

# Introduction to the Random Phase Approximation in DFT

János G. Ángyán

CRM2, Institut Jean Barriol, Faculté des Sciences,  
Université Lorraine & CNRS, Vandœuvre-lès-Nancy, France

June 20, 2015

## Contents

<b>1</b>	<b>Introduction</b>	<b>2</b>
1.1	History . . . . .	2
<b>2</b>	<b>Adiabatic Connection-Fluctuation Dissipation Theorem</b>	<b>4</b>
2.1	Adiabatic Connection (AC) . . . . .	4
2.2	AC correlation energy with Kohn-Sham reference . . . . .	6
2.3	AC correlation energy with Hartree-Fock reference . . . . .	7
2.4	Fluctuation Dissipation Theorem (FDT) . . . . .	8
<b>3</b>	<b>RPA correlation energy</b>	<b>12</b>
3.1	Kohn-Sham reference: direct RPA . . . . .	13
3.2	Hartree-Fock reference: RPA with exchange . . . . .	18
3.3	Ring CCD and RPA . . . . .	21
3.4	Approximate RPA schemes with exchange . . . . .	26
	<b>Bibliography</b>	<b>28</b>

# 1 Introduction

These notes provide an overview of the basic formalism of the random phase approximation (RPA) as it is used in density functional calculations to evaluate the correlation energy. Some more advanced subjects will be treated as well and the state-of-the-art performance will be shortly discussed. There are several excellent recent review papers available [1, 2, 3, 4, 5, 6] covering different aspects of the RPA, where the interested reader can complete and deepen his/her knowledge.

## 1.1 History

When dealing with RPA, it is perhaps more appropriate to speak about *random phase approximations* (plural), since there is a whole family of approaches used in many-body physics, which are referred to in the literature under the name RPA. Although the pioneering works are due to Bohm and Pines in the early fifties [7, 8, 9] in the context of the homogeneous electron gas (HEG), which can be classified as a subject of electronic structure of solids, nuclear physicists improved and refined this methodology for the study of the correlated nuclear matter [10]. In the early sixties, McLachlan and Ball reformulated RPA for quantum chemists [11], and it became a popular approach for the study of excited states under the name of time-dependent Hartree-Fock (TDHF) method. Although before the late seventies quantum chemistry articles on RPA/TDHF mention that RPA can be used to obtain approximate ground state electron correlation energies, from the eighties on such a use of the RPA became obsolete. The fact that the RPA has been completely ignored in quantum chemistry as a correlation method is mostly due to the fast developments in coupled-cluster and other many-body methods and to its poor performance in a wave function context, when it is based on Hartree-Fock reference orbitals. The last significant quantum chemical contribution was due to Szabo and Ostlund [12] and Oddershede reviewed the state-of-the-art in 1978 [13]. After that, the usage of RPA for correlation energies has been limited to the nuclear physicist community, although it survived also in electronic structure theory in relation to the studies of the HEG, often in view of designing correlation functionals for density functional theory (DFT). The works of Langreth and Perdew [14] and of Harris [15] had a strong influence on the interpretation of Kohn-Sham DFT, by introducing the adiabatic connection-fluctuation dissipation theorem approach for the definition of the exact exchange-correlation functional. At this time, disregarded from the simplest electronic systems, AC-FDT was used only in theoretical analyses, without attempting to perform numerical calculations on the correlation energy starting from Kohn-Sham orbitals.

A renaissance of RPA applied for inhomogeneous electronic systems, such as molecules and real solids, appeared around the year 2000. This breakthrough was due to the discovery that RPA can be formulated as a relatively efficient practical computational method which provides reasonable estimates of the many-body, infinite order, correlation energy and can be implemented by algorithms that scale advantageously with the number of electrons. In the quantum chemistry community, Furche published the first successful calculations on small molecules [16], and several other authors came upon with application to real solids [17, 18, 19]. Although these first calculations were rather inefficient computationally, they provided a convincing proof of

principle, and within a few years more efficient computational procedures were developed and implemented for solids [20, 21] and for molecules [22, 23, 24].

## 2 Adiabatic Connection-Fluctuation Dissipation Theorem

The derivation of the ground state RPA correlation energy may be done following several different paths. The first one has a DFT flavor and is based on the adiabatic connection-fluctuation-dissipation theorem, which has been already presented during these courses (in the DFT lecture). A second method is rooted in the coupled-cluster formalism correlation energy, and therefore seems to be closer to the wave-function theories (WFT). Another approach is based on the Green's functions.

The most important results obtained by the different derivations are strictly equivalent, but some differences exist in particular cases, giving different insights and leading to different RPA methods and algorithms. The equivalence of some of the formulations of RPA is far from being obvious for a non-initiated reader of the relevant literature, therefore it could be interesting to understand the hidden relationships among the various ways of expressing the RPA correlation energy.

In order to prepare ourselves to this task, the adiabatic connection fluctuation dissipation theorem (AC-FDT) approach will be overviewed. In principle it gives a general formulation for the exact correlation energy, and will be the starting point to introduce the random phase approximation.

### 2.1 Adiabatic Connection (AC)

The approach of the adiabatic connection (AC) as a way of expressing the exact exchange-correlation energy functional has already been exposed in chapter 2.1.2 of the DFT course. Here, the AC will be exposed in a slightly more general context.

The central idea is to construct an interpolation Hamiltonian,  $\hat{H}^\lambda$ , which connects smoothly an independent particle  $\hat{H}_{i.p.}$  and the physical  $\hat{H}_{phys.}$  Hamiltonians:

$$\hat{H}^\lambda = \hat{T} + \hat{V}_{ne} + \hat{V}^\lambda + \lambda \hat{W}_{ee} \quad (2.1.1)$$

$$\hat{H}_{i.p.} = \hat{H}^{\lambda=0} = \hat{T} + \hat{V}_{ne} + \hat{V}^{\lambda=0} \quad \Rightarrow \quad \hat{H}_{phys.} = \hat{H}^{\lambda=1} = \hat{T} + \hat{V}_{ne} + \hat{W}_{ee} \quad (2.1.2)$$

The connection path is controlled by a single parameter  $\lambda$  which gradually switches on the electron-electron interaction  $\hat{W}_{ee}$  and simultaneously changes the effective one-electron potential  $\hat{V}_{ne} + \hat{V}^\lambda$ , which is equal to the electron-nuclear attraction for  $\lambda = 1$ , i.e.  $\hat{V}^{\lambda=1} = 0$ .<sup>1</sup>

#### General AC expression of the correlation energy

Let  $\Psi$  be the exact many-body wave-function, eigenfunction of the physical Hamiltonian  $\hat{H}_{phys.}$ , so that the physical energy is  $E(\lambda = 1) = \langle \Psi | \hat{H}_{phys.} | \Psi \rangle$  and let  $\Phi^0$  be the independent particle

---

<sup>1</sup>The linear scaling of the electron-electron interaction, which is the most popular one and will be used in the present notes, is not the only possibility. More complicated, non-linear paths can be constructed, e.g. using a screened Coulomb interaction [25].

(single determinant) wave function, eigenfunction of  $\hat{H}_{i.p.}$ , with the corresponding energy  $E(\lambda = 0) = \langle \Phi^0 | \hat{H}_{i.p.} | \Phi^0 \rangle$ . In general, for any  $\lambda$ , let  $\Psi^\lambda$  be the eigenfunction of  $\hat{H}^\lambda$ .

The difference of the physical and independent particle energies,  $E(\lambda = 1) - E(\lambda = 0) = \langle \Psi | \hat{H}_{phys.} | \Psi \rangle - \langle \Psi^0 | \hat{H}_{i.p.} | \Psi^0 \rangle$ , can be obtained via an adiabatic connection path:

$$\begin{aligned} E(\lambda = 1) - E(\lambda = 0) &= \int_0^1 \frac{\partial E(\lambda)}{\partial \lambda} d\lambda \\ &= \int_0^1 \langle \Psi^\lambda | \frac{\partial \hat{H}^\lambda}{\partial \lambda} | \Psi^\lambda \rangle d\lambda \\ &= \int_0^1 \langle \Psi^\lambda | \hat{W}_{ee} + \frac{\partial V^\lambda}{\partial \lambda} | \Psi^\lambda \rangle d\lambda \end{aligned} \quad (2.1.3)$$

where in the second equality we have used the *Hellmann-Feynman theorem*.

**Exercise #:** Prove the differential Hellmann-Feynman theorem

$$\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial \hat{H}}{\partial \lambda} | \Psi \rangle \langle \Psi | \Psi \rangle^{-1}. \quad (2.1.4)$$

and specify the conditions of its validity.

On the other hand, the correlation energy can be defined as the difference of the expectation values of the physical Hamiltonian taken on the one side with the exact many-electron wave function and on the other side with the independent particle wave function:

$$E_{\text{corr}} = \langle \Psi | \hat{H}_{phys.} | \Psi \rangle - \langle \Phi^0 | \hat{H}_{phys.} | \Phi^0 \rangle. \quad (2.1.5)$$

This definition can be transformed by adding and subtracting the effective one-electron potential at  $\lambda = 0$ :

$$E_{\text{corr}} = \langle \Psi | \hat{H}_{phys.} | \Psi \rangle - \langle \Phi^0 | \hat{H}_{i.p.} | \Phi^0 \rangle - \langle \Phi^0 | \hat{W}_{ee} - \hat{V}^0 | \Phi^0 \rangle \quad (2.1.6)$$

**Exercise #:** Show that the general correlation energy definition Eq.(2.1.5) coincides with the conventional Löwdin's expression in the WFT case and with the correlation energy functional in the DFT case (Eq. 25 of the DFT course).

Thus we are in measure of writing a general expression for the correlation energy:

$$E_{\text{corr}} = \int_0^1 \langle \Psi^\lambda | \hat{W}_{ee} + \frac{\partial V^\lambda}{\partial \lambda} | \Psi^\lambda \rangle d\lambda - \langle \Phi^0 | \hat{W}_{ee} - \hat{V}^0 | \Phi^0 \rangle \quad (2.1.7)$$

Remark that in contrast to a simple “algebraic” decomposition of the correlation energy, involving both kinetic and potential energy contributions, the kinetic correlation energy has been eliminated and transformed to a potential energy term by virtue of the integration along the adiabatic connection path.

