# Linear Response Theory

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Mainly based on [LL19].

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# **1** Preliminaries

For a Hamiltonian H (viewed as a self-adjoint operator on  $L^2$  space), we additionally assume that H has a discrete spectrum. Then the spectral decomposition of H can be formally written as

$$H = \sum_{n} \lambda_n |\psi_n\rangle \langle\psi_n|, \quad \lambda_n \in \mathbb{R},$$
(1)

with  $\{\psi_n\}$  being a set of Hilbert basis of  $L^2$ . We denote the resolvent set of H by  $\rho(H)$  and the resolvent operator by  $G_{\lambda} = (\lambda I - H)^{-1}$  for  $\lambda \in \rho(H)$ . We also call the resolvent operator the Green's function, which is a common term in physics and PDE. We can also write down the spectral decomposition of  $G_{\lambda}$  as

$$G_{\lambda} = \sum_{n} \frac{|\psi_n\rangle \langle \psi_n|}{\lambda - \lambda_n}, \quad \lambda \in \rho(H).$$
<sup>(2)</sup>

For the operator  $G_{\lambda}$  as a bounded operator on  $L^2$ , we can also view it as an integral operator with kernel  $G_{\lambda}(\mathbf{r}, \mathbf{r}')$  given by

$$G_{\lambda}(\mathbf{r},\mathbf{r}') = \sum_{n} \frac{\psi_{n}(\mathbf{r})\psi_{n}^{*}(\mathbf{r}')}{\lambda - \lambda_{n}}, \quad \lambda \in \rho(H).$$
(3)

That is because  $G_{\lambda}f \in L^2$  can be written as the following integral form

$$G_{\lambda}f(\mathbf{r}) = \int G_{\lambda}(\mathbf{r},\mathbf{r}')f(\mathbf{r}')d\mathbf{r}' = \sum_{n} \frac{\psi_{n}(\mathbf{r})}{\lambda - \lambda_{n}} \int \psi_{n}^{*}(\mathbf{r}')f(\mathbf{r}')d\mathbf{r}' = \sum_{n} \frac{\psi_{n}(\mathbf{r})}{\lambda - \lambda_{n}} \left\langle \psi_{n} | f \right\rangle.$$
(4)

A very useful property of the resolvent operator is that it satisfies the following relation, which is called the resolvent identity:

$$(\lambda_1 - H)^{-1} - (\lambda_2 - H)^{-1} = \frac{(\lambda_1 - \lambda_2)}{(\lambda_1 - H)(\lambda_2 - H)},$$
(5)

$$(\lambda - H_1)^{-1} - (\lambda - H_2)^{-1} = \frac{(H_2 - H_1)}{(\lambda - H_1)(\lambda - H_2)}.$$
(6)

In electronic structure theory, we often need to consider the density operator. For a single-particle system, or independent particle system such as Hartree-Fock or Kohn-Sham density functional theory, the zero-temperature density operator is defined as

$$P = \sum_{n=1}^{N} |\psi_n\rangle \langle\psi_n|, \qquad (7)$$

where  $\{\psi_n\}$  are the occupied orbitals and N is the number of electrons. The density operator is a projection operator, i.e.,  $P^2 = P$ . The range of P is also called the occupied subspace, which is exactly  $\text{Span}(\{\psi_n\}_{n=1}^N)$ . The occupied space is very important in the context of mean-field calculations of electronic structure, since the HF or KSDFT energy functional is precisely defined on it. To be more specific, the energy functionals are

$$\mathcal{E}_{\rm HF} = \mathcal{E}_{\rm HF}(\{\psi_n\}), \quad \mathcal{E}_{\rm DFT} = \mathcal{E}_{\rm DFT}(\{\psi_n\}). \tag{8}$$

At first glance, it seems that those functionals are defined on the whole set of Hilbert basis with respect to the HF or KSDFT Hamiltonian operator. However, we know that they are in fact gauge-invariant, i.e., they are invariant under the unitary transformation of the orbitals. Hence, the *physical* (not *gauge*) quantity is actually the occupied space.

Again, the density operator can be viewed as a bounded operator on  $L^2$  space, and it can be written as an integral operator with kernel  $P(\mathbf{r}, \mathbf{r}')$  given by

$$P(\mathbf{r}, \mathbf{r}') = \sum_{n=1}^{N} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}').$$
(9)

We can also obtain the particle number by taking the trace of the density operator, i.e.,

$$\operatorname{Tr}(P) = \int P(\mathbf{r}, \mathbf{r}) \mathrm{d}\mathbf{r} = \sum_{n=1}^{N} \int \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}) \mathrm{d}\mathbf{r} = N.$$
(10)

In fact, the integral kernel  $P(\mathbf{r}, \mathbf{r})$  or the "diagonal" part of the density operator is the electron density, which is a function of  $\mathbf{r}$  and can be written as

$$\rho(\mathbf{r}) = \sum_{n=1}^{N} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}) = \sum_{n=1}^{N} |\psi_n(\mathbf{r})|^2,$$
(11)

which is pivotal in the density functional theory.

For any Borel measurable function F on the real line, we can in principle employ the functional calculus to define the operator F(H). Recall that H has a discrete spectrum, we can then define the zero-temperature density operator as

$$P = \mathbf{1}_{(-\infty,\mu]}(H) = \sum_{\lambda_n \le \mu} |\psi_n\rangle \langle \psi_n|, \quad \mu \in \mathbb{R},$$
(12)

where  $\mu$  is called the chemical potential or Fermi level. Here we also assume that the spectrum of H satisfies the gapped condition i.e.

$$\lambda_1 \le \dots \le \lambda_N \le \mu < \lambda_{N+1} \le \dots . \tag{13}$$

In physics literature this characteristic function is often called the zero-temperature Fermi-Dirac function denoted as  $f_{\infty}$  ( $f_{\beta}$  when  $\beta = \infty$  is used to denote the zero-temperature limit).

We can avoid the use of Borel functional calculus by equivalently defining the density operator using a contour integral representation

$$P = \frac{1}{2\pi i} \oint_{\Gamma} G_{\lambda} d\lambda = \frac{1}{2\pi i} \oint_{\Gamma} (\lambda - H)^{-1} d\lambda,$$
(14)

where the Jordan curve  $\Gamma$  is a closed contour that encloses only the first N eigenvalues of H which is the eigenvalues corresponding to the occupied orbitals.

TDDFT is proposed in 1984 by Runge and Gross [RG84] for solving the time-dependent Schrödinger equation. However, the rigorous mathematical foundation of TDDFT is much less clear than that of DFT. The main conclusion of TDDFT is the following coupled equations:

$$i\partial_t \psi_j(\mathbf{x}, t) = \left( -\frac{1}{2} \Delta + V_{\text{ext}}(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}[\{\rho(s)\}_{t_0 \le s \le t}](\mathbf{r}) \right) \psi_j(\mathbf{x}, t),$$

$$\rho(\mathbf{r}, t) = \sum_{\sigma} \sum_{j=1}^N |\psi_j(\mathbf{x}, t)|^2.$$
(15)

In practical Runge-Gross TDDFT, the exchange-correlation potential  $V_{\rm xc}$  is often approximated by the adiabatic approximation, i.e.

$$V_{\rm xc}[\{\rho(s)\}_{t_0 \le s \le t}](\mathbf{r}) \approx V_{\rm xc}^{\rm KS}[\rho(t)](\mathbf{r}).$$
(16)

Finally, if we rewrite the Runge-Gross TDDFT equations eq. (15) in terms of the time-dependent density matrix

$$P(t) = \sum_{j=1}^{N} |\psi_j(t)\rangle \langle \psi_j(t)|, \qquad (17)$$

then we can obtain the following closed equation:

$$i\partial_t P(t) = [H[\rho(t)](t), P(t)].$$
(18)

This is the (self-consistent) quantum Liouville equation, which can be seen as an intrinsic representation of TDDFT.

