 0 - 1 & \text{if } j' = i' \to k' = a' \\ f_{k'} - f_{j'} = 1 - 0 & \text{if } j' = a' \to k' = i' \end{cases} \tag{1.68}$$

$$\begin{aligned}\Omega\beta_{ia\sigma}(\Omega) = \sum_{\sigma'}\sum_{i',a'}^{\infty}\Big\{&\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}(\omega_{i'a'\sigma'} - i\eta)\beta_{i'a'\sigma'}(\Omega) - K_{ia\sigma,i'a'\sigma'}(\Omega)\beta_{i'a'\sigma'}(\Omega) \\ &+ K_{ia\sigma,a'i'\sigma'}(\Omega)\beta_{a'i'\sigma'}(\Omega)\Big\} \\ \Omega\beta_{ia\sigma}(\Omega) = \sum_{\sigma'}\sum_{i',a'}^{\infty}\Big\{&\Big(\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}(\omega_{i'a'\sigma'} - i\eta) - K_{ia\sigma,i'a'\sigma'}(\Omega)\Big)\beta_{i'a'\sigma'}(\Omega) \\ &+ K_{ia\sigma,a'i'\sigma'}(\Omega)\beta_{a'i'\sigma'}(\Omega)\Big\}\end{aligned} \tag{1.69}$$

ii. when f_j is unoccupied and f_k is ocuppied the same reasoning applies:

$$\Omega\beta_{ai\sigma}(\Omega) = \sum_{\sigma'}\sum_{j',k'}^{\infty}\Big\{\delta_{aj'}\delta_{ik'}\delta_{\sigma\sigma'}(\omega_{j'k'\sigma'} - i\eta) + \gamma_{j'k'\sigma'}K_{ai\sigma,j'k'\sigma'}(\Omega)\Big\}\beta_{j'k'\sigma'}(\Omega) \tag{1.70}$$

$$\Omega\beta_{ai\sigma}(\Omega) = \sum_{\sigma'}\sum_{j',k'}^{\infty}\Big\{\delta_{aj'}\delta_{ik'}\delta_{\sigma\sigma'}(\omega_{j'k'\sigma'} - i\eta)\beta_{j'k'\sigma'}(\Omega) + \gamma_{j'k'\sigma'}K_{ai\sigma,j'k'\sigma'}(\Omega)\beta_{j'k'\sigma'}(\Omega)\Big\} \tag{1.71}$$

$$ \tag{1.72} $$

$$\gamma_{j'k'\sigma'} = \begin{cases} f_{k'} - f_{j'} = 1 - 0 & \text{if } j' = a' \to k' = i' \\ f_{k'} - f_{j'} = 0 - 1 & \text{if } j' = i' \to k' = a' \end{cases} \tag{1.73}$$

$$\begin{aligned} \Omega\beta_{ai\sigma}(\Omega) &= \sum_{\sigma'} \sum_{i',a'}^{\infty} \Big\{ \delta_{aa'}\delta_{ii'}\delta_{\sigma\sigma'}(\omega_{a'i'\sigma'} - i\eta)\beta_{a'i'\sigma'}(\Omega) - K_{ai\sigma,i'a'\sigma'}(\Omega)\beta_{i'a'\sigma'}(\Omega) \Big\} \\ &\quad + K_{ai\sigma,a'i'\sigma'}(\Omega)\beta_{a'i'\sigma'}(\Omega) \Big\} \\ \Omega\beta_{ai\sigma}(\Omega) &= \sum_{\sigma'} \sum_{i',a'}^{\infty} \Big\{ \Big(\delta_{aa'}\delta_{ii'}\delta_{\sigma\sigma'}(\omega_{a'i'\sigma'} - i\eta) + K_{ai\sigma,a'i'\sigma'}(\Omega)\Big)\beta_{a'i'\sigma'}(\Omega) \\ &\quad - K_{ai\sigma,i'a'\sigma'}(\Omega)\beta_{i'a'\sigma'}(\Omega) \Big\} \end{aligned} \tag{1.74}$$

Finally we re-name the variables: $X_{ia\sigma} = -\beta_{ia\sigma}$ and $Y_{ia\sigma} = \beta_{ai\sigma}$ to get

$$\begin{aligned} -\Omega X_{ia\sigma}(\Omega) &= \sum_{\sigma'} \sum_{i',a'}^{\infty} \Big\{ \Big(\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}(\omega_{i'a'\sigma'} - i\eta) - K_{ia\sigma,i'a'\sigma'}(\Omega)\Big)(-X_{i'a'\sigma'}(\Omega)) \\ &\quad + K_{ia\sigma,a'i'\sigma'}(\Omega)Y_{a'i'\sigma'}(\Omega) \Big\} \end{aligned} \tag{1.75}$$

$$\begin{aligned} \Omega Y_{ia\sigma}(\Omega) &= \sum_{\sigma'} \sum_{i',a'}^{\infty} \Big\{ \Big(\delta_{aa'}\delta_{ii'}\delta_{\sigma\sigma'}(\omega_{a'i'\sigma'} - i\eta) + K_{ai\sigma,a'i'\sigma'}(\Omega)\Big)Y_{a'i'\sigma'}(\Omega) \\ &\quad + K_{ai\sigma,i'a'\sigma'}(\Omega)X_{i'a'\sigma'}(\Omega) \Big\} \end{aligned} \tag{1.76}$$