## Pair density operator

Any multiplicative one-electron operator can be easily expressed using the electron density operator  $\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$ . For instance, the electron-nuclei attraction operator  $\hat{V}_{\text{en}} = \sum_i \sum_A Z_A / |\mathbf{r}_i - \mathbf{R}_A|$  becomes

$$\hat{V}_{\text{en}} = \int d\mathbf{r} \hat{\rho}(\mathbf{r}) v_{\text{ne}}(\mathbf{r}) \quad (2.1.8)$$

The electron-electron repulsion operator  $\hat{W}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j} |\mathbf{r}_i - \mathbf{r}_j|$  can be expressed with the help of the electron density operator, as

$$\hat{W}_{\text{ee}} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \{ \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') - \hat{\rho}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \} w_{\text{ee}}(\mathbf{r}, \mathbf{r}') \quad (2.1.9)$$

where the second term in curly brackets removes the Coulomb singularity of  $w_{\text{ee}}(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ . If one introduces the pair density operator

$$\hat{n}_2(\mathbf{r}, \mathbf{r}') = \{ \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}') \hat{\rho}(\mathbf{r}) \} \quad (2.1.10)$$

the electron repulsion operator becomes

$$\hat{W}_{\text{ee}} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \hat{n}_2(\mathbf{r}, \mathbf{r}') w_{\text{ee}}(\mathbf{r}, \mathbf{r}') \quad (2.1.11)$$

## 2.2 AC correlation energy with Kohn-Sham reference

In DFT the natural choice for the independent particle model is the Kohn-Sham determinant,  $\Phi_{\text{KS}}^0$ . The effective potential  $V_{\text{DFT}}^0$  is constructed to produce the exact one particle density  $\rho(\mathbf{r})$  and at intermediate values of  $\lambda$  the potential  $\hat{V}_{\text{DFT}}^\lambda$  is chosen to maintain the density at its exact value, i.e. for all  $\lambda$ :  $\langle \Psi^\lambda | \hat{\rho}(\mathbf{r}) | \Psi^\lambda \rangle = \rho(\mathbf{r})$ . At  $\lambda = 1$  the effective potential is vanishing ( $\hat{V}_{\text{DFT}}^1 = 0$ ): the nuclear attraction potential of the physical Hamiltonian ensures that  $\langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \rho(\mathbf{r})$ .

The integral involving the derivative of  $\hat{V}_{\text{DFT}}^\lambda$  in Eq.(2.1.7) is easy to obtain, as:

$$\int_0^1 \langle \Psi^\lambda | \frac{\partial V^\lambda}{\partial \lambda} | \Psi^\lambda \rangle d\lambda = \langle \Psi | \hat{V}_{\text{DFT}}^1 | \Psi \rangle - \langle \Phi_{\text{KS}}^0 | \hat{V}_{\text{DFT}}^0 | \Phi_{\text{KS}}^0 \rangle = 0 - \langle \Phi_{\text{KS}}^0 | \hat{V}_{\text{DFT}}^0 | \Phi_{\text{KS}}^0 \rangle \quad (2.2.1)$$

After cancellation of the  $\langle \Phi_{\text{KS}}^0 | \hat{V}_{\text{DFT}}^0 | \Phi_{\text{KS}}^0 \rangle$  terms, one obtains the simple expression

$$\boxed{E_{\text{corr}}^{\text{DFT}} = \int_0^1 \langle \Psi^\lambda | \hat{W}_{\text{ee}} | \Psi^\lambda \rangle d\lambda - \langle \Phi_{\text{KS}}^0 | \hat{W}_{\text{ee}} | \Phi_{\text{KS}}^0 \rangle} \quad (2.2.2)$$

It remains to calculate the expectation values of the electron repulsion operator with the  $\lambda$ -dependent many-electron wave function and with the KS determinant. The second term is equal to the sum of the exact Hartree and the exact exchange energies, provided we have the exact KS determinant.

**Exercise #:** Show that the expectation value of the electron repulsion operator taken with the KS determinant gives the sum of the exact Hartree and exact exchange energies. Use Slater rules.

In order to obtain the electron repulsion expectation value, it is sufficient to calculate the expectation value of the pair density operator. The pair density function along the adiabatic path  $n_2^\lambda(\mathbf{r}, \mathbf{r}') = \langle \Psi^\lambda | \hat{n}_2(\mathbf{r}, \mathbf{r}') | \Psi^\lambda \rangle$  can be decomposed (see DFT course) into the Hartree energy and a non-trivial exchange-correlation part:

$$n_2^\lambda(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r})h_{xc}^\lambda(\mathbf{r}, \mathbf{r}') \quad (2.2.3)$$

The hole function  $h_{xc}^\lambda(\mathbf{r}, \mathbf{r}')$  is further decomposed into a  $\lambda$ -independent exchange hole and a  $\lambda$ -dependent correlation hole:  $h_{xc}^\lambda(\mathbf{r}, \mathbf{r}') = h_x(\mathbf{r}, \mathbf{r}') + h_c^\lambda(\mathbf{r}, \mathbf{r}')$ .

Remember (DFT courses) that the DFT correlation energy can be written with the coupling strength averaged correlation hole,  $\bar{h}_c(\mathbf{r}, \mathbf{r}') = \int_0^1 d\lambda h_c^\lambda(\mathbf{r}, \mathbf{r}')$  as

$$E_{\text{corr}}^{\text{DFT}} = \frac{1}{2} \iint d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\bar{h}_c(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.2.4)$$

Instead of this form of the correlation energy, we are going to follow a different method. For this purpose, we are going to transform the pair density operator in a more convenient form for the following developments. Introduce the *density fluctuation* operator  $\Delta\hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \rho(\mathbf{r})$  to get

$$\hat{n}_2(\mathbf{r}, \mathbf{r}') = \{ \Delta\hat{\rho}(\mathbf{r})\Delta\hat{\rho}(\mathbf{r}') + \hat{\rho}(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r})\hat{\rho}(\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')\hat{\rho}(\mathbf{r}) \} \quad (2.2.5)$$

This form is particularly useful to express the expectation value in the the AC integrand, because in the DFT case one can take profit of the constancy of the electron density along the adiabatic path:

$$E_{\text{corr}}^{\text{DFT}} = \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{r}d\mathbf{r}' \frac{\langle \Psi^\lambda | \Delta\hat{\rho}(\mathbf{r})\Delta\hat{\rho}(\mathbf{r}') | \Psi^\lambda \rangle - \langle \Phi_{\text{KS}}^0 | \Delta\hat{\rho}(\mathbf{r})\Delta\hat{\rho}(\mathbf{r}') | \Phi_{\text{KS}}^0 \rangle}{|\mathbf{r} - \mathbf{r}'|} \quad (2.2.6)$$

## 2.3 AC correlation energy with Hartree-Fock reference

In wave function theory, the usual independent particle reference is the Hartree-Fock (HF) determinant,  $\Phi_{\text{HF}}^0$ . The HF one-electron density,  $\langle \Phi_{\text{HF}}^0 | \hat{\rho}(\mathbf{r}) | \Phi_{\text{HF}}^0 \rangle = \rho_{\text{HF}}(\mathbf{r})$ , is *not* equal to the exact density. The effective potential at  $\lambda = 0$  is the (nonlocal) Hartree-Fock potential  $\hat{V}_{\text{WFT}}^0 = \hat{V}_{\text{HF}} = \hat{V}_H + \hat{V}_{x,\text{HF}}$  and the adiabatic connection path can be defined by scaling the fluctuation potential,  $\Delta\hat{W} = \hat{W}_{\text{ee}} - \hat{V}_{\text{HF}}$  from  $\lambda = 0$  to  $\lambda = 1$ . This choice corresponds to  $\hat{V}_{\text{WFT}}^\lambda = (1 - \lambda)\hat{V}_{\text{HF}}$  and the correlation energy of Eq. (2.1.7) becomes:

$$E_{\text{corr}}^{\text{WFT}} = \int_0^1 \langle \Psi^\lambda | \hat{W}_{\text{ee}} - \hat{V}_{\text{HF}} | \Psi^\lambda \rangle d\lambda - \langle \Phi_{\text{HF}}^0 | \hat{W}_{\text{ee}} - \hat{V}_{\text{HF}} | \Phi_{\text{HF}}^0 \rangle \quad (2.3.1)$$

In contrast to the DFT case, where the adiabatic connection integrand contains only the electron repulsion operator, the WFT integrand also contains one-electron terms. This is a consequence of the fact that, in the context of WFT, the electron density (and the one-particle density matrix) varies along the adiabatic connection path. Remark that the integration constant is the expectation value of the fluctuation potential taken with the HF determinant, which is the first-order Møller-Plesset energy.

The non-constancy of the density gives rise to various corrective terms. To demonstrate this, we write the fluctuation potential operator as

$$\begin{aligned} \hat{W}_{\text{ee}} - \hat{V}_{\text{HF}} &= \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\hat{n}_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \left\{ \frac{\hat{\rho}(\mathbf{r})\rho_{\text{HF}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\hat{\gamma}(\mathbf{r}, \mathbf{r}')\gamma_{\text{HF}}^*(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right\} \end{aligned} \quad (2.3.2)$$

where  $\hat{\gamma}(\mathbf{r}, \mathbf{r}')$  is the one-particle density matrix operator, with diagonal elements  $\hat{\gamma}(\mathbf{r}, \mathbf{r}) = \hat{\rho}(\mathbf{r})$  the density operator. In contrast to the DFT case, the density and density matrix expectation values are  $\lambda$ -dependent, so one should keep them in the integrand:

$$\begin{aligned} \langle \Psi_\lambda | \hat{W}_{\text{ee}} - \hat{V}_{\text{HF}} | \Psi_\lambda \rangle - \langle \Phi_{\text{HF}} | \hat{W}_{\text{ee}} - \hat{V}_{\text{HF}} | \Phi_{\text{HF}} \rangle &= \\ \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\langle \Psi_\lambda | \Delta\hat{\rho}(\mathbf{r})\Delta\hat{\rho}(\mathbf{r}') | \Psi_\lambda \rangle - \langle \Phi_{\text{HF}} | \Delta\hat{\rho}(\mathbf{r})\Delta\hat{\rho}(\mathbf{r}') | \Phi_{\text{HF}} \rangle}{|\mathbf{r} - \mathbf{r}'|} &+ \\ + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{(\rho_\lambda(\mathbf{r}) - \rho_{\text{HF}}(\mathbf{r}))\rho_\lambda(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} &- \\ - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\delta(\mathbf{r} - \mathbf{r}')(\rho_\lambda(\mathbf{r}) - \rho_{\text{HF}}(\mathbf{r}))}{|\mathbf{r} - \mathbf{r}'|} &+ \\ + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{(\gamma_\lambda(\mathbf{r}, \mathbf{r}') - \gamma_{\text{HF}}(\mathbf{r}, \mathbf{r}'))\gamma_{\text{HF}}^*(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (2.3.3)$$

If one supposes that the one particle exact and HF density matrices are equal, which is a very strong assumption (it would mean e.g. that there is no kinetic energy contribution to the correlation energy) one gets an analogous expression to the DFT case. With the considerably weaker assumption that the Hartree-Fock density is a good approximation of the exact one, only the last correction term, corresponding to an exchange energy, survives.