### 2 Perturbation of the Green's function

The perturbation of the Green's function can be characterized mathematically using the Neumann-series expansion. For a bounded operator A on a Hilbert space, we can write down the Neumann series as

$$\sum_{n=0}^{\infty} A^n = (I - A)^{-1}, \quad \text{for } ||A|| < 1.$$
(19)

In the context of electronic structure theory, we often need to consider the perturbation of the original Hamiltonian H by a perturbation via a potential (i.e. multiplicative operator)  $\varepsilon W$ 

$$H_{\varepsilon} = H + \varepsilon W. \tag{20}$$

By the argument of Neumann-series expansion we know that  $\rho(H)$  is open in  $\mathbb{C}$ , therefore for any  $\lambda \in \rho(H)$  and  $\varepsilon$  sufficiently small, by the resolvent indentity we can guarantee that  $G_{\lambda,\varepsilon}$  is also well-defined. Specifically, we can then define the perturbed Green's function as

$$G_{\lambda,\varepsilon} = (\lambda I - H_{\varepsilon})^{-1} = (\lambda I - H - \varepsilon W)^{-1} = G_{\lambda} (I - \varepsilon W (\lambda I - H)^{-1})^{-1} = \sum_{n=0}^{\infty} G_{\lambda} (WG_{\lambda})^n \varepsilon^n.$$
(21)

We can see from the above equation that  $G_{\lambda,\varepsilon}$  is well-defined when  $W(\lambda I - H)^{-1}$  is bounded and  $\varepsilon$  is sufficiently small. We can also get an important insight on how to calculate the perturbed Green's function. It is equivalent to solving a Dyson equation iteratively, i.e.

$$G_{\lambda,\varepsilon}^{(n)} = G_{\lambda} + G_{\lambda}(\varepsilon W)G_{\lambda,\varepsilon}^{(n-1)}, \quad n \ge 1.$$
(22)

We also see that the coefficient of  $\varepsilon$  is  $G_{\lambda}WG_{\lambda}$ , which is the linear response function.

## **3** Perturbation of the density matrix

By the resolvent indentity, we can compute the perturbed density matrix

$$P_{\varepsilon} - P = \frac{1}{2\pi i} \oint_{\Gamma} (G_{\lambda,\varepsilon} - G_{\lambda}) d\lambda$$

$$\stackrel{\text{resolvent indentity}}{=} \frac{1}{2\pi i} \oint_{\Gamma} G_{\lambda,\varepsilon} (\varepsilon W) G_{\lambda} d\lambda$$

$$\stackrel{\text{Neumann series}}{=} \frac{1}{2\pi i} \oint_{\Gamma} \sum_{n=0}^{\infty} G_{\lambda} (WG_{\lambda})^{n} \varepsilon^{n} . (\varepsilon W) G_{\lambda} d\lambda$$

$$= \frac{1}{2\pi i} \oint_{\Gamma} \sum_{n=1}^{\infty} G_{\lambda} (WG_{\lambda})^{n} \varepsilon^{n} d\lambda$$

$$= \frac{\varepsilon}{2\pi i} \int_{\Gamma} G_{\lambda} WG_{\lambda} d\lambda + \mathcal{O}(\varepsilon^{2}).$$
(23)

It is easy to see that the linear response of the density operator is given by

$$\mathfrak{X}_{0}(W) := \frac{1}{2\pi \mathrm{i}} \oint_{\Gamma} G_{\lambda} W G_{\lambda} \mathrm{d}\lambda = \frac{1}{2\pi \mathrm{i}} \int_{\Gamma} (\lambda - H)^{-1} W (\lambda - H)^{-1} \mathrm{d}\lambda.$$
(24)

That is to say, the Frechét derivative of the density operator with respect to the potential perturbation W is given by

$$\frac{\delta P}{\delta V}(W) = \left. \frac{\mathrm{d}P(H + \varepsilon W)}{\mathrm{d}\varepsilon} \right|_{\varepsilon = 0} = \mathfrak{X}_0(W).$$
(25)

By applying the specral decomposition, we can derive

$$\mathfrak{X}_{0}W = \frac{1}{2\pi \mathrm{i}} \oint_{\Gamma} (\lambda I - H)^{-1} W(\lambda I - H)^{-1} \mathrm{d}\lambda = \frac{1}{2\pi \mathrm{i}} \oint_{\Gamma} \sum_{p,q} \frac{|\psi_{p}\rangle\langle\psi_{p}| W |\psi_{q}\rangle\langle\psi_{q}|}{(\lambda - \lambda_{p})(\lambda - \lambda_{q})} \mathrm{d}\lambda$$

$$= \frac{1}{2\pi \mathrm{i}} \sum_{p,q} \oint_{\Gamma} \left( (\lambda - \lambda_{p})^{-1} - (\lambda - \lambda_{q})^{-1} \right) \mathrm{d}\lambda \frac{|\psi_{p}\rangle\langle\psi_{p}| W |\psi_{q}\rangle\langle\psi_{q}|}{\lambda_{p} - \lambda_{q}}.$$
(26)

Note that the integral above is non-vanishing if and only if one of  $\lambda_p$  and  $\lambda_q$  is enclosed by the contour  $\Gamma$ . In other words, one of p and q is occupied and the other is unoccupied. We change the indices to the conventional notation i and a for occupied and unoccupied states respectively. We can then write down the linear response function as

$$\mathfrak{X}_{0}(W) = \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \frac{|\psi_{i}\rangle\langle\psi_{i}| W |\psi_{a}\rangle\langle\psi_{a}|}{\lambda_{i} - \lambda_{a}} + \text{h.c.}$$
(27)

Here h.c. denotes the Hermitian conjugate of the first term.

By taking the diagonal part of the linear response operator, we can obtain the linear response of the electron density. That is, the Frechét derivative of the electron density with respect to the potential perturbation W is given by

$$\frac{\delta\rho}{\delta V}(W) = \operatorname{diag}(\mathfrak{X}_0 W) =: \chi_0 W.$$
(28)

That is, the  $L^2$ -function  $\chi_0 W$  is the kernel function of the operator  $\mathfrak{X}_0 W$  evaluated at the point  $(\mathbf{r}, \mathbf{r})$ 

$$\chi_0 W(\mathbf{r}) = (\mathfrak{X}_0 W)(\mathbf{r}, \mathbf{r}) = \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \langle \psi_i | W | \psi_a \rangle \, \frac{\psi_i(\mathbf{r}) \psi_a^*(\mathbf{r})}{\lambda_i - \lambda_a} + \text{c.c.}$$
(29)

We claim that the operator  $\chi$  is a non-positive operator lower-bounded below by  $-\frac{1}{\Delta}$  where  $\Delta$  is the spectral gap of the Hamiltonian. To see this, we evaluate

$$\operatorname{Tr}(W\chi_{0}W) = \int W(\mathbf{r})(\chi_{0}W)(\mathbf{r}) = \int W(\mathbf{r}) \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \langle \psi_{i} | W | \psi_{a} \rangle \frac{\psi_{i}(\mathbf{r})\psi_{a}^{*}(\mathbf{r})}{\lambda_{i} - \lambda_{a}} d\mathbf{r} + \text{c.c.}$$

$$= \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \frac{|\langle \psi_{i} | W | \psi_{a} \rangle|^{2}}{\lambda_{i} - \lambda_{a}} + \text{c.c.} = -2 \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \frac{|\langle \psi_{i} | W | \psi_{a} \rangle|^{2}}{\lambda_{a} - \lambda_{i}} \leq 0.$$
(30)

Here we note that  $\lambda_a - \lambda_i \ge \Delta \ge 0$  for any  $a \ge N + 1$  and  $i \le N$ . Hence  $\chi_0$  is a non-positive operator. Also, for the bound below, we have

$$-\operatorname{Tr}(W\chi_{0}W) \leq \frac{1}{\Delta} \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} |\langle \psi_{i}|W|\psi_{a}\rangle|^{2} = \frac{1}{\Delta} \sum_{p,q} |\langle \psi_{p}|W|\psi_{q}\rangle|^{2} = \frac{\|W\|_{2}^{2}}{\Delta}.$$
(31)

Here we use the Parseval's identity to obtain the last equality since  $\{\psi_p\}$  and  $\{\psi_q\}$  are both the Hilbert basis of the space. This implies that

$$-\frac{1}{\Delta} \le \sup_{W} \frac{\operatorname{Tr}(W\chi_0 W)}{\|W\|_2^2} \le 0 \Rightarrow -\frac{1}{\Delta} \le \chi_0 \le 0.$$
(32)

In other words, for gapped systems, the linear response of the density with respect to the perturbation of the potential cannot be arbitrarily large.