That we can rewrite in a matrix form:

$$\boxed{\Omega \begin{pmatrix} -\mathbb{1} & \mathbb{0} \\ \mathbb{0} & \mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{C} & \mathbb{D} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}} \tag{1.77}$$

where

$$\mathbb{A} = -\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}(\omega_{i'a'\sigma'} - i\eta) + K_{ia\sigma,i'a'\sigma'}(\Omega) \tag{1.78}$$

$$\mathbb{B} = K_{ia\sigma,a'i'\sigma'}(\Omega) \tag{1.79}$$

$$\mathbb{C} = K_{ai\sigma,i'a'\sigma'}(\Omega) \tag{1.80}$$

$$\mathbb{D} = \delta_{aa'}\delta_{ii'}\delta_{\sigma\sigma'}(\omega_{a'i'\sigma'} - i\eta) + K_{ai\sigma,a'i'\sigma'}(\Omega) \tag{1.81}$$

F. Analysing Casida equation

The first observation we can make on the matrix formulation of Casida equation 1.84 is that

$$\omega_{i'a'\sigma'} = \epsilon_{i'\sigma'} - \epsilon_{a'\sigma'} = -(\epsilon_{a'\sigma'} - \epsilon_{i'\sigma'}) = -\omega_{a'i'\sigma'}. \tag{1.82}$$

The second thing to notice is that, since Ω are the real excitation energies, we can safely take the small imaginary part $i\eta \to 0$ (the density-density response function will be finite at $\omega_{jk\sigma}$).
The third thing to notice is that, if the Kohn-Sham orbitals are real, then the we have

$$K_{ia\sigma,i'a'\sigma'}(\Omega) = K_{ia\sigma,a'i'\sigma'}(\Omega) = K_{ai\sigma,i'a'\sigma'}(\Omega) = K_{ai\sigma,a'i'\sigma'}(\Omega) \tag{1.83}$$

therefore we arrive to a more literature-common Casida equation

$$\boxed{\Omega \begin{pmatrix} -\mathbb{1} & \mathbb{0} \\ \mathbb{0} & \mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B} & \mathbb{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}} \tag{1.84}$$

Appendix A: Problematic integrals

In this section we are going to perform the following integral

$$\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau} \tag{A.1}$$

We start by introducing an imaginary part to the frequency and take the limit when it goes to zero

$$\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau} = \lim_{\eta\to 0+}\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i(\omega+i\eta)\tau} \tag{A.2}$$

$$\lim_{\eta\to 0+}\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i(\omega+i\eta)\tau} = \lim_{\eta\to 0+}\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau}e^{i^2\eta\tau} \tag{A.3}$$

$$= \lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} \tag{A.4}$$

$$\tag{A.5}$$

now we integrate by parts choosing

$$u = e^{-\eta\tau} \tag{A.6}$$

$$du = -\eta e^{-\eta\tau}d\tau \tag{A.7}$$

$$dv = e^{i\omega\tau}d\tau \tag{A.8}$$

$$v = \frac{e^{i\omega\tau}}{i\omega} \tag{A.9}$$

$$\begin{aligned}
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} &= \lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty - \lim_{\eta\to 0+}\int_{0}^{\infty} \frac{e^{i\omega\tau}}{i\omega}\left(-\eta e^{-\eta\tau}\right)d\tau \\
&= \lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty + \lim_{\eta\to 0+}\int_{0}^{\infty} \frac{\eta}{i\omega}\left(e^{i\omega\tau}e^{-\eta\tau}\right)d\tau \\
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} - \lim_{\eta\to 0+}\int_{0}^{\infty} \frac{\eta}{i\omega}e^{i\omega\tau}e^{-\eta\tau}d\tau &= \lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty \\
\lim_{\eta\to 0+}\left(1-\frac{\eta}{i\omega}\right)\left(\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau}\right) &= \lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty \\
\left(\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau}\right) &= \lim_{\eta\to 0+}\left(1-\frac{\eta}{i\omega}\right)^{-1}\lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty \\
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} &= \lim_{\eta\to 0+}\left(\frac{i\omega-\eta}{i\omega}\right)^{-1}\lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty \\
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} &= \lim_{\eta\to 0+}\left(\frac{i\omega}{i\omega-\eta}\right)\lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{i\omega}\Big|_0^\infty \\
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} &= \lim_{\eta\to 0+}\left(\frac{\cancel{i\omega}}{i\omega-\eta}\right)\lim_{\eta\to 0+} e^{-\eta\tau}\frac{e^{i\omega\tau}}{\cancel{i\omega}}\Big|_0^\infty \\
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} &= \lim_{\eta\to 0+}\left(\frac{1}{i(\omega+i\eta)}\right)\lim_{\eta\to 0+} e^{-\eta\tau}e^{i\omega\tau}\Big|_0^\infty \\
\lim_{\eta\to 0+}\int_{0}^{\infty} d\tau e^{i\omega\tau}e^{-\eta\tau} &= \lim_{\eta\to 0+}\left(\frac{-i}{\omega+i\eta}\right)\lim_{\eta\to 0+} e^{-\eta\tau}e^{i\omega\tau}\Big|_0^\infty
\end{aligned}$$

$$\lim_{\eta\to 0+}\int_0^\infty d\tau e^{i\omega\tau}e^{-\eta\tau} = \lim_{\eta\to 0+}\left(\frac{-i}{\omega+i\eta}\right)\lim_{\eta\to 0+}\underbrace{e^{-\eta\tau}}_{0\text{ or }1}\underbrace{e^{i\omega\tau}}_{\leq|1|}\Big|_0^\infty$$

$$\boxed{\int_{-\infty}^{\infty} d\tau\theta(\tau)e^{i\omega\tau} = \lim_{\eta\to 0+}\int_0^\infty d\tau e^{i\omega\tau}e^{-\eta\tau} = \lim_{\eta\to 0+}\left(\frac{-i}{\omega+i\eta}\right)} \tag{A.10}$$

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