## 2.4 Fluctuation Dissipation Theorem (FDT)

The density fluctuation at a given value  $\lambda$  of the AC parameter is related to the linear charge density response function  $\chi$  through the *zero temperature fluctuation-dissipation theorem*, which states that the frequency integral of the linear response function along the imaginary axis is equal to the correlation function of the spontaneous charge density fluctuations of the system. Note that this still lies, in principle, in the realm of the exact theory. In this section, the DFT-based response theory, TDDFT, will be discussed. This would be exact if the exact frequency-dependent



exchange-correlation kernel was known. In the WFT case the density matrix response is given by the “four-point” polarization propagator. This latter is actually more convenient to use even in DFT calculations with a basis, where four-index quantities appear (the density response can easily be extracted from the polarization propagator).

## AC-FDT formula

The frequency-dependent response function for real wave functions and imaginary frequencies takes the form

$$\chi_\lambda(\mathbf{r}, \mathbf{r}'; i\omega) = -2 \sum_{n \neq 0} \frac{E_n^\lambda - E_0^\lambda}{(E_n^\lambda - E_0^\lambda)^2 + \omega^2} \langle \Psi_0^\lambda | \hat{\rho}(\mathbf{r}) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{\rho}(\mathbf{r}') | \Psi_0^\lambda \rangle \quad (2.4.1)$$

The frequency integration can be carried out using that  $\int_0^\infty d\omega \frac{a}{a^2 + \omega^2} = \frac{\pi}{2}$  (for positive  $a$ ) to obtain

$$- \int_0^\infty \frac{d\omega}{2\pi} \chi_\lambda(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2} \sum_{n \neq 0} \langle \Psi_0^\lambda | \hat{\rho}(\mathbf{r}) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{\rho}(\mathbf{r}') | \Psi_0^\lambda \rangle \quad (2.4.2)$$

which can be rewritten as:

$$\boxed{- \int_0^\infty \frac{d\omega}{2\pi} \chi_\lambda(\mathbf{r}, \mathbf{r}'; i\omega) = \frac{1}{2} \langle \Psi_0^\lambda | \Delta \hat{\rho}(\mathbf{r}) \Delta \hat{\rho}(\mathbf{r}') | \Psi_0^\lambda \rangle} \quad (2.4.3)$$

known as the zero temperature FDT.

**Exercise #:** Prove the identity

$$\sum_{n \neq 0} \langle \Psi_0^\lambda | \hat{\rho}(\mathbf{r}) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{\rho}(\mathbf{r}') | \Psi_0^\lambda \rangle = \langle \Psi_0^\lambda | \Delta \hat{\rho}(\mathbf{r}) \Delta \hat{\rho}(\mathbf{r}') | \Psi_0^\lambda \rangle \quad (2.4.4)$$

which permitted us to complete the proof of the FDT.

The importance of the FDT is that it offers a convenient method to evaluate or approximate the AC integrand for different coupling strengths, avoiding the difficult task of solving a many-body Schrödinger equation for each value of the coupling strength. The AC-FDT correlation energy expression is obtained by the combination of the adiabatic connection method and the fluctuation-dissipation theorem, and reads as

$$E_{\text{corr}}^{\text{DFT}} = - \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \iint d\mathbf{r} d\mathbf{r}' \frac{\chi_\lambda(\mathbf{r}, \mathbf{r}'; i\omega) - \chi_0(\mathbf{r}, \mathbf{r}'; i\omega)}{|\mathbf{r} - \mathbf{r}'|} \quad (2.4.5)$$

An analogous expression exists for the polarization propagator.

## Interacting density response

Time-dependent density functional theory (TDDFT) provides a convenient framework to obtain the frequency-dependent linear charge density response function. Suppose that the exact exchange-correlation functional and its functional derivative (the exchange-correlation potential) is known and the solution of the KS equations produce the exact ground state density of the system,  $\rho^{(0)}(\mathbf{r})$ . The first order density response,  $\rho_\lambda^{(1)}(\mathbf{r}, \omega)$ , to an external field  $v^{(1)}(\mathbf{r}, \omega)$  oscillating with a given frequency is given by

$$\rho_\lambda^{(1)}(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi_\lambda(\mathbf{r}, \mathbf{r}'; \omega) v_\lambda^{(1)}(\mathbf{r}', \omega) \quad (2.4.6)$$

We assume that the first order density response can be written in an independent particle form and there exist an effective one-particle potential, such that

$$\rho_\lambda^{(1)}(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}'; \omega) v_\lambda^{(1, \text{eff})}(\mathbf{r}', \omega) \quad (2.4.7)$$

where the non-interacting response function is known and takes the form:

$$\chi_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} \left\{ \frac{\phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_a^*(\mathbf{r}) \phi_i(\mathbf{r}')}{\epsilon_{ia} - \omega + i0^+} + \frac{\phi_a^*(\mathbf{r}) \phi_i(\mathbf{r}') \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}')}{\epsilon_{ia} + \omega + i0^+} \right\} \quad (2.4.8)$$

The first order effective potential is decomposed into an external, an Hartree and a first-order exchange-correlation contribution:

$$v_\lambda^{(1, \text{eff})}(\mathbf{r}, \omega) = v^{(1)}(\mathbf{r}, \omega) + \int d\mathbf{r}' \frac{\rho_\lambda^{(1)}(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}^{(1)}(\mathbf{r}, \omega) = v^{(1)}(\mathbf{r}, \omega) + v_{\text{Hxc}}^{(1)}(\mathbf{r}, \omega) \quad (2.4.9)$$

In the spirit of linear response,  $v_{\text{Hxc}}^{(1)}(\mathbf{r}, \omega)$  will be considered in the form

$$v_{\text{Hxc}}^{(1)}(\mathbf{r}, \omega) = \int d\mathbf{r}' f_{\text{Hxc}}^\lambda(\mathbf{r}, \mathbf{r}'; \omega) \rho^{(1)}(\mathbf{r}', \omega) \quad (2.4.10)$$

where  $f_{\text{Hxc}}^\lambda(\mathbf{r}, \mathbf{r}'; \omega)$  is the Hartree-exchange-correlation kernel, which is a functional of  $\rho^{(0)}$ .

All what remains to do is to establish the relationship between the non-interacting and the interacting response functions. Compare the right-hand sides of relationships 2.4.6 and 2.4.7

$$\int d\mathbf{r}' \chi_\lambda(\mathbf{r}, \mathbf{r}'; \omega) v^{(1)}(\mathbf{r}', \omega) = \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}'; \omega) v^{(1, \text{eff})}(\mathbf{r}', \omega) \quad (2.4.11)$$

where substituting the decomposition of the effective first order potential and the definition of the kernels leads to

$$\boxed{\chi_0^{-1}(\mathbf{r}, \mathbf{r}'; \omega) = \chi_\lambda^{-1}(\mathbf{r}, \mathbf{r}'; \omega) + f_{\text{Hxc}}^\lambda(\mathbf{r}, \mathbf{r}'; \omega)} \quad (2.4.12)$$

**Exercise #:** Derive equation 2.4.12 relating non-interacting and exact linear response functions via the Hartree-exchange-correlation kernel.

In practice, instead of attempting the exact resolution of the equation for the linear response, one tries to obtain reasonably good correlation energies using some approximation for  $f_{\text{Hxc}}^\lambda$ . Among such approximations to get the response function are RPA or some higher RPA method, the time-dependent Hartree-Fock (TDHF), BSE, etc.

The direct space coordinate representation of the response function, discussed here, is very convenient for formal developments. In material science, people use the reciprocal space representation obtained by Fourier transformation. In quantum chemical calculations using atomic orbital basis functions, it is more convenient to work in matrix representation, i.e. with the polarization propagator, as will be discussed in the following sections.

## Interacting density matrix response

The exact DFT correlation energy is the following multiple integral involving the AC parameter  $\lambda$  and the imaginary frequency:

$$E_c^{\text{ACFDT}} = -\frac{1}{2} \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} \{ \mathbb{P}_\lambda(i\omega) \mathbb{V} - \mathbb{P}_0(i\omega) \mathbb{V} \}. \quad (2.4.13)$$

where  $\mathbb{P}_\lambda(z)$  is the four-index matrix representation of the density matrix response function (also called dynamic polarization propagator) at interaction strength  $\lambda$ , and  $\mathbb{P}_0(z)$  is the polarization propagator of the non-interacting reference system given by (see equation 2.4.12):

$$\mathbb{P}_0(z) = -(\mathbb{A}_0 - z \mathbb{\Delta})^{-1}, \quad (2.4.14)$$

with

$$\mathbb{A}_0 = \begin{pmatrix} \boldsymbol{\epsilon} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\epsilon} \end{pmatrix} \quad \text{and} \quad \mathbb{\Delta} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}. \quad (2.4.15)$$

The elements of the  $\mathbb{A}_0$  matrix are independent one-particle excitation energies:  $(\boldsymbol{\epsilon})_{ia,jb} = \epsilon_{ia} \delta_{ij} \delta_{ab}$ , where  $\epsilon_{ia} = \epsilon_a - \epsilon_i$ ,  $\epsilon_a$  is the energy of a virtual orbital and  $\epsilon_i$  the energy of an occupied orbital. This can be written:

$$\mathbb{P}_0(z) = \begin{pmatrix} -(\boldsymbol{\epsilon} - z\mathbf{1})^{-1} & \mathbf{0} \\ \mathbf{0} & -(\boldsymbol{\epsilon} + z\mathbf{1})^{-1} \end{pmatrix} = \begin{pmatrix} \mathbb{\Pi}_0^+(z) & \mathbf{0} \\ \mathbf{0} & \mathbb{\Pi}_0^-(z) \end{pmatrix}, \quad (2.4.16)$$

which introduces a compact notation  $\mathbb{\Pi}_0^\pm$  for the diagonal blocks.