Recall that the physical quantity we are interested in the regimes of HF or KSDFT is the occupied space. Although it appears that the linear response of the electron density involves the unoccupied states, we can in fact derive an equation that only involves the occupied states. For the kernel function of  $\chi_0$ , we have (assume that all the orbitals are real-valued)

$$\chi_{0}(\mathbf{r},\mathbf{r}') = \sum_{i,a} \frac{\psi_{i}(\mathbf{r})\psi_{a}^{*}(\mathbf{r})\psi_{a}(\mathbf{r}')\psi_{i}^{*}(\mathbf{r}')}{\lambda_{i}-\lambda_{a}} + \text{c.c.}$$

$$= 2\sum_{i,a} \frac{\psi_{i}(\mathbf{r})\psi_{a}(\mathbf{r})\psi_{a}(\mathbf{r}')\psi_{i}(\mathbf{r}')}{\lambda_{i}-\lambda_{a}}$$

$$= 2\sum_{i\in\mathcal{S}_{\text{occ}}} \psi_{i}(\mathbf{r}) \left(\sum_{a\in\mathcal{S}_{\text{unocc}}} \frac{\psi_{a}(\mathbf{r}')\psi_{a}(\mathbf{r})}{\lambda_{i}-\lambda_{a}}\right)\psi_{i}(\mathbf{r}')$$

$$= 2\sum_{i\in\mathcal{S}_{\text{occ}}} \psi_{i}(\mathbf{r})[(I-P)G_{\lambda_{i}}(I-P)](\mathbf{r},\mathbf{r}')\psi_{i}(\mathbf{r}').$$
(33)

Note that the density operator P is also defined only using the occupied states, hence the whole expression above only involves the occupied states. The last equality is obtained by noting that the unoccupied-related term has the form of the kernel function of the Green's function truncated using the projection to the unoccupied space which is Q = I - P.

Once we have the expression of  $\chi_0(\mathbf{r}, \mathbf{r}')$ , the linear response of the electron density with respect to the potential operator W is

$$\chi_0 W(\mathbf{r}) = \int \chi_0(\mathbf{r}, \mathbf{r}') W(\mathbf{r}') d\mathbf{r}' = 2 \sum_{i \in \mathcal{S}_{occ}} \psi_i(\mathbf{r}) \int [(I-P)G_{\lambda_i}(I-P)](\mathbf{r}, \mathbf{r}') \psi_i(\mathbf{r}') W(\mathbf{r}') d\mathbf{r}' =: 2 \sum_{i \in \mathcal{S}_{occ}} \psi_i(\mathbf{r}) \xi_i(\mathbf{r})$$
(34)

Here  $\xi_i$  is the operator  $QG_{\lambda_i}Q$  acting on  $W\psi_i$ , i.e.  $\xi_i$  solves the following Sternheimer equation

$$[Q(\lambda_i I - H)Q]\xi_i = QW\psi_i.$$
(35)

Although the operator at the left-hand side is not invertible since it is truncated by the projection Q, the equation is in fact well-posed since the right-hand side has a vanishing component in the kernel space of  $Q(\lambda_i I - H)Q$ due to the presence of the projection operator Q. Moreover,  $Q(\lambda_i I - H)Q$  is always invertible restricted to the unoccupied space. Therefore the solution is unique.

### **4** Density functional perturbation theory (DFPT)

Recall that in DFT, the effective Hamiltonian depends (*self-consistently*) on the electron density. When considering the perturbation of the Hamiltonian by a potential operator, the change of the electron density will also affect the effective potential. This leads to self-consistent equations similar to the self-consistent KS equations.

The electron density can be implicitly calculated by

$$\rho(\mathbf{r}) = f_{\infty}(H[\rho])(\mathbf{r}, \mathbf{r}). \tag{36}$$

This is a nonlinear equation and  $H[\rho]$  can be written more explicitly as

$$H[\rho] = -\frac{1}{2} \triangle + V_{\text{ext}} + V_{\text{Hxc}}[\rho].$$
(37)

Here,  $V_{\text{ext}}$  denotes the external potential that does not depend on the electron density, and  $V_{\text{Hxc}}$  is the Hartreeexchange-correlation potential that depends on the electron density. We assume that the perturbation of the effective ponetial causes a change of the electron density of  $\delta\rho$ , then

$$V_{\rm Hxc}[\rho + \delta\rho] = V_{\rm Hxc}[\rho] + \frac{\delta V_{\rm Hxc}}{\delta\rho}\delta\rho + \mathcal{O}(\delta\rho^2) =: V_{\rm Hxc}[\rho] + f_{\rm Hxc}[\delta\rho] + \mathcal{O}(\delta\rho^2).$$
(38)

The linearization operator  $f_{\text{Hxc}}$  can be explicitly calculated for some types of exchange-correlation functionals. For example, for the local density approximation (LDA), we have

$$V_{\rm Hxc}[\rho](\mathbf{r}) = \int \mathcal{K}(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}' + v_{\rm xc}(\rho(\mathbf{r})).$$
(39)

Here  $\mathcal{K}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$  is the Coulomb kernel and  $v_{xc}$  is the exchange-correlation potential. The linearization operator  $f_{Hxc}$  can be calculated as

$$(f_{\text{Hxc}}[g])(\mathbf{r}) = \int \mathcal{K}(\mathbf{r}, \mathbf{r}') g(\mathbf{r}') d\mathbf{r}' + \frac{\partial v_{\text{xc}}}{\partial \rho}(\rho(\mathbf{r})) g(\mathbf{r}).$$
(40)

Here we note that the first term in eq. (39) is a linear integral operator and the second term is a multiplication operator. Thus, when considering the change of  $\rho$ , the Hamiltonian operator  $H[\rho + \delta\rho]$  then becomes

$$H[\rho + \delta\rho] = H[\rho] + \delta V_{\text{ext}} + f_{\text{Hxc}}[\delta\rho] + \mathcal{O}(\delta\rho^2).$$
(41)

Here  $\delta V_{\text{ext}}$  is the direct perturbation of the external potential.

Recall that the linear response of the density operator with respect to the perturbation of the potential operator W is given by (eq. (28))

$$\frac{\delta\rho}{\delta V}(W) = \chi_0(W). \tag{42}$$

Here we call  $\chi_0$  the *irreducible polarizability operator*. If we view  $\delta V_{\text{ext}} + f_{\text{Hxc}}[\delta \rho]$  as the perturbation of the Hamiltonian (up to the leading order), we can arrive at the following self-consistent equation for the change of the electron density  $\delta \rho$ :

$$\delta \rho = \chi_0 (\delta V_{\text{ext}} + f_{\text{Hxc}}[\delta \rho]). \tag{43}$$

Formally, we can rewrite the above equation as

$$\delta \rho = (I - \chi_0 f_{\text{Hxc}}[\delta \rho])^{-1} \chi_0 \delta V_{\text{ext}}.$$
(44)

We sometime denote  $\chi := (I - \chi_0 f_{\text{Hxc}})^{-1} \chi_0$  as the *reducible polarizability operator*, which means the linear response of the electron density with respect to the external potential perturbation  $\delta V_{\text{ext}}$ , i.e.

$$\delta \rho = \chi[\delta \rho](\delta V_{\text{ext}}). \tag{45}$$

Note that if we consider the many-body Hamiltonian with *exact* exchange-correlation functional, then the reducible polarizability operator  $\chi$  defined above should *agree* with the *exact* polarizability operator  $\chi_{\text{exact}}$ , which is the many-body linear response.

We mentioned that the above is a formal definition of the reducible polarizability operator. From a physical point of view, if  $I - \chi_0 f_{\text{Hxc}}$  is not invertible, it means that it is possible that a small perturbation of the external potential can cause a large change of the electron density. The invertibility of this operator is called the *stability* condition of electronic structure in the context of KSDFT.

In practice, we often need to calculate the reducible polarizability operator  $\chi$  applying to some vector (function) g, i.e.

$$u(\mathbf{r}) = (\chi g)(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') g(\mathbf{r}') d\mathbf{r}'.$$
(46)

In the form of integral operator, we write

$$u = \chi g = (I - \chi_0 f_{\text{Hxc}})^{-1} \chi_0 g \Rightarrow u - \chi_0 f_{\text{Hxc}} u = \chi_0 g.$$
(47)

This is equation can be solved using fixed-point iteration of u, say

$$u^{(n+1)} = \chi_0 g + \chi_0 f_{\text{Hxc}} u^{(n)}, \quad n \ge 0.$$
(48)

Or equivalently, we can also write down the Dyson series as

$$u = \chi_0 g + \chi_0 f_{\text{Hxc}} u = \chi_0 g + \chi_0 f_{\text{Hxc}} \chi_0 g + \chi_0 f_{\text{Hxc}} \chi_0 g + \cdots .$$
(49)

We can see that we only need to compute  $\chi_0$  applied to some function. This can be directly obtained by solving the Sternheimer equation eq. (35), hence only involes the occupied states in the context of DFPT.

Some important applications of DFPT can be found in [LL19].

#### **5** Time-dependent DFPT

To deal with the quantum Liouville equation, we define the time-ordered exponential operator

$$A(t) = \mathcal{T} \exp\left(-i \int_0^t H(s) ds\right) A(0).$$
(50)

Here the  $\mathcal{T}$  is applied such that A(t) solves the following time-dependent linear equation

$$i\partial_t A(t) = [H(t), A(t)], \quad A(0) = A.$$
 (51)

We also denote the "time-ordered exponential propagator" as

$$\mathcal{U}(t_2, t_1) = \mathcal{T} \exp\left(-i \int_{t_1}^{t_2} H(t) dt\right)$$
(52)

which is a unitary operator such that  $\mathcal{U}(t_2, t_1) = \mathcal{U}(t_1, t_2)^*$  if  $t_1 > t_2$ . We can then express the solution to the quantum Liouville equation as

$$P(t) = \mathcal{U}(t,0)P(0)\mathcal{U}(0,t).$$
(53)

Now we consider the perturbation of the Hamiltonian by  $\varepsilon W(t)$ , i.e.

$$H_{\varepsilon}(t) = H(t) + \varepsilon W(t), \quad P_{\varepsilon}(t) = \mathcal{U}_{\varepsilon}(t,0)P(0)\mathcal{U}_{\varepsilon}(0,t).$$
(54)

Here  $\mathcal{U}_{\varepsilon}(t_2, t_1)$  is defined such that  $A_{\varepsilon}(t) = \mathcal{U}_{\varepsilon}(t, 0)A_{\varepsilon}(0)$  solves  $i\partial_t A_{\varepsilon}(t) = H_{\varepsilon}(t)A_{\varepsilon}(t) = H(t)A_{\varepsilon}(t) + \varepsilon W(t)A_{\varepsilon}(t)$ . By Duhamel's principle, we have

$$A_{\varepsilon}(t) = \mathcal{U}(t,0)A_{\varepsilon}(0) - \mathrm{i}\varepsilon \int_{0}^{t} \mathcal{U}(t,s)W(s)A_{\varepsilon}(s)\mathrm{d}s = \mathcal{U}(t,0)A_{\varepsilon}(0) - \mathrm{i}\varepsilon \int_{0}^{t} \mathcal{U}(t,s)W(s)\mathcal{U}_{\varepsilon}(s,0)A_{\varepsilon}(0)\mathrm{d}s.$$
 (55)

Therefore

$$\mathcal{U}_{\varepsilon}(t,0) = \mathcal{U}(t,0) - \mathrm{i}\varepsilon \int_{0}^{t} \mathcal{U}(t,s)W(s)\mathcal{U}_{\varepsilon}(s,0)\mathrm{d}s = \mathcal{U}(t,0) - \mathrm{i}\varepsilon \int_{0}^{t} \mathcal{U}(t,s)W(s)\mathcal{U}(s,0)\mathrm{d}s + \mathcal{O}(\varepsilon^{2}).$$
(56)

Note that this can be viewed as the time-dependent generalization of the Dyson equation eq. (21).

Hence, up to  $\mathcal{O}(\varepsilon^2)$ , we have

$$P_{\varepsilon}(t) = \mathcal{U}_{\varepsilon}(t,0)P(0)\mathcal{U}_{\varepsilon}(0,t)$$
$$= \mathcal{U}(t,0)P(0)\mathcal{U}(0,t) - \mathrm{i}\varepsilon \int_{0}^{t} \mathcal{U}(t,s)W(s)\mathcal{U}(s,0)P(0)\mathcal{U}(0,t)\mathrm{d}s + \mathrm{i}\varepsilon\mathcal{U}(t,0)P(0)\int_{0}^{t} \mathcal{U}(0,s)W(s)\mathcal{U}(s,t)\mathrm{d}s + \mathcal{O}(\varepsilon^{2}).$$
(57)

Now we are at the place to compute the Frechét derivative of the density operator with respect to the perturbation of the potential operator W. We have

$$(\mathfrak{X}_{0}W)(t) = \frac{\delta P}{\delta V}(W) = \left.\frac{\mathrm{d}P_{\varepsilon}}{\mathrm{d}\varepsilon}\right|_{\varepsilon=0} = -\mathrm{i}\int_{0}^{t}\mathcal{U}(t,s)W(s)\mathcal{U}(s,0)P(0)\mathcal{U}(0,t)\mathrm{d}s + \mathrm{h.c.}$$
(58)

Let us now consider a system that lies in the ground state before the perturbation. That is, the unperturbed Hamiltonian is time-independent and the initial density matrix is the zero-temperature density matrix

$$H(t) \equiv H, \quad P(0) \equiv P_0 = f_{\infty}(H - \mu), \quad \mathcal{U}(t, s) = \exp(-i(t - s)H).$$
 (59)

Note additionally that  $P_0$  is obtained via functional calculus of the unperturbed Hamiltonian H, it commutes with U(t, s). Then eq. (58) can be simplified as

$$(\mathfrak{X}_{0}W)(t) = -i\left(\int_{-\infty}^{t} e^{-i(t-s)H}W(s)\exp(-i(s-0)H)e^{i(t-s)H}ds\right)P_{0} + \text{h.c.} = -i\int_{-\infty}^{t} e^{-i(t-s)H}[W(s), P_{0}]e^{i(t-s)H}ds.$$
(60)

Here we imagine that the perturbation starts at some time after  $t = -\infty$ . Note that the starting time 0 above is arbitrarily and we may relabel it and remove the arbitrarity by setting  $-\infty$  starting point. This will also significantly simplify the derivation of the linear response function.

Applying the spectral decomposition of H, we may rewrite eq. (60) as

$$(\mathfrak{X}_{0}W)(t) = -\mathrm{i}\sum_{p,q} |\psi_{p}\rangle\langle\psi_{p}| \int_{-\infty}^{t} e^{-\mathrm{i}(t-s)(\lambda_{p}-\lambda_{q})} [W(s), P_{0}] \mathrm{d}s \, |\psi_{q}\rangle\langle\psi_{q}| \,.$$
(61)

We want to rewrite this expression in the frequency domain. To do this, we need to compute the Fourier transform of the function  $e^{-i(t-s)\omega_0}W(s)\Theta(t-s)$ , i.e.

$$\int_{-\infty}^{t} e^{-\mathrm{i}(t-s)\omega_0} W(s) \mathrm{d}s = \int_{-\infty}^{\infty} e^{-\mathrm{i}(t-s)\omega_0} W(s) \Theta(t-s) \mathrm{d}s = \left[ e^{-\mathrm{i}\omega_0 t} \Theta(t) * W(t) \right] (\omega).$$
(62)

Note that the Fourier transform of a convolution is the product of the Fourier transforms. Hence we can write down the Fourier transform of the above expression as

$$\mathcal{F}\left(\int_{-\infty}^{t} e^{-\mathrm{i}(t-s)\omega_0} W(s) \mathrm{d}s\right) = e^{-\widehat{\mathrm{i}\omega_0 t}\Theta}(t)(\omega)\widehat{W}(\omega).$$
(63)

For the Fourier transform of the Heaviside function, we have

$$\int_{-\infty}^{\infty} e^{-\mathrm{i}\omega_0 t} \Theta(t) e^{\mathrm{i}\omega t} \mathrm{d}t \sim \lim_{\eta \to 0+} \int_{-\infty}^{0} e^{-(\eta + \mathrm{i}(\omega - \omega_0))t} \mathrm{d}t = \lim_{\eta \to 0+} \frac{1}{\omega - \omega_0 + \mathrm{i}\eta} = \pi \delta(\omega - \omega_0) + \mathrm{i}\mathcal{P}\left(\frac{1}{\omega - \omega_0}\right).$$
(64)

Here we denote  $\mathcal{P}$  as the Cauchy principal value. Hence we can write down the Fourier transform of the above expression as

$$\mathcal{F}\left(\int_{-\infty}^{t} e^{-\mathrm{i}(t-s)\omega_0} W(s) \mathrm{d}s\right) = \lim_{\eta \to 0+} \frac{\hat{W}(\omega)}{\omega - \omega_0 + \mathrm{i}\eta} = \pi \widehat{W}(\omega_0)\delta(\omega - \omega_0) + \mathrm{i}\mathcal{P}\left(\frac{\widehat{W}(\omega)}{\omega - \omega_0}\right).$$
(65)