The interacting polarization propagator  $\mathbb{P}_\lambda(z)$  is obtained from a Dyson-like equation (see 2.4.12),

$$\mathbb{P}_\lambda^{-1}(z) = \mathbb{P}_0^{-1}(z) - \mathbb{F}_{\text{Hxc}}^\lambda(z), \quad (2.4.17)$$

where  $\mathbb{F}_{\text{Hxc}}^\lambda(z)$  is the kernel matrix. Again, this expression is exact only if one knows the exact Hxc kernel, which is usually not the case.

The correlation energy expression has been written with the direct Coulomb interaction, which has a representation  $\mathbb{V}$  with simple two-electron integrals as matrix elements. Since the exact (and some of the approximate) polarization propagator matrix is a properly antisymmetric object an equivalent energy expression can be written down by replacing  $\mathbb{V}$  by its antisymmetrized counterpart, denoted in the following notes by  $\mathbb{W}$ . In order to maintain the same value of the correlation energy the prefactor of 1/2 should be changed to 1/4.

### 3 RPA correlation energy

In short, the RPA, or rather the DFT-flavored RPA, consists in completely neglecting the exchange-correlation kernel and retaining only the Hartree-kernel in the determination of the interacting response function:

$$\mathbb{F}_{\text{Hxc}}^{\text{dRPA},\lambda}(z) = \lambda\mathbb{V} \quad (3.0.18)$$

In the quantum chemistry language, RPA can have a slightly different meaning (as a synonym of TDHF) and means retaining the Hartree kernel and approximating the exchange kernel by the nonlocal exchange potential:

$$\mathbb{F}_{\text{Hxc}}^{\text{RPAx},\lambda}(z) = \lambda\mathbb{W} \quad (3.0.19)$$

For the sake of the clarity, in the former case we are going to speak about direct RPA (dRPA), while the second case will be referred to as RPA with exchange (RPAx).

RPA (both RPAx and dRPA) is a quite crude approximation, which leads to a loss of the proper antisymmetry of the polarization propagator. Therefore one cannot take advantage of the equivalence of the energy expression with simple two-electron integrals,  $\langle ij|ab \rangle$  (“single-bar”) and antisymmetrized integrals  $\langle ij||ab \rangle$  (“double-bar”). In our notational conventions the type of integrals used in the energy expression will be referred to by “I” and “II”. For instance, dRPA-I means that the response function has been evaluated by a Dyson-like equation where the kernel is a simple Coulomb interaction and the energy expression is formed by a contraction using non-antisymmetrized “single-bar” two-electron integrals. The notation RPAx-II means a method, where the response equations are the TDHF equations with antisymmetrized two-electron integrals in the kernel, and the energy is calculated also with antisymmetrized “double-bar” integrals.

In this chapter first we are going to overview the main types of the RPA correlation energy formulations on the example of the dRPA-I. The different RPA “flavors” can be classified according to the way the interaction strength and the frequency integrations are carried out: either analytically or numerically. Anyhow, it would be impractical to leave both integrals on numerical quadratures. After a first analytical integration we are left with different physical objects. It is possible also to perform both integrations analytically, leading to again a very differently looking expression. Three other topics will be discussed in this chapter: the relationship to the coupled cluster doubles (CCD) theory, the Hartree-Fock based energy expression and various attempts to include at least partly some exchange effects in the RPA scheme via antisymmetrized integrals.

### 3.1 Kohn-Sham reference: direct RPA

The polarization propagator matrix expression will be used in the following. This formalism has the double advantage that the matrix expression can be directly implemented in quantum chemical codes and the incorporation of exchange effects is quite obvious. Our starting point will be the formally exact ACFDT expression, Eq.(2.4.13), where we have to calculate first the response function in dRPA. This consists in changing the kernel to a simple Coulomb matrix:

$$\mathbb{\Pi}_\lambda^{-1}(z) = \mathbb{\Pi}_0^{-1}(z) - \mathbb{F}_{Hxc}^\lambda(z) \quad \Rightarrow \quad \mathbb{\Pi}_{\text{RPA},\lambda}^{-1}(z) = \mathbb{\Pi}_0^{-1}(z) - \lambda \mathbb{V} \quad (3.1.1)$$

In dRPA the interaction kernel matrix is constituted from four identical blocks,

$$\mathbb{V} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}, \quad (3.1.2)$$

where  $K_{ia,jb} = \langle ij|ab \rangle$  are the non-antisymmetrized two-electron integrals (physicist's notation) in spin-orbitals. The solution of Eq. (3.1.1), required in the AC-FDT formula, Eq.(2.4.13) is

$$\mathbb{\Pi}_\lambda(i\omega) = (\mathbb{1} - \lambda \mathbb{\Pi}_0(i\omega) \mathbb{V})^{-1} \mathbb{\Pi}_0(i\omega). \quad (3.1.3)$$

The matrices appearing in the above formulae have doubled linear dimensions with respect to the necessary minimal number  $N_{exc} = N_{occ} \times N_{virt}$ . It is a nontrivial but straightforward exercise to show that with the help of the non-interacting reduced dimension response function  $\mathbb{\Pi}_0(i\omega) = \mathbb{\Pi}_0^+(i\omega) + \mathbb{\Pi}_0^-(i\omega)$  the reduced dimension interacting response function is given by

$$\mathbb{\Pi}_\lambda(i\omega) = (\mathbf{I} - \lambda \mathbb{\Pi}_0(i\omega) \mathbf{K})^{-1} \mathbb{\Pi}_0(i\omega). \quad (3.1.4)$$

Accordingly, the dRPA-I correlation energy is

$$E_c^{\text{dRPA-I}} = -\frac{1}{2} \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \{ \mathbb{\Pi}_\lambda(i\omega) \mathbf{K} - \mathbb{\Pi}_0(i\omega) \mathbf{K} \}. \quad (3.1.5)$$

which will be used as starting point to in the forthcoming derivations concerning dRPA-I.

To avoid the double numerical integration (adiabatic connection parameter and frequency) we will examine the possibilities of integrating analytically at least according to one of the variables.

#### Adiabatic connection dRPA-I formulation

After the analytical integration according to the frequency parameter, the adiabatic connection integral can usually be calculated on a few numerical quadrature points.

Starting from Eq. (3.1.5) and using that

$$\mathbb{\Pi}_0(i\omega) = \mathbb{\Pi}_0^+(i\omega) + \mathbb{\Pi}_0^-(i\omega) = -2\epsilon^{1/2}(\epsilon^2 + \omega^2 \mathbf{I})^{-1} \epsilon^{1/2}, \quad (3.1.6)$$

we have from the ‘‘dimension-reduced’’ Dyson equation  $\mathbb{\Pi}_\lambda^{-1}(i\omega) = \mathbb{\Pi}_0^{-1}(i\omega) - \lambda \mathbf{K}$  that

$$\mathbb{\Pi}_\lambda^{-1}(i\omega) = -\frac{1}{2} \epsilon^{-1/2} (\mathbf{M}_\lambda + \omega^2 \mathbf{I}) \epsilon^{-1/2}, \quad (3.1.7)$$

where

$$\mathbf{M}_\lambda = \boldsymbol{\epsilon}^{1/2}(\boldsymbol{\epsilon} + 2\lambda\mathbf{K})\boldsymbol{\epsilon}^{1/2}. \quad (3.1.8)$$

The symmetric matrix  $\mathbf{M}_\lambda$  can be brought to a diagonal form using its eigenvectors and eigenvalues:

$$\mathbf{M}_\lambda \mathbf{Z}_\lambda = \mathbf{Z}_\lambda \boldsymbol{\Omega}_\lambda^2, \quad \mathbf{Z}_\lambda \mathbf{Z}_\lambda^T = \mathbf{Z}_\lambda^T \mathbf{Z}_\lambda = \mathbf{I}. \quad (3.1.9)$$

Thus we find:

$$\begin{aligned} \boldsymbol{\Pi}_\lambda^{-1}(i\omega) &= -\frac{1}{2}\boldsymbol{\epsilon}^{-1/2}\mathbf{Z}_\lambda\mathbf{Z}_\lambda^T(\mathbf{M}_\lambda + \omega^2\mathbf{1})\mathbf{Z}_\lambda\mathbf{Z}_\lambda^T\boldsymbol{\epsilon}^{-1/2} \\ &= -\frac{1}{2}\boldsymbol{\epsilon}^{-1/2}\mathbf{Z}_\lambda(\boldsymbol{\Omega}_\lambda^2 + \omega^2\mathbf{I})\mathbf{Z}_\lambda^T\boldsymbol{\epsilon}^{-1/2}, \end{aligned} \quad (3.1.10)$$

and furthermore:

$$\boldsymbol{\Pi}_\lambda(i\omega) = -2\boldsymbol{\epsilon}^{1/2}\mathbf{Z}_\lambda(\boldsymbol{\Omega}_\lambda^2 + \omega^2\mathbf{I})^{-1}\mathbf{Z}_\lambda^T\boldsymbol{\epsilon}^{1/2}. \quad (3.1.11)$$

Noting that

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{1}{\Omega_{\lambda,k}^2 + \omega^2} = \frac{1}{2}\Omega_{\lambda,k}^{-1},$$

where  $k$  labels the eigenvalues of  $\mathbf{M}_\lambda$ , we get

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \boldsymbol{\Pi}_\lambda(i\omega) &= -2\boldsymbol{\epsilon}^{1/2}\mathbf{Z}_\lambda \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (\boldsymbol{\Omega}_\lambda + \omega^2\mathbf{I})^{-1} \right\} \mathbf{Z}_\lambda^T\boldsymbol{\epsilon}^{1/2} \\ &= -\boldsymbol{\epsilon}^{1/2}\mathbf{Z}_\lambda\boldsymbol{\Omega}_\lambda^{-1}\mathbf{Z}_\lambda^T\boldsymbol{\epsilon}^{1/2} = -\boldsymbol{\epsilon}^{1/2}\mathbf{M}_\lambda^{-1/2}\boldsymbol{\epsilon}^{1/2} \end{aligned} \quad (3.1.12)$$

Furthermore, since  $\mathbf{M}_0 = \boldsymbol{\epsilon}^2$ , we have

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \boldsymbol{\Pi}_0(i\omega) = -\boldsymbol{\epsilon}^{1/2}\boldsymbol{\epsilon}^{-1}\boldsymbol{\epsilon}^{1/2} = -\mathbf{I}, \quad (3.1.13)$$

which finally leads to

$$\boxed{\mathbf{E}_c^{\text{dRPA-I}} = \frac{1}{2} \int_0^1 d\lambda \operatorname{tr} \{ (\boldsymbol{\epsilon}^{1/2}\mathbf{M}_\lambda^{-1/2}\boldsymbol{\epsilon}^{1/2} - \mathbf{I})\mathbf{K} \}} \quad (3.1.14)$$

or

$$\boxed{\mathbf{E}_c^{\text{dRPA-I}} = \frac{1}{2} \int_0^1 d\lambda \operatorname{tr} \{ \mathbf{P}_{c,\lambda}^{\text{dRPA}} \mathbf{K} \}} \quad (3.1.15)$$

This method has been proposed first and implemented in a quantum chemical program package (Turbomole) by Furche [16].

**Exercise #:** Demonstrate the physical meaning of the frequency integral

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr}\{\Pi_0(i\omega)\mathbf{K}\} = \sum_i \sum_a \langle ii|aa \rangle$$

which plays the role of an integration constant for the AC integral.

### Example of the minimal basis H<sub>2</sub> molecule

In minimal basis H<sub>2</sub> we have only one occupied and one virtual orbital, so the matrices are one-dimensional for spin-adapted singlet, which is the only contribution to the correlation energy. This simple model is discussed in the textbook Modern Quantum Chemistry by Szabo and Ostlund. The "full CI" correlation energy is given by

$$E_c^{\text{FCI}} = \Delta - \sqrt{\Delta^2 + K^2} \quad (3.1.16)$$

with

$$2\Delta = 2\Delta\varepsilon + J_{11} + J_{22} - 4J_{12} + 2K \quad (3.1.17)$$

Considering the occupied/virtual orbital energy difference,  $\Delta\varepsilon$  and the two-electron integral,  $K = \langle 11|22 \rangle$ ,  $M = \Delta\varepsilon^{1/2}(\Delta\varepsilon + 4\lambda K)\Delta\varepsilon^{1/2} = \Delta\varepsilon^2 + 4\lambda\Delta\varepsilon K$ . The correlation energy is given by the integral

$$E_c^{\text{dRPA-I}} = \int_0^1 d\lambda \frac{\Delta\varepsilon K}{\sqrt{\Delta\varepsilon(\Delta\varepsilon + 4\lambda K)}} - K \quad (3.1.18)$$

Analytical integration gives:

$$E_c^{\text{dRPA-I}} = -\frac{1}{2} \left( 2K + \Delta\varepsilon - \sqrt{\Delta\varepsilon(\Delta\varepsilon + 4K)} \right) \quad (3.1.19)$$

### Dielectric matrix expression

An alternative possibility is to perform analytically the adiabatic connection integral analytically and use a numerical quadrature for the frequency integration.

Start again from the double integral form after substituting the formal solution of the Dyson-like response equation:

$$E_c^{\text{dRPA-I}} = -\frac{1}{2} \int_0^1 d\lambda \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr}\left\{ \left( (\mathbf{I} - \lambda \Pi_0(i\omega)\mathbf{K})^{-1} \Pi_0(i\omega) - \Pi_0(i\omega) \right) \mathbf{K} \right\} \quad (3.1.20)$$

The general definition of a matrix function is  $f(\mathbf{A}) = \mathbf{Q} f(\mathbf{D}) \mathbf{Q}^{-1}$ , where  $\mathbf{A} = \mathbf{Q}\mathbf{D}\mathbf{Q}^{-1}$ ,  $\mathbf{D}$  is the diagonal matrix of the eigenvalues of  $\mathbf{A}$  and  $\mathbf{Q}$  is the matrix of eigenvectors, respectively.

$$\Pi_\lambda(i\omega)\mathbf{K} = \mathbf{Q}(i\omega)(\mathbf{I} - \lambda\mathbf{D}(i\omega))^{-1}\mathbf{D}(i\omega)\mathbf{Q}^{-1}(i\omega). \quad (3.1.21)$$

Using the cyclic invariance of the trace and denoting by  $d_i$  the  $i$ -th diagonal element of  $\mathbf{D}$ , Eq. (3.1.5) becomes

$$\begin{aligned} E_c^{\text{dRPA-I}} &= -\frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int_0^1 d\lambda \sum_{i=1}^n \left\{ \frac{d_i(i\omega)}{1 - \lambda d_i(i\omega)} - d_i(i\omega) \right\} \\ &= \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{i=1}^n \left\{ \log(1 - d_i(i\omega)) + d_i(i\omega) \right\}, \end{aligned} \quad (3.1.22)$$

where  $n$  denotes the total number of eigenvalues; specifically, in the occupied-virtual state representation used up to this point  $n = N_{exc}$ .

In matrix form Eq. (3.1.22) can be written as

$$E_c^{\text{dRPA-I}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \left\{ \log(\mathbf{I} - \Pi_0(i\omega)\mathbf{K}) + \Pi_0(i\omega)\mathbf{K} \right\}. \quad (3.1.23)$$

We recognize here the matrix representation of the dielectric function,  $\varepsilon(i\omega) = \mathbf{I} - \Pi_0(i\omega)\mathbf{K}$ , and the dRPA-I correlation energy can be written as:

$$E_c^{\text{dRPA-I}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \left\{ \log(\varepsilon(i\omega)) + \mathbf{I} - \varepsilon(i\omega) \right\} \quad (3.1.24)$$

This expression may be called the *dielectric matrix formulation* of the dRPA-I correlation energy.

### Example of the minimal basis $\text{H}_2$ molecule

The noninteracting response function is simply

$$\Pi_0(i\omega) = -\frac{\Delta\varepsilon}{\Delta\varepsilon^2 + \omega^2} \quad (3.1.25)$$

The correlation energy is given by the frequency integral

$$E_c^{\text{dRPA-I}} = -\int_0^\infty \frac{d\omega}{2\pi} \log(1 - \Pi_0(i\omega)K) + \Pi_0(i\omega)K = \int_0^\infty \frac{d\omega}{2\pi} \frac{4K\Delta\varepsilon}{\Delta\varepsilon^2 + \omega^2} \quad (3.1.26)$$

which can be carried out again analytical and yields the same result as the dielectric matrix formulation

$$\begin{aligned} E_c^{\text{dRPA-I}} &= \int_0^\infty \frac{d\omega}{2\pi} \left\{ \log\left(1 + \frac{4K\Delta\varepsilon}{\Delta\varepsilon^2 + \omega^2}\right) - \frac{4K\Delta\varepsilon}{\Delta\varepsilon^2 + \omega^2} \right\} \\ &= -\frac{1}{2} \left( 2K + \Delta\varepsilon - \sqrt{\Delta\varepsilon(\Delta\varepsilon + 4K)} \right) \end{aligned} \quad (3.1.27)$$



## Plasmonic expression

Both integrations can be performed analytically, leading to another, different RPA energy expression, which does not require any numerical quadrature. One can integrate either the AC expression or the dielectric one, both methods lead to the same result.

Let us consider the generalized non-hermitian RPA eigenvalue equation

$$\mathbb{A}_\lambda \mathbb{C}_{\lambda,n} = \omega_{\lambda,n} \mathbb{A} \mathbb{C}_{\lambda,n}, \quad (3.1.28)$$

whose solutions come in pairs: positive excitation energies  $\omega_{\lambda,n}$  with eigenvectors  $\mathbb{C}_{\lambda,n} = (\mathbf{x}_{\lambda,n}, \mathbf{y}_{\lambda,n})$  and negative excitation energies  $\omega_{\lambda,-n} = -\omega_{\lambda,n}$  with eigenvectors  $\mathbb{C}_{\lambda,-n} = (\mathbf{y}_{\lambda,n}, \mathbf{x}_{\lambda,n})$ . The spectral representation of  $\mathbb{P}_\lambda^{\text{RPA}}(\omega)$  then writes

$$\mathbb{P}_\lambda^{\text{RPA}}(\omega) = \sum_n \left\{ \frac{\mathbb{C}_{\lambda,n} \mathbb{C}_{\lambda,n}^T}{\omega - \omega_{\lambda,n} + i0^+} - \frac{\mathbb{C}_{\lambda,-n} \mathbb{C}_{\lambda,-n}^T}{\omega - \omega_{\lambda,-n} - i0^+} \right\}, \quad (3.1.29)$$

where the sum is over eigenvectors  $n$  with positive excitation energies  $\omega_{\lambda,n} > 0$ . The fluctuation-dissipation theorem leads to the supermatrix representation of the correlation density matrix  $\mathbb{P}_{c,\lambda}^{\text{RPA}}$  (using contour integration in the upper half of the complex plane)

$$\mathbb{P}_{c,\lambda}^{\text{RPA}} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega 0^+} [\mathbb{P}_\lambda^{\text{RPA}}(\omega) - \mathbb{P}_0(\omega)] = \sum_n \{ \mathbb{C}_{\lambda,-n} \mathbb{C}_{\lambda,-n}^T - \mathbb{C}_{0,-n} \mathbb{C}_{0,-n}^T \}, \quad (3.1.30)$$

with the non-interacting eigenvectors  $\mathbb{C}_{0,-n} = (\mathbf{y}_{0,n}, \mathbf{x}_{0,n})$  with  $\mathbf{y}_{0,n} = \mathbf{0}$  and  $\mathbf{x}_{0,n} = \mathbf{1}_n$  (where  $\mathbf{1}_n$  is the vector whose  $n^{\text{th}}$  component is 1 and all other components are zero). The explicit supermatrix expression of the RPA correlation density matrix is thus

$$\mathbb{P}_{c,\lambda}^{\text{RPA}} = \begin{pmatrix} \mathbf{Y}_\lambda \mathbf{Y}_\lambda^T & \mathbf{Y}_\lambda \mathbf{X}_\lambda^T \\ \mathbf{X}_\lambda \mathbf{Y}_\lambda^T & \mathbf{X}_\lambda \mathbf{X}_\lambda^T \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}, \quad (3.1.31)$$

where  $\mathbf{X}_\lambda$  and  $\mathbf{Y}_\lambda$  are the matrices whose columns contain the eigenvectors  $\mathbf{x}_{\lambda,n}$  and  $\mathbf{y}_{\lambda,n}$ .