Plugging this back into eq. (61), we can obtain the linear response function in the frequency domain as

$$\mathcal{F}(\mathfrak{X}_{0}W)(\omega) = \lim_{\eta \to 0+} \sum_{p,q} \frac{|\psi_{p}\rangle\langle\psi_{p}| [\hat{W}(\omega), P_{0}] |\psi_{q}\rangle\langle\psi_{q}|}{\omega - (\lambda_{p} - \lambda_{q}) + i\eta} = \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{occ}, a \in \mathcal{S}_{unocc}} \frac{|\psi_{a}\rangle\langle\psi_{a}| \hat{W}(\omega) |\psi_{i}\rangle\langle\psi_{i}|}{\omega - (\lambda_{a} - \lambda_{i}) + i\eta} - \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{occ}, a \in \mathcal{S}_{unocc}} \frac{|\psi_{i}\rangle\langle\psi_{i}| \hat{W}(\omega) |\psi_{a}\rangle\langle\psi_{a}|}{\omega - (\lambda_{i} - \lambda_{a}) + i\eta}.$$
(66)

Here we use the fact that  $P_0 |\psi_i\rangle\langle\psi_i| = |\psi_i\rangle\langle\psi_i|$  and  $P_0 |\psi_a\rangle\langle\psi_a| = 0$  for occupied and unoccupied states respectively. We can also write down the kernel function of the linear response function in the frequency domain as

$$\mathcal{F}(\mathfrak{X}_{0}W)(\mathbf{r},\mathbf{r}') = \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \frac{\langle \psi_{a} | W(\omega) | \psi_{i} \rangle \psi_{a}(\mathbf{r}) \psi_{i}^{*}(\mathbf{r}')}{\omega - (\lambda_{a} - \lambda_{i}) + \mathrm{i}\eta} - \frac{\langle \psi_{i} | W(\omega) | \psi_{a} \rangle \psi_{i}(\mathbf{r}) \psi_{a}^{*}(\mathbf{r}')}{\omega - (\lambda_{i} - \lambda_{a}) + \mathrm{i}\eta}.$$
 (67)

Taking the diagonal part, we obtain

$$\chi_0 W(\mathbf{r};\omega) = \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \frac{\langle \psi_a | \dot{W}(\omega) | \psi_i \rangle \, \psi_a(\mathbf{r}) \psi_i^*(\mathbf{r})}{\omega - (\lambda_a - \lambda_i) + \mathrm{i}\eta} - \frac{\langle \psi_i | \dot{W}(\omega) | \psi_a \rangle \, \psi_i(\mathbf{r}) \psi_a^*(\mathbf{r})}{\omega - (\lambda_i - \lambda_a) + \mathrm{i}\eta}. \tag{68}$$

Here we use the notation  $\chi_0(\mathbf{r}, \mathbf{r}'; \omega)$  to denote the kernel function of the operator  $\chi_0$  in the frequency domain, with a little bit of abuse of notation. Again, the kernel of irreducible *dynamic* polarizability operator  $\chi_0$  in the frequency domain is given by

$$\chi_0(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \frac{\psi_a^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_a(\mathbf{r})\psi_i^*(\mathbf{r})}{\omega - (\lambda_a - \lambda_i) + \mathrm{i}\eta} - \frac{\psi_i^*(\mathbf{r}')\psi_a(\mathbf{r}')\psi_i(\mathbf{r})\psi_a^*(\mathbf{r})}{\omega - (\lambda_i - \lambda_a) + \mathrm{i}\eta}.$$
 (69)

eq. (69) is related to eq. (68) by noting that

$$\chi_0 W(\mathbf{r}; \omega) = \int \chi_0(\mathbf{r}, \mathbf{r}'; \omega) W(\mathbf{r}') \mathrm{d}\mathbf{r}'.$$
(70)

The procedure of obtaining the expression of the irreducible dynamic polarizability operator eq. (69) can be summarized as

Derive  $\mathcal{F}(\mathfrak{X}_0 W)(\omega) \to \text{Taking the kernel function } \mathcal{F}(\mathfrak{X}_0 W)(\omega)(\mathbf{r}, \mathbf{r}') \to \text{Taking the diagonal part } \chi_0 W(\mathbf{r}; \omega) \to \text{Taking the kernel function } \chi_0(\mathbf{r}, \mathbf{r}'; \omega)$ 

In TDDFT, again, we take into account the change of the potential induced by the change of density, where the latter is described using the *reducible dynamic polarizability operator* denoted as  $\chi(\omega)$ . Following the same derivation as in DFPT, we have

$$\chi(\omega) = (I - \chi_0(\omega) f_{\text{Hxc}}[\delta\rho](\omega))^{-1} \chi_0(\omega).$$
(71)

In almost all practical TDDFT calculations, we apply *adiabatic approximation* to make  $f_{\rm Hxc}$  frequency-independent.

If we want to calculate  $u(\mathbf{r}) = (\chi g)(\mathbf{r})$ , we only need to employ the following iteration scheme to solve the Dyson equation

$$u^{(n+1)} = \chi_0 g + \chi_0 f_{\text{Hxc}} u^{(n)}, \quad n \ge 0.$$
(72)

To calculate the irreducible dynamic polarizability operator  $\chi_0$  applying to a function, we note that

$$\begin{aligned} (\chi_{0}g)(\mathbf{r},\omega) &= \int \chi_{0}(\mathbf{r},\mathbf{r}';\omega)g(\mathbf{r}')d\mathbf{r}' = \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}},a \in \mathcal{S}_{\text{unocc}}} \frac{\langle \psi_{a}|g|\psi_{i} \rangle \psi_{a}(\mathbf{r})\psi_{i}^{*}(\mathbf{r})}{\omega - (\lambda_{a} - \lambda_{i}) + \mathrm{i}\eta} - \frac{\langle \psi_{i}|g|\psi_{a} \rangle \psi_{i}(\mathbf{r})\psi_{a}^{*}(\mathbf{r})}{\omega - (\lambda_{i} - \lambda_{a}) + \mathrm{i}\eta} \\ &= \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}} \int [Q(\omega - H + \lambda_{i} + \mathrm{i}\eta)^{-1}Q](\mathbf{r},\mathbf{r}')\psi_{i}(\mathbf{r}')g(\mathbf{r}')d\mathbf{r}'\psi_{i}^{*}(\mathbf{r}) \\ &= \sum_{i \in \mathcal{S}_{\text{occ}}} \psi_{i}(\mathbf{r}) \int [Q(\omega + H - \lambda_{i} + \mathrm{i}\eta)^{-1}Q](\mathbf{r},\mathbf{r}')\psi_{i}^{*}(\mathbf{r}')g(\mathbf{r}')d\mathbf{r}' \\ &= \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}} [Q(\omega - H + \lambda_{i} + \mathrm{i}\eta)^{-1}Q](\psi_{i}g)(\mathbf{r})\psi_{i}^{*}(\mathbf{r}) + \psi_{i}(\mathbf{r})[Q(\omega + H - \lambda_{i} + \mathrm{i}\eta)^{-1}Q](\psi_{i}^{*}g)(\mathbf{r}) \\ &=: \left(\lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}} [\xi_{i,+}(\omega)\psi_{i}^{*} + \psi_{i}\xi_{i,-}(\omega)]\right)(\mathbf{r}). \end{aligned}$$

$$(73)$$

Here, just like eq. (35),  $\xi_{i,\pm}(\omega)$  solves the frequency-dependent Sternheimer equation

$$Q(\omega - H + \lambda_i + i\eta)Q\xi_{i,+}(\omega) = Q(\psi_i g(\omega)), \quad Q(\omega + H - \lambda_i + i\eta)Q\xi_{i,-}(\omega) = Q(\psi_i^* g(\omega)).$$
(74)

The numerical solution of the above frequency-dependent equation is much more difficult than the frequencyindependent equation, though they are formally similar.

### 6 Moving forward to many-body perturbation theory

In this section we consider a N-body Hamiltonian H with eigenpairs  $(E_k, \Psi_k)$ . The perturbation of the many-body density matrix also has the following form

$$P_{\varepsilon} - P = \frac{\varepsilon}{2\pi i} \int_{\Gamma} G_{\lambda} W G_{\lambda} d\lambda + \mathcal{O}(\varepsilon^2).$$
(75)

Here  $G_{\lambda} = (\lambda I - H)^{-1}$  is a many-body Green's function. Note that the many-body ground state is given by  $P = |\Psi_0\rangle\langle\Psi_0|$ , so the contour  $\Gamma$  is chosen such that it encloses only the ground state energy. Therefore, in spectral decomposition form, we have

$$P_{\varepsilon} - P = \varepsilon \left( \sum_{k \neq 0} \frac{|\Psi_0\rangle \langle \Psi_0| W |\Psi_k\rangle \langle \Psi_k|}{E_0 - E_k} \right) + \text{h.c.}$$
(76)

As a result, we have the following N-body polarizability operator

$$\mathfrak{X}W = \sum_{k \neq 0} \frac{|\Psi_0\rangle \langle \Psi_0| W |\Psi_k\rangle \langle \Psi_k|}{E_0 - E_k} + \text{h.c.}$$
(77)

Note that the many-body polarizability operator is linear, therefore there is *NO* distinction between the irreducible and reducible polarizability operator.