In the following we show the second analytic integration starting from the AC expression, which is rewritten in an equivalent form as

$$E_c^{\text{dRPA-I}} = \frac{1}{2} \int_0^1 d\lambda \sum_n \text{Tr} \{ \mathbb{C}_{\lambda,-n}^T \mathbb{V} \mathbb{C}_{\lambda,-n} - \mathbb{C}_{0,-n}^T \mathbb{V} \mathbb{C}_{0,-n} \}, \quad (3.1.32)$$

obtained by a cyclic permutation of the matrices in the trace. Since the positive excitation energies can be written as [11, 22]

$$\omega_{\lambda,n}^{\text{dRPA}} = \mathbb{C}_{\lambda,-n}^T \mathbb{A}_\lambda^{\text{dRPA}} \mathbb{C}_{\lambda,-n}, \quad (3.1.33)$$

the derivative of  $\omega_{\lambda,n}$  with respect to  $\lambda$  gives

$$\frac{d\omega_{\lambda,n}^{\text{dRPA}}}{d\lambda} = \mathbb{C}_{\lambda,-n}^T \frac{d\mathbb{A}_\lambda^{\text{dRPA}}}{d\lambda} \mathbb{C}_{\lambda,-n} = \mathbb{C}_{\lambda,-n}^T \mathbb{V} \mathbb{C}_{\lambda,-n}, \quad (3.1.34)$$

which allows one to perform the integral over  $\lambda$  in 3.1.32 analytically, leading to the plasmon formula

$$\begin{aligned} E_c^{\text{dRPA-I}} &= \frac{1}{2} \sum_n (\omega_{1,n}^{\text{dRPA}} - \omega_{0,n} - \mathbb{C}_{0,-n}^T \mathbb{V} \mathbb{C}_{0,-n}) \\ &= \frac{1}{2} \sum_n (\omega_{1,n}^{\text{dRPA}} - \omega_n^{\text{dTDA}}), \end{aligned} \quad (3.1.35)$$

where  $\sum_n \omega_n^{\text{dTDA}} = \sum_n \mathbb{C}_{0,-n}^T \mathbb{A}_1^{\text{dRPA}} \mathbb{C}_{0,-n} = \sum_n \omega_{0,n} + \mathbb{C}_{0,-n}^T \mathbb{V} \mathbb{C}_{0,-n}$  is the sum of the (positive) excitation energies in the direct Tamm-Dancoff approximation (dTDA). The sum of the dTDA excitation energies can also be expressed as  $\sum_n \omega_n^{\text{dTDA}} = \text{tr}\{\boldsymbol{\varepsilon} + \mathbf{K}\}$ .

**Exercise #:** When taking the derivative in Eq. (3.1.34) we have used an analog of the Hellmann-Feynman theorem for the excitation energies:

$$\frac{d\omega_{\lambda,n}^{\text{RPA}}}{d\lambda} = \mathbb{C}_{\lambda,-n}^T \frac{\mathbb{A}_{\lambda}^{\text{RPA}}}{d\lambda} \mathbb{C}_{\lambda,-n}$$

which holds as a consequence of the fact that  $\omega_{\lambda,n}^{\text{RPA}}$  excitation energies are solutions of a (non-Hermitian) eigenvalue problem Prove the theorem.

The correlation energy expression, Eq. (3.1.35) has a direct physical interpretation as the shift of the zero-point energy of a set of noninteracting harmonic oscillators upon the switching on of their interaction.

### Example of the minimal basis $\text{H}_2$ molecule

Using the results derived in the course on Green's function, the time-dependent Hartree excitation energies are given by the spin-adapted dRPA  ${}^1\mathbf{A}$  and  ${}^1\mathbf{B}$  matrices. In our 1-dimensional case

$$\omega^{\text{dRPA}} = \sqrt{({}^1\mathbf{A} + {}^1\mathbf{B})({}^1\mathbf{A} - {}^1\mathbf{B})} = \sqrt{(4K + \Delta\varepsilon)\Delta\varepsilon} \quad (3.1.36)$$

and the TDA excitation energy,  $\omega^{\text{dTDA}} = {}^1\mathbf{A} = \Delta\varepsilon + 2K$ . The correlation energy given by the plasmon formula is:

$$E_c^{\text{dRPA-I}} = \frac{1}{2} (\sqrt{(4K + \Delta\varepsilon)\Delta\varepsilon} - \Delta\varepsilon - 2K), \quad (3.1.37)$$

which agrees with the dielectric matrix and density matrix values.

## 3.2 Hartree-Fock reference: RPA with exchange

We have seen that the exact AC-DFT formula in the WFT case must involve one-electron correction terms, which are necessary to take into account the non-constancy of the density along this connection path. Crude approximations would be necessary to remove these correction terms and the resulting approximate AC-FDT formula, which involves only the frequency-dependent

response function is not only difficult to calculate, but it is doomed to fail because of the neglected terms. It can be anticipated that an approximate calculation of the response function, more precisely of the polarization propagator based on the Hartree-Fock independent particle reference, is not going to lead precise estimates of the correlation energy.

In spite of these facts, it is of some interest to briefly overview the Hartree-Fock based RPA approach, where, in contrast to the dRPA, exchange effects are consistently taken into account. According to the common usage in quantum chemistry, RPA is used as a synonym of the time-dependent Hartree-Fock method, while the dRPA would correspond to a time-dependent Hartree approach. In the following, in order to make clear the distinction between the two types of methods the acronym RPAX will be used when the response function is calculated at the TDHF level.

The RPAX equations are fully analogous to the dRPA variant, the only difference is that the  $\mathbf{A}$  and  $\mathbf{B}$  matrices are defined with antisymmetrized two-electron integrals and the orbitals are supposed to satisfy the Hartree-Fock equations. In the case of non-HF orbitals the definition of  $\mathbf{A}$  and  $\mathbf{B}$  matrices should be, in principle, modified.

### RPAX equations

In order to fix notations, we recall that the RPAX polarization propagator at interaction strength  $\lambda$  writes as

$$\mathbb{P}_\lambda^{\text{RPAX}}(\omega) = -(\mathbb{A}_\lambda - \omega \mathbb{A})^{-1}, \quad (3.2.1)$$

where the supermatrix  $\mathbb{A}_\lambda$  is calculated with the Hartree-Fock kernel  $\mathbb{W}$ ,

$$\mathbb{A}_\lambda^{\text{RPAX}} = \mathbb{A}_0 + \lambda \mathbb{W}. \quad (3.2.2)$$

The Hartree-Fock kernel is

$$\mathbb{W} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix}, \quad (3.2.3)$$

with the antisymmetrized two-electron integrals

$$A'_{ia,jb} = \langle ib||aj \rangle = \langle ib|aj \rangle - \langle ib|ja \rangle = K_{ia,jb} - J_{ia,jb}, \quad (3.2.4)$$

and

$$B_{ia,jb} = \langle ab||ij \rangle = \langle ab|ij \rangle - \langle ab|ji \rangle = K_{ia,jb} - K'_{ia,jb}. \quad (3.2.5)$$

### AC-RPAX-II energy expression

The RPAX-II correlation energy can be written in terms of the eigenvectors of the RPAX polarization propagator

$$E_c^{\text{RPAX-II}} = \frac{1}{4} \int_0^1 d\lambda \sum_n \text{Tr} \{ \mathbb{W} \mathbf{C}_{\lambda,-n} \mathbf{C}_{\lambda,-n}^T - \mathbb{W} \mathbf{C}_{0,-n} \mathbf{C}_{0,-n}^T \}, \quad (3.2.6)$$

or, using the block structure of  $\mathbb{W}$  [3.2.3],

$$E_c^{\text{RPAX-II}} = \frac{1}{4} \int_0^1 d\lambda \text{tr} \{ (\mathbf{Y}_\lambda \mathbf{Y}_\lambda^T + \mathbf{X}_\lambda \mathbf{X}_\lambda^T - \mathbf{I}) \mathbf{A}' + (\mathbf{Y}_\lambda \mathbf{X}_\lambda^T + \mathbf{X}_\lambda \mathbf{Y}_\lambda^T) \mathbf{B} \}. \quad (3.2.7)$$