#### 6.1 Connection to effective one-body DFT

In this section, we use  $W^N$  to denote the many-body potential operator and W to denote the one-body potential operator.

To see the connection to effective one-body DFT, we consider the real-space representation of the perturbation of the effective potential. For simplicity, we assume that  $W^N$  is a local potential operator i.e.

$$W^{N}(\{\mathbf{r}_{i}\}) = \sum_{i=1}^{N} W(\mathbf{r}_{i}) = \sum_{i=1}^{N} \int W(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}_{i})d\mathbf{r} = \int W(\mathbf{r})\hat{\rho}(\mathbf{r})d\mathbf{r}, \quad \hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_{i}).$$
(78)

Note that

$$\operatorname{Tr}(\hat{\rho}(\mathbf{r}) |\Psi_0\rangle\!\langle\Psi_0|) = \rho(\mathbf{r}).$$
(79)

Here the right-hand side is the single-particle density.

We compute the bilinear form w.r.t. the many-body polarizability operator

$$\operatorname{Tr}(U^{N}\mathfrak{X}W^{N}) = \sum_{k\neq 0} \frac{\langle \Psi_{k}|U^{N}|\Psi_{0}\rangle \ \langle \Psi_{0}|W^{N}|\Psi_{k}\rangle}{E_{0} - E_{k}} + \sum_{k\neq 0} \frac{\langle \Psi_{0}|U^{N}|\Psi_{k}\rangle \ \langle \Psi_{k}|W^{N}|\Psi_{0}\rangle}{E_{0} - E_{k}}.$$
(80)

Assume that the test function  $U^N$  is also a local potential with  $U^N({\mathbf{r}_i}) = \sum_{i=1}^N U(\mathbf{r}_i)$ , then we can (e.g.) compute

$$\langle \Psi_k | U^N | \Psi_0 \rangle = \int \langle \Psi_k | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle U(\mathbf{r}) d\mathbf{r},$$
(81)

$$\langle \Psi_k | U^N | \Psi_0 \rangle \, \langle \Psi_0 | W^N | \Psi_k \rangle = \int \langle \Psi_k | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \, U(\mathbf{r}) \, \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_k \rangle \, W(\mathbf{r}') \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}'. \tag{82}$$

Induced by this, we define an integral operator  $\chi^{exact}$  with kernel function

$$\chi^{\text{exact}}(\mathbf{r},\mathbf{r}') = \sum_{k\neq 0} \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_k \rangle \, \langle \Psi_k | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{E_0 - E_k} + \sum_{k\neq 0} \frac{\langle \Psi_k | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \, \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_k \rangle}{E_0 - E_k}.$$
(83)

Then for any bilinear form  $Tr(U^N \mathfrak{X} W^N)$ , we have

$$\operatorname{Tr}(U^{N}\mathfrak{X}W^{N}) = \int \chi^{\operatorname{exact}}(\mathbf{r}, \mathbf{r}')U(\mathbf{r})W(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' =: \operatorname{Tr}(U\chi^{\operatorname{exact}}W).$$
(84)

We point out that eq. (83) can be viewed as the many-body generalization of the irreducible polarizability operator  $\chi_0$  in the one-body case eq. (29). However, we should also note that in the context of DFT, the reducible polarizability operator  $\chi$  is actually a better approximation to the many-body polarizability operator  $\chi^{\text{exact}}$ , given that the exchange-correlation functional is exact.

#### 6.2 Casida formalism

Similar to the static case, we can also derive the time-dependent perturbation theory for many-body systems. This can be done by considering first the many-body dynamics exact polarizability operator

$$\mathfrak{X}^{\text{exact}}(t) = -\mathrm{i} \int_{-\infty}^{t} e^{-\mathrm{i}(t-s)H} [W(s), P] e^{\mathrm{i}(t-s)H} \mathrm{d}s = -\mathrm{i} \sum_{p,q} |\Psi_p\rangle \langle \Psi_p| \int_{-\infty}^{t} e^{-\mathrm{i}(t-s)(E_p - E_q)} [W(s), P] \mathrm{d}s |\Psi_q\rangle \langle \Psi_q|$$
(85)

By Fourier transform, we can obtain the frequency-dependent polarizability operator

$$(\mathfrak{X}^{\text{exact}}W)(\omega) = \lim_{\eta \to 0+} \sum_{p,q} \frac{|\Psi_p\rangle \langle \Psi_p| [W(\omega), P] |\Psi_q\rangle \langle \Psi_q|}{\omega - (E_p - E_q) + i\eta}$$

$$= \lim_{\eta \to 0+} \sum_{k \neq 0} \frac{|\Psi_k\rangle \langle \Psi_k| \hat{W}(\omega) |\Psi_0\rangle \langle \Psi_0|}{\omega - (E_k - E_0) + i\eta} - \sum_{k \neq 0} \frac{|\Psi_0\rangle \langle \Psi_0| \hat{W}(\omega) |\Psi_k\rangle \langle \Psi_k|}{\omega - (E_0 - E_k) + i\eta}.$$
(86)

Again, we take the kernel function, take the diagonal part and take the kernel function once more, we have the following exact many-body dynamics polarizability operator

$$\chi^{\text{exact}}(\mathbf{r},\mathbf{r}';\omega) = \lim_{\eta \to 0+} \sum_{k \neq 0} \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_k \rangle \, \langle \Psi_k | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{\omega - (E_k - E_0) + \mathrm{i}\eta} - \frac{\langle \Psi_k | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \, \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_k \rangle}{\omega - (E_0 - E_k) + \mathrm{i}\eta}.$$
(87)

From this, we can get a very important insight. We can see in eq. (87) that the poles of  $\chi^{\text{exact}}(\omega)$  take the form of  $E_k - E_0$ , which is the neutral excitation energy. In the context of TDDFPT, since the reducible polarizability operator  $\chi$  is a good approximation to the exact polarizability operator  $\chi^{\text{exact}}$ , we can also expect that the poles of  $\chi(\omega)$  take the form of  $E_k - E_0$ . This is the basis of Casida formalism.

Recall eq. (71), we have

$$\chi(\omega)f = (I - \chi_0(\omega)f_{\text{Hxc}}(\omega))^{-1}f$$
(88)

for some function f. To evaluate the poles of  $\chi(\omega)$ , we only need to evaluate the zeros of  $\chi^{-1}(\omega)$ . Again, we consider the test function f, then the candidate of the zero of  $\chi^{-1}(\omega)$  solves the following equation

$$\chi_0(\omega) f_{\rm Hxc}(\omega) f = f. \tag{89}$$

In order to solve this equation, we do the following steps:

- We first truncate the set of unoccupied orbitals up to some fixed energy level  $E_{\rm cut}$ .
- We consider the following set of test functions:

$$\Psi_{ai} := \psi_a \psi_i^*, \quad \Psi_{ia} := \Psi_{ai}^* = \psi_i \psi_a^*, \quad i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}.$$
(90)

• We expand the test function f in the above basis set, i.e.

$$f = \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} (f_{ai} \Psi_{ai} + f_{ia} \Psi_{ia}).$$
(91)

• Recall the definition of the irreducible polarizability operator  $\chi_0$  in eq. (69) and note that the Heisenberg evolution of  $|\Psi_{ai}\rangle\langle\Psi_{ai}|$  will give a Bohr frequency  $\omega_{ai} = E_a - E_i$ , we have

$$\chi_0 W(\omega) = \lim_{\eta \to 0+} \sum_{i \in \mathcal{S}_{\text{occ}}, a \in \mathcal{S}_{\text{unocc}}} \sum_{pq} \frac{\langle \Psi_{ai} | W(\omega) | \Psi_{pq} \rangle | \Psi_{ai} \rangle \langle \Psi_{pq} |}{\omega - \omega_{ai} + \mathrm{i}\eta} - \frac{\langle \Psi_{ia} | W(\omega) | \Psi_{pq} \rangle | \Psi_{ia} \rangle \langle \Psi_{pq} |}{\omega - \omega_{ia} + \mathrm{i}\eta}.$$
(92)

Therefore, eq. (89) can be rewritten as

$$\lim_{\eta \to 0^{+}} \sum_{i,j \in \mathcal{S}_{\text{occ}},a,b \in \mathcal{S}_{\text{unocc}}} \left( \frac{\langle \Psi_{ai} | f_{\text{Hxc}} | \Psi_{bj} \rangle}{\omega - \omega_{ai} + i\eta} | \Psi_{ai} \rangle - \frac{\langle \Psi_{ia} | f_{\text{Hxc}} | \Psi_{bj} \rangle}{\omega + \omega_{ai} + i\eta} | \Psi_{ia} \rangle \right) f_{bj} 
+ \sum_{i,j \in \mathcal{S}_{\text{occ}},a,b \in \mathcal{S}_{\text{unocc}}} \left( \frac{\langle \Psi_{ai} | f_{\text{Hxc}} | \Psi_{jb} \rangle}{\omega - \omega_{ai} + i\eta} | \Psi_{ai} \rangle - \frac{\langle \Psi_{ia} | f_{\text{Hxc}} | \Psi_{jb} \rangle}{\omega + \omega_{ai} + i\eta} | \Psi_{ia} \rangle \right) f_{jb}$$

$$= \sum_{i \in \mathcal{S}_{\text{occ}},a \in \mathcal{S}_{\text{unocc}}} f_{ai} | \Psi_{ai} \rangle + f_{ia} | \Psi_{ia} \rangle .$$
(93)

• Finally, we match the coefficients of  $\Psi_{ai}$  and  $\Psi_{ia}$  to obtain the following non-Hermitian eigenvalue equation

$$\begin{cases} \lim_{\eta \to 0+} \sum_{j \in \mathcal{S}_{\text{occ}}, b \in \mathcal{S}_{\text{unocc}}} \frac{\langle \Psi_{ai} | f_{\text{Hxc}} | \Psi_{bj} \rangle}{\omega - \omega_{ai} + i\eta} f_{bj} + \frac{\langle \Psi_{ia} | f_{\text{Hxc}} | \Psi_{jb} \rangle}{\omega - \omega_{ai} + i\eta} f_{jb} = f_{ai}, \\ -\lim_{\eta \to 0+} \sum_{j \in \mathcal{S}_{\text{occ}}, b \in \mathcal{S}_{\text{unocc}}} \frac{\langle \Psi_{ai} | f_{\text{Hxc}} | \Psi_{bj} \rangle}{\omega + \omega_{ai} + i\eta} f_{bj} - \frac{\langle \Psi_{ia} | f_{\text{Hxc}} | \Psi_{jb} \rangle}{\omega + \omega_{ai} + i\eta} f_{jb} = f_{ia}. \end{cases}$$
(94)

Or equivalently, we can write down the following eigenvalue equation

$$\begin{cases} \sum_{j \in \mathcal{S}_{\text{occ}}, b \in \mathcal{S}_{\text{unocc}}} \langle \Psi_{ai} | f_{\text{Hxc}} | \Psi_{bj} \rangle f_{bj} + \langle \Psi_{ai} | f_{\text{Hxc}} | \Psi_{jb} \rangle f_{jb} = (\omega - \omega_{ai}) f_{ai}, \\ \sum_{j \in \mathcal{S}_{\text{occ}}, b \in \mathcal{S}_{\text{unocc}}} \langle \Psi_{ia} | f_{\text{Hxc}} | \Psi_{bj} \rangle f_{bj} + \langle \Psi_{ia} | f_{\text{Hxc}} | \Psi_{jb} \rangle f_{jb} = -(\omega + \omega_{ai}) f_{ia}. \end{cases}$$
(95)

The equation eq. (95) is known as the Casida equation.

One of the important applications of TDDFT is to calculate the *absorption spectrum* which is directly related to the excitation energies, i.e. the poles of the the reducible polarizability operator  $\chi(\omega)$ , which in the context of TDDFT is viewed as a good approximation to the many-body exact polarizability operator  $\chi^{\text{exact}}(\omega)$ . Specifically, we can define the polarizability tensor as

$$A_{ij}(\omega) = -\int r_{\alpha} \chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega) r'_{\beta} \mathrm{d}\mathbf{r}.$$
(96)

The absorption spectrum cross section denoted by  $\sigma(\omega)$  is given by

$$\sigma(\omega) = \frac{4\pi\omega}{c} \operatorname{Im} \operatorname{Tr}[A(\omega)].$$
(97)

Here c is the speed of light which is approximately 137 (the reciprocal of the fine-structure constant) in atomic units.

We note that only the poles of  $\chi(\omega)$  (or all the possible excitation energies) contribute to the imaginary part of  $\text{Tr}(A(\omega))$ . Therefore, the Casida equation eq. (95) may readily give us the absorption spectrum. However, the Casida equation requires the diagonalization of a non-Hermitian matrix of size  $N_{\text{occ}}N_{\text{unocc}}$  where  $N_{\text{occ}}$  is the number of occupied states and  $N_{\text{unocc}}$  is the number of unoccupied states within the energy cutoff. This is a very large matrix and the diagonalization is very expensive.

#### 6.3 Random phase approximation (RPA)

Random phase approximation is another application of the time-dependent perturbation theory from a very different perspective. In RPA, we aim to *improve* the accuracy of the calculation of the many-body ground state energy using TDPT. RPA can be viewed as the starting point of various algorithms based on many-body perturbation theory. We remark the the term "RPA" is merely a legacy term and has lost its original meaning in the current context of DFT.

We consider the adiabatic connection between the non-interacting Hamiltonian (such as KSDFT) with the interacting Hamiltonian. The adiabatic connection is given by the following family of Hamiltonians

$$H_{\lambda} = T + V_{\text{ext}} + V_{\lambda} + \lambda V_{\text{ee}}, \quad \lambda \in [0, 1].$$
(98)

Here T and  $V_{\text{ext}}$  are the kinetic and external potential operators respectively.  $V_{\lambda}$  is the effective one-body potential such that  $V_{\lambda=0}$  is given by the non-interacting potential term in one-body theory and  $V_{\lambda=1} = 0$ .

Given a density  $\rho$ , we can obtain the many-body ground state  $\Psi_{\lambda}$  of each  $H_{\lambda}$  by minimizing the energy functional. We denote  $E(\lambda) = \langle \Psi_{\lambda} | H_{\lambda} | \Psi_{\lambda} \rangle$  as the ground state energy, then we have

$$E(1) - E(0) = \int_0^1 \frac{\partial E(\lambda)}{\partial \lambda} d\lambda = \int_0^1 \langle \Psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \Psi_\lambda \rangle d\lambda = \int_0^1 \langle \Psi_\lambda | V_{ee} + \frac{\partial V_\lambda}{\partial \lambda} | \Psi_\lambda \rangle d\lambda.$$
(99)

Here E(1) is the exact ground state energy of the many-body system which is the quantity we want to calculate. E(0) is the ground state energy of the non-interacting system which can be calculated using KSDFT. The second equality uses the Hellmann-Feynman theorem.

We recall that for the many-body wavefunction  $\Psi$ , the Coulomb energy can be expressed as

$$\langle \Psi | \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle = \frac{1}{2} \iint \frac{\rho^{(2)}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}'.$$
(100)

Here  $\rho^{(2)}(\mathbf{r},\mathbf{r}')$  denotes the two-body electron density, which is given by

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{(N-1)N}{2} \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n)|^2 \mathrm{d}\mathbf{r}_3 \cdots \mathrm{d}\mathbf{r}_N.$$
(101)

Note that  $V_{\lambda}$  is a single-body term, therefore we have

$$\int_{0}^{1} \langle \Psi_{\lambda} | \frac{\partial V_{\lambda}}{\partial \lambda} | \Psi_{\lambda} \rangle \, \mathrm{d}\lambda = \int_{0}^{1} \int \rho \frac{\partial V_{\lambda}}{\partial \lambda} \mathrm{d}\mathbf{r} \mathrm{d}\lambda = \int \rho (V_{1} - V_{0}) \mathrm{d}\mathbf{r} = -\int \rho V_{0} \mathrm{d}\mathbf{r}.$$
(102)

Here we use the assumption that  $\rho$  does not depend on  $\lambda$  and the fact that  $V_1 = 0$ . Plugging these back to eq. (99), we have

$$E(1) = E(0) - \int \rho V_0 d\mathbf{r} + \int_0^1 \langle \Psi_\lambda | V_{ee} | \Psi_\lambda \rangle d\lambda = E(0) - \int \rho V_0 d\mathbf{r} + \frac{1}{2} \int_0^1 \iint \frac{\rho_\lambda^{(2)}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' d\lambda.$$
(103)

From this equation, we see that E(0) can be obtained just by solving the KSDFT equations. Therefore, to get the "exact" functional  $E(1)[\rho]$ , we only need to know  $\rho_{\lambda}^{(2)}(\mathbf{r}, \mathbf{r}')$ . The idea of random phase approximation is to approximate  $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$  via the approximation of the exact many-body polarizability operator  $\chi^{\text{exact}}$  using the irreducible polarizability operator  $\chi_0$ . In this way, the energy functional can be expressed using only the electron density and the one-particle density matrix. This bridges the gap between the many-body ground state problem and the time-dependent perturbation theory.