Using the matrix  $\mathbf{Q}_\lambda$  which is given by

$$\begin{aligned}\mathbf{Q}_\lambda^{\text{RPax}} &= (\mathbf{X}_\lambda + \mathbf{Y}_\lambda) (\mathbf{X}_\lambda + \mathbf{Y}_\lambda)^{\text{T}} \\ &= (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' - \lambda \mathbf{B})^{1/2} (\mathbf{M}_\lambda^{\text{RPax}})^{-1/2} (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' - \lambda \mathbf{B})^{1/2},\end{aligned}\quad (3.2.8)$$

with

$$\mathbf{M}_\lambda^{\text{RPax}} = (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' - \lambda \mathbf{B})^{1/2} (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' + \lambda \mathbf{B}) (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' - \lambda \mathbf{B})^{1/2}, \quad (3.2.9)$$

and the inverse  $\mathbf{Q}_\lambda^{-1}$

$$(\mathbf{Q}_\lambda^{\text{RPax}})^{-1} = (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' - \lambda \mathbf{B})^{-1/2} (\mathbf{M}_\lambda^{\text{RPax}})^{1/2} (\boldsymbol{\varepsilon} + \lambda \mathbf{A}' - \lambda \mathbf{B})^{-1/2}, \quad (3.2.10)$$

we arrive at the adiabatic-connection formula for the RPax-II correlation energy

$$E_c^{\text{RPax-II}} = \frac{1}{4} \int_0^1 d\lambda \operatorname{tr} \left\{ \frac{1}{2} \mathbf{Q}_\lambda^{\text{RPax}} (\mathbf{A}' + \mathbf{B}) + \frac{1}{2} (\mathbf{Q}_\lambda^{\text{RPax}})^{-1} (\mathbf{A}' - \mathbf{B}) - \mathbf{A}' \right\}. \quad (3.2.11)$$

which is much more complicated as the dRPA-I correlation energy. The above expressions are written in spinorbitals. In practical applications for closed-shell systems a spin-adapted formulation is more advantageous. Details are given in Ref. [26], only the final result is cited here:

$$\begin{aligned}E_c^{\text{RPax-II}} &= \frac{1}{4} \int_0^1 d\lambda \operatorname{tr} \left\{ \frac{1}{2} ({}^1\mathbf{Q}_\lambda^{\text{RPax}}) ({}^1\mathbf{A}' + {}^1\mathbf{B}) + \frac{1}{2} ({}^1\mathbf{Q}_\lambda^{\text{RPax}})^{-1} ({}^1\mathbf{A}' - {}^1\mathbf{B}) - {}^1\mathbf{A}' \right\} \\ &+ \frac{3}{4} \int_0^1 d\lambda \operatorname{tr} \left\{ \frac{1}{2} ({}^3\mathbf{Q}_\lambda^{\text{RPax}}) ({}^3\mathbf{A}' + {}^3\mathbf{B}) + \frac{1}{2} ({}^3\mathbf{Q}_\lambda^{\text{RPax}})^{-1} ({}^3\mathbf{A}' - {}^3\mathbf{B}) - {}^3\mathbf{A}' \right\}.\end{aligned}\quad (3.2.12)$$

which is a sum of singlet and triplet contributions.

### RPax-II plasmon formula

The plasmon formula for the RPax-II correlation energy is found by taking profit of the cyclic invariance of the trace to rewrite 3.2.6 as

$$E_c^{\text{RPax-II}} = \frac{1}{4} \int_0^1 d\lambda \sum_n \operatorname{Tr} \left\{ \mathbb{C}_{\lambda,-n}^{\text{T}} \mathbb{W} \mathbb{C}_{\lambda,-n} - \mathbb{C}_{0,-n}^{\text{T}} \mathbb{W} \mathbb{C}_{0,-n} \right\}, \quad (3.2.13)$$

and then using  $d\omega_{\lambda,n}^{\text{RPax}}/d\lambda = \mathbb{C}_{\lambda,-n}^{\text{T}} (d\Lambda_\lambda^{\text{RPax}}/d\lambda) \mathbb{C}_{\lambda,-n} = \mathbb{C}_{\lambda,-n}^{\text{T}} \mathbb{W} \mathbb{C}_{\lambda,-n}$  the analytical integration over  $\lambda$  leads to

$$\begin{aligned}E_c^{\text{RPax-II}} &= \frac{1}{4} \sum_n (\omega_{1,n}^{\text{RPax}} - \omega_{0,n} - \mathbb{C}_{0,-n}^{\text{T}} \mathbb{W} \mathbb{C}_{0,-n}) \\ &= \frac{1}{4} \sum_n (\omega_{1,n}^{\text{RPax}} - \omega_n^{\text{TDAx}}),\end{aligned}\quad (3.2.14)$$

where  $\sum_n \omega_n^{\text{TDAX}} = \sum_n \mathbb{C}_{0,-n}^{\text{T}} \hat{\Lambda}_1^{\text{RPAX}} \mathbb{C}_{0,-n} = \sum_n \omega_{0,n} + \mathbb{C}_{0,-n}^{\text{T}} \mathbb{W} \mathbb{C}_{0,-n}$  is the sum of the (positive) excitation energies in the Tamm-Dancoff approximation with exchange (TDAX) or configuration interaction singles (CIS). The sum of the TDAX excitation energies can also be expressed as  $\sum_n \omega_n^{\text{TDAX}} = \text{tr} \{ \boldsymbol{\varepsilon} + \mathbf{A}' \}$ . This plasmon formula was first presented by McLachlan and Ball [11] in the quantum chemistry literature.

The RPAX-II plasmon formula decomposes into sums over singlet and triplet excitation energies

$$E_c^{\text{RPAX-II}} = \frac{1}{4} \sum_n ({}^1\omega_{1,n}^{\text{RPAX}} - {}^1\omega_n^{\text{TDAX}}) + \frac{3}{4} \sum_n ({}^3\omega_{1,n}^{\text{RPAX}} - {}^3\omega_n^{\text{TDAX}}), \quad (3.2.15)$$

### 3.3 Ring CCD and RPA

The possibility of a close connection between the RPA and ring coupled cluster doubles correlation energies has been remarked by several authors in the past. In certain cases the close connection becomes strict identity, which might seem to be surprising. In the section we explore these relationships.

#### CCD

The coupled cluster doubles method is based on the following form of the correlated wave function:

$$|\Psi_{\text{CCD}}\rangle = \exp(\hat{T}_2)|\Phi_{\text{HF}}\rangle \quad (3.3.1)$$

where double excitations operator  $\hat{T}_2 = \frac{1}{4} \sum t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_i \hat{a}_b^\dagger \hat{a}_j$  is parametrized by the amplitudes  $t_{ij}^{ab}$ . The CCD correlation energy is

$$E_c^{\text{CCD}} = \langle \Phi_{\text{HF}} | \hat{H} | \Psi_{\text{CCD}} \rangle - \langle \Phi_{\text{HF}} | \hat{H} | \Phi_{\text{HF}} \rangle = \frac{1}{4} \sum \langle ab || ij \rangle t_{ij}^{ab} = \frac{1}{4} \text{tr}[\mathbf{BT}] \quad (3.3.2)$$

where  $B_{ia,jb} = \langle ab || ij \rangle$  are antisymmetrized two-electron integrals. The CCD amplitudes satisfy the nonlinear equations,

$$0 = \langle \Phi_{ij}^{ab} | \exp(-\hat{T}_2) \hat{H} \exp(\hat{T}_2) | \Phi \rangle. \quad (3.3.3)$$

The CCD equations can be simplified by keeping only certain kind of terms. One speaks about *ring coupled cluster doubles* approximation, when only the terms corresponding to the particle-hole ring contractions are retained. The rCCD equations can be expressed as

$$\mathbf{0} = \mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} \quad (3.3.4)$$

with  $A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + \langle ib || aj \rangle$ .

Although CCD and rCCD, when they are derived from a Hartree-Fock reference naturally involve exchange, a further approximation can be introduced in a DFT context: the antisymmetrized two-electron integrals are replaced by non-antisymmetrized integrals. The resulting

direct ring CCD (ddccd) method is similar to the rCCD, excepted the definition of the  $\mathbf{A}$  and  $\mathbf{B}$  matrices:  $B_{ia,jb}^{\text{drCCD}} = \langle ab|ij \rangle$  and  $A_{ia,jb}^{\text{ddccd}} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + \langle ib|aj \rangle$ , and the energy expression, which takes a pre-factor of 1/2 instead of 1/4:

$$E_c^{\text{drCCD}} = \frac{1}{2}\text{tr}[\mathbf{B}^{\text{drCCD}}\mathbf{T}^{\text{drCCD}}] \quad (3.3.5)$$

## Equivalence of RPA and ring CCD

In 2008, Kresse and his coworkers implemented the rCCD method in VASP and realized that the obtained correlation energies systematically agreed with the RPA results. It was obvious that such an agreement cannot be a question of hazard. Inspired by the numerical observations of the VASP group, presented at a conference in september 2008, Scuseria [27] succeeded in proving formally the equivalence of these methods.

Write the RPA generalized eigenvalue problem in the following form:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \omega, \quad (3.3.6)$$

Multiply from the right by  $\mathbf{X}^{-1}$  and introduce the notations  $\mathbf{R} = \mathbf{X}\omega\mathbf{X}^{-1}$  and  $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{I} \\ \mathbf{T} \end{pmatrix} = \begin{pmatrix} \mathbf{I} \\ \mathbf{T} \end{pmatrix} \mathbf{R}, \quad (3.3.7)$$

Alter multiplication from the left by  $(\mathbf{T} - \mathbf{I})$

$$(\mathbf{T} - \mathbf{I}) \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{I} \\ \mathbf{T} \end{pmatrix} = (\mathbf{T} - \mathbf{I}) \begin{pmatrix} \mathbf{I} \\ \mathbf{T} \end{pmatrix} \mathbf{R}, \quad (3.3.8)$$

and carrying out the matrix multiplications we obtain the rCCD equation:

$$\mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0} \quad (3.3.9)$$

From the RPA equations we obtain the relationship  $\mathbf{A} + \mathbf{BT} = \mathbf{R}$  which allows us to rewrite the energy expression:

$$E_c = \frac{1}{2}\text{tr}[\mathbf{BT}] = \frac{1}{2}\text{tr}[\mathbf{R} - \mathbf{A}] = \frac{1}{2}\text{tr}[\omega - \mathbf{A}] \quad (3.3.10)$$

which is just the dRPA plasmon formula.

## RPAX-II and ring-CCD

The ring CCD approximation corresponding to the RPAX-II plasmon formula can be derived in full analogy with the dRPA-I case. The rCCD correlation energy in spin-adapted formulation is

$$E_{c,\text{RPAX-II}} = \frac{1}{4}\text{tr} \{ {}^1\mathbf{B} {}^1\mathbf{T}_{\text{RPAX}} + 3 {}^3\mathbf{B} {}^3\mathbf{T}_{\text{RPAX}} \}, \quad (3.3.11)$$

where the singlet and triplet amplitudes  ${}^1\mathbf{T}_{\text{RPAX}}$  and  ${}^3\mathbf{T}_{\text{RPAX}}$  satisfy the equations

$${}^1\mathbf{B} + {}^1\mathbf{A} {}^1\mathbf{T}_{\text{RPAX}} + {}^1\mathbf{T}_{\text{RPAX}} {}^1\mathbf{A} + {}^1\mathbf{T}_{\text{RPAX}} {}^1\mathbf{B} {}^1\mathbf{T}_{\text{RPAX}} = \mathbf{0}, \quad (3.3.12)$$

and

$${}^3\mathbf{B} + {}^3\mathbf{A} {}^3\mathbf{T}_{\text{RPAX}} + {}^3\mathbf{T}_{\text{RPAX}} {}^3\mathbf{A} + {}^3\mathbf{T}_{\text{RPAX}} {}^3\mathbf{B} {}^3\mathbf{T}_{\text{RPAX}} = \mathbf{0}, \quad (3.3.13)$$

where  ${}^1A_{ia,jb} = \Delta\epsilon_{ia,jb} + 2\langle ib|aj\rangle - \langle ib|ja\rangle$ ,  ${}^1B_{ia,jb} = 2\langle ab|ij\rangle - \langle ab|ji\rangle$ ,  ${}^3A_{ia,jb} = \Delta\epsilon_{ia,jb} - \langle ib|ja\rangle$ , and  ${}^3B_{ia,jb} = -\langle ab|ji\rangle$ .

### First order limit: MP2

The amplitude equations in spinorbitals are solved iteratively starting with the first approximation

$$\mathbf{B} + \Delta\epsilon \mathbf{T}_{\text{RPAX}}^{(1)} + \mathbf{T}_{\text{RPAX}}^{(1)} \Delta\epsilon = \mathbf{0}, \quad (3.3.14)$$

leading to the MP2 energy by substitution of  $\mathbf{T}_{\text{RPAX}}^{(1)}$

$$\mathbf{T}_{ia,jb}^{(1)} = \frac{\langle ab|ij\rangle - \langle ab|ji\rangle}{\Delta\epsilon_{ia,jb} + \Delta\epsilon_{jb,ia}} \quad (3.3.15)$$

in the energy formula

$$E_{c,\text{MP2}} = \frac{1}{4} \text{tr} \left\{ \mathbf{B} \mathbf{T}_{\text{RPAX}}^{(1)} \right\} = \frac{1}{4} \sum_{iajb} \frac{|\langle ij||ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (3.3.16)$$

which is the usual MP2 energy expression in spinorbitals. Remark that the exchange-free drCCD approximation leads to a ‘‘direct MP2’’ energy, instead of the usual MP2, at the first order.

### Corrections to RPAX-II

The Hartree-Fock based rCCD method provides rather poor results. A diagrammatic analysis of the rCCD energy expression, Fukuda was the first to realize that although the second order result is correct, higher order contributions appear with an incorrect, too low by a factor of 2, coefficient. Szabo and Ostlund showed in 1977 that the RPAX-II method predicts a wrong asymptotic behavior of the intermolecular dispersion energy: the vdW coefficient is an average of the TDHF(RPA) and MP2 dispersion coefficients. Moszynski and coworkers analyzed the RPAX-II energy expression from the viewpoint of intermolecular interactions and proposed independently the same correction as Fukuda:

$$E_c^{\text{Fukuda}} = 2E_c^{\text{RPAX-II}} - E_c^{\text{MP2}} \quad (3.3.17)$$

This correction repairs the asymptotic behavior of the  $R^{-6}$  contribution to the intermolecular forces. Szabo and Ostlund showed that there are other problems: e.g. RPAX-II introduces nonphysical contributions as well.

## Amplitudes and correlation density matrix elements

If we compare the drCCD and dRPA(AC) correlation energy expressions

$$E_c^{\text{drCCD}} = \frac{1}{2} \text{tr}[\mathbf{B}\mathbf{T}^{\text{drCCD}}] \quad E_c^{\text{dRPA}} = \frac{1}{2} \text{tr}[\mathbf{B}\bar{\mathbf{P}}_c^{\text{dRPA}}] \quad (3.3.18)$$

where we define the adiabatic connection averaged correlation density matrix,  $\bar{\mathbf{P}}_c = \int_0^1 d\lambda \mathbf{P}_{c,\lambda}$ . At first glance one may think that the correlation density matrix  $\bar{\mathbf{P}}_c$  and the amplitude matrix  $\mathbf{T}$  are the same. This is not the case at all,  $\bar{\mathbf{P}}_c \neq \mathbf{T}$ , a fact that is less surprising if we consider that they obey quite different equations.

The Riccati equation at arbitrary interaction strength reads as

$$\lambda \mathbf{K} + (\epsilon + \lambda \mathbf{K}), \mathbf{T}_\lambda + \mathbf{T}_\lambda (\epsilon + \lambda \mathbf{K}) + \lambda \mathbf{T}_\lambda \mathbf{K} \mathbf{T}_\lambda = \mathbf{0}.$$

Using the normalization conditions

$$\mathbf{X}_\lambda^T \mathbf{X}_\lambda - \mathbf{Y}_\lambda^T \mathbf{Y}_\lambda = \mathbf{I} \quad \text{and} \quad \mathbf{Y}_\lambda^T \mathbf{X}_\lambda = \mathbf{X}_\lambda^T \mathbf{Y}_\lambda$$

from the expression of the density matrix

$$\mathbf{P}_\lambda = (\mathbf{X}_\lambda + \mathbf{Y}_\lambda)(\mathbf{X}_\lambda + \mathbf{Y}_\lambda)^T - \mathbf{I}. \quad (3.3.19)$$

and the definition of the amplitude  $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$ , one obtains the following expression for the density matrix:

$$\mathbf{P}_\lambda = 2\mathbf{T}_\lambda(\mathbf{I} - \mathbf{T}_\lambda)^{-1} = 2(\mathbf{T}_\lambda + \mathbf{T}_\lambda^2 + \mathbf{T}_\lambda^3 + \mathbf{T}_\lambda^4 + \dots)$$

such that the AC energy can be expressed by  $\lambda$ -dependent drCCD amplitudes

$$E_c^{\text{AC-dRPA}} = \frac{1}{2} \int_0^1 d\lambda \text{tr}\{\mathbf{K} \mathbf{P}_\lambda\} = \frac{1}{2} \int_0^1 d\lambda \text{tr}\{\mathbf{K} 2\mathbf{T}_\lambda(\mathbf{I} - \mathbf{T}_\lambda)^{-1}\}$$

First, we show that the series expansion of the interaction strength averaged density matrix is term-by-term different from the series expansion of the amplitude. Inserting the expansion

$$\mathbf{T}_\lambda = \lambda \mathbf{T}^{(1)} + \lambda^2 \mathbf{T}^{(2)} + \lambda^3 \mathbf{T}^{(3)} + \dots$$

in the coupling strength averaged density matrix expansion, one obtains

$$\begin{aligned} \bar{\mathbf{P}}_c = 2 \int_0^1 d\lambda \mathbf{T}_\lambda (\mathbf{I} - \mathbf{T}_\lambda)^{-1} = & \mathbf{T}^{(1)} + \frac{2}{3} (\mathbf{T}^{(2)} + (\mathbf{T}^{(1)})^2) + \\ & + \frac{2}{4} (\mathbf{T}^{(3)} + \mathbf{T}^{(2)} \mathbf{T}^{(1)} + \mathbf{T}^{(1)} \mathbf{T}^{(2)} + (\mathbf{T}^{(1)})^3) + \dots \end{aligned} \quad (3.3.20)$$

Disregarded from the first term  $\mathbf{T}^{(1)}$ , all higher order terms appear with different prefactors in the two expansions, proving that these matrices are different.



In spite of that lack of equality of the amplitude and density matrices, the drCCD and dRPA-I correlation energies are the same. To show that, we consider the expanded form of the drCCD energy by substituting  $\mathbf{T}_\lambda$  at  $\lambda = 1$ :

$$E_c^{\text{drCCD}} = \frac{1}{2} (\text{tr}(\mathbf{K} \mathbf{T}^{(1)}) + \text{tr}(\mathbf{K} \mathbf{T}^{(2)}) + \text{tr}(\mathbf{K} \mathbf{T}^{(3)}) + \text{tr}(\mathbf{K} \mathbf{T}^{(4)}) + \dots)$$

and calculate the coupling strength integral of the AC-dRPA-I energy using the same expansion

$$\begin{aligned} E_c^{\text{dRPA-I}} &= \frac{1}{2} \int_0^1 d\lambda \, 2\text{tr}(\mathbf{K} (\mathbf{T}_\lambda + \mathbf{T}_\lambda^2 + \mathbf{T}_\lambda^3 + \mathbf{T}_\lambda^4 \dots)) \\ &= \frac{1}{2} \left( \text{tr}\{\mathbf{K}\mathbf{T}^{(1)}\} + \frac{2}{3}\text{tr}\{\mathbf{K}\mathbf{T}^{(2)}\} + \frac{2}{3}\text{tr}\{\mathbf{K}(\mathbf{T}^{(1)})^2\} \right. \\ &\quad + \frac{1}{4}\text{tr}\{\mathbf{K}(\mathbf{T}^{(3)} + (\mathbf{T}^{(1)})^3 + \mathbf{T}^{(1)}\mathbf{T}^{(2)} + \mathbf{T}^{(2)}\mathbf{T}^{(1)})\} \\ &\quad + \frac{1}{5}\text{tr}\{\mathbf{K}(\mathbf{T}^{(4)} + \mathbf{T}^{(1)}\mathbf{T}^{(2)}\mathbf{T}^{(1)} + (\mathbf{T}^{(1)})^2\mathbf{T}^{(2)} + \mathbf{T}^{(2)}(\mathbf{T}^{(1)})^2)\} \\ &\quad \left. + \frac{1}{5}\text{tr}\{\mathbf{K}(\mathbf{T}^{(1)}\mathbf{T}^{(3)} + \mathbf{T}^{(3)}\mathbf{T}^{(1)} + (\mathbf{T}^{(2)})^2 + (\mathbf{T}^{(1)})^4)\} + \dots \right) \end{aligned}$$

It can be demonstrated order by order that the two expansions are equal. For this purpose, we use the  $n$ th order Riccati equations:

$$\lambda^1 : \mathbf{K} + \Delta\epsilon\mathbf{T}^{(1)} + \mathbf{T}^{(1)}\Delta\epsilon = \mathbf{0} \quad (3.3.21)$$

$$\lambda^2 : \Delta\epsilon\mathbf{T}^{(2)} + \mathbf{T}^{(2)}\Delta\epsilon + \mathbf{K}\mathbf{T}^{(1)} + \mathbf{T}^{(1)}\mathbf{K} = \mathbf{0} \quad (3.3.22)$$

$$\lambda^3 : \Delta\epsilon