This can be down using the following steps

• We recall the definition of the irreducible polarizability operator  $\chi_0$  in eq. (69). We extend it to imaginary frequency i $\omega$  and assume that all the orbital functions are real just as in eq. (33)

$$\chi_{0}(\mathbf{r}, \mathbf{r}'; i\omega) = \sum_{i \in \mathcal{S}_{occ}, a \in \mathcal{S}_{unocc}} \frac{\psi_{a}(\mathbf{r}')\psi_{i}(\mathbf{r}')\psi_{a}(\mathbf{r})\psi_{i}(\mathbf{r})}{i\omega - (\lambda_{a} - \lambda_{i})} + c.c.$$

$$= -2\sum_{i \in \mathcal{S}_{occ}, a \in \mathcal{S}_{unocc}} \frac{(\lambda_{a} - \lambda_{i})\psi_{a}(\mathbf{r}')\psi_{i}(\mathbf{r}')\psi_{a}(\mathbf{r})\psi_{i}(\mathbf{r})}{\omega^{2} + (\lambda_{a} - \lambda_{i})^{2}}.$$
(104)

• Similarly, we also recall the definition of the exact polarizability operator  $\chi^{\text{exact}}$  in eq. (87) and extend it to imaginary frequency  $i\omega$  as

$$\chi^{\text{exact}}(\mathbf{r}, \mathbf{r}'; i\omega) = \sum_{k \neq 0} \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_k \rangle \langle \Psi_k | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{i\omega - (E_k - E_0)} + \text{c.c.}$$

$$= -2 \sum_{k \neq 0} \frac{\langle E_k - E_0 \rangle \langle \Psi_k | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_k \rangle}{\omega^2 + (E_k - E_0)^2}.$$
(105)

• We integrate  $\chi$  and  $\chi_0$  along the imaginary axis and note that  $\int_{\mathbb{R}^+} \frac{a}{a^2 + \omega^2} d\omega = \frac{\pi}{2}$ . We have

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \chi_0(\mathbf{r}, \mathbf{r}'; \mathrm{i}\omega) \mathrm{d}\omega = -\sum_{i \in \mathcal{S}_{\mathrm{occ}}, a \in \mathcal{S}_{\mathrm{unocc}}} \psi_a(\mathbf{r}) \psi_i(\mathbf{r}') \psi_a(\mathbf{r}') \psi_i^*(\mathbf{r}) = -\sum_{i \in \mathcal{S}_{\mathrm{occ}}} \langle \psi_i | \delta_{\mathbf{r}'} \sum_{a \in \mathcal{S}_{\mathrm{unocc}}} |\psi_a \rangle \langle \psi_a | \delta_{\mathbf{r}} | \psi_i \rangle$$
(106)

Using the similar argument as in eq. (33), we express the above equation in terms of occupied orbitals

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \chi_0(\mathbf{r}, \mathbf{r}'; i\omega) d\omega = \sum_{i,j \in \mathcal{S}_{occ}} \langle \psi_i | \delta_{\mathbf{r}'} | \psi_a \rangle \langle \psi_a | \delta_{\mathbf{r}} | \psi_i \rangle - \sum_{i \in \mathcal{S}_{occ}} \langle \psi_i | \delta_{\mathbf{r}} | \psi_i \rangle \delta(\mathbf{r} - \mathbf{r}') = \left| P_s(\mathbf{r}, \mathbf{r}') \right|^2 - \rho_s(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$$
(107)

Here,  $P_s$  denotes the kernel function of the single-particle density matrix  $P_s = \sum_{i \in S_{occ}} |\psi_i\rangle\langle\psi_i|$ ,  $\rho_s$  denotes the single-particle density.

Similarly, we have

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \chi^{\text{exact}}(\mathbf{r}, \mathbf{r}'; i\omega) d\omega = -\sum_{k \neq 0} \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_k \rangle \langle \Psi_k | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle$$

$$= \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle - \langle \Psi_0 | \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle$$

$$= \rho(\mathbf{r}) \rho(\mathbf{r}') - \rho^{(2)}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}').$$
(108)

This is because

$$\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') = \sum_{i,j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_i) + \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j)$$

$$= \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r} - \mathbf{r}') + \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) = \hat{\rho}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + \hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}').$$
(109)

Thus

$$\langle \Psi_0 | \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle = \rho^{(2)}(\mathbf{r}, \mathbf{r}') + \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') = \rho^{(2)}(\mathbf{r}, \mathbf{r}') + \rho(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}').$$
(110)

• Next, we compare eq. (107) and eq. (108). If we approximate  $\chi^{\text{exact}}$  using  $\chi_0$ , we get an approximation of  $\rho^{(2)}$  by

$$\rho^{(2)}(\mathbf{r},\mathbf{r}') \approx \rho_s^{(2)}(\mathbf{r},\mathbf{r}') := \rho_s(\mathbf{r})\rho_s(\mathbf{r}') - \left|P_s(\mathbf{r},\mathbf{r}')\right|^2.$$
(111)

This gives

$$\frac{1}{2} \iint \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' \approx \frac{1}{2} \iint \frac{\rho^{(2)}_{s}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' = \frac{1}{2} \iint \frac{\rho_{s}(\mathbf{r})\rho_{s}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' - \frac{1}{2} \iint \frac{|P_{s}(\mathbf{r},\mathbf{r}')|^{2}}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}'.$$
(112)

The right-hand side is exactly the Hartree-Fock approximation of the Coulomb energy! This trivialty motivates us to look for a better approximation of  $\chi$  so that we can expect a better approximation of the many-body correlation energy, which is completely missing when we just replace  $\chi^{\text{exact}}$  with  $\chi_0$ .

• To improve the approximation, we examine the additional contribution beyond  $\chi_0$ 

$$E_{\text{correlation}} = \int_0^1 \frac{1}{2} \iint \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left( -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \chi_\lambda(\mathbf{r}, \mathbf{r}'; i\omega) - \chi_0(\mathbf{r}, \mathbf{r}'; i\omega) \mathrm{d}\omega \right) \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' \mathrm{d}\lambda.$$
(113)

Recall that  $\chi_{\lambda}$  is the polarizability operator of the many-body Hamiltonian  $H_{\lambda}$ , which can be approximated using the reducible polarizability operator. This suggests that we can solve the following equation (recall eq. (71))

$$\chi_{\lambda}^{-1} = \chi_0^{-1} - \lambda v_C - f_{\rm xc}^{\lambda}.$$
(114)

Here the Coulomb kernel  $\mathcal{K}(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$  in eq. (113) is changed to  $\lambda v_C := \lambda \cdot \frac{\delta V_{\text{ext}}}{\delta \rho}$  due to the adiabatic path.

• In RPA, we neglect  $f_{\rm xc}^{\lambda}$  and obtain the following Dyson equation

$$\chi_{\lambda}^{-1} = \chi_0^{-1} - \lambda v_C \Rightarrow \chi_{\lambda} = \chi_0 + \lambda \chi_0 v_C \chi_{\lambda}.$$
(115)

Thus

$$\int_0^1 \chi_\lambda(\mathrm{i}\omega) v_C \mathrm{d}\lambda - \chi_0(\mathrm{i}\omega) v_C = \int_0^1 (1 - \lambda \chi_0(\mathrm{i}\omega) v_C)^{-1} \chi_0(\mathrm{i}\omega) v_C \mathrm{d}\lambda - \chi_0(\mathrm{i}\omega) v_C = -\log(1 - \chi_0(\mathrm{i}\omega) v_C) - \chi_0(\mathrm{i}\omega) v_C.$$
(116)

Therefore, in RPA, the correction energy is given by

$$E_{\text{correlation}}^{\text{RPA}} = \frac{1}{4\pi} \int_{-\infty}^{+\infty} \text{Tr} \left[ \log(1 - \chi_0(i\omega)v_C) - \chi_0(i\omega)v_C \right] d\omega.$$
(117)

eq. (117) is the fundamental equation of RPA. It strongly relies on the time-dependent perturbation theory. The matrix logarithm can be computed by exact diagonalization or contour integral.

We remark that the one we just discussed about is actually the DFT-flavored RPA. There are various other formulations under the umbrella term of RPA.

# References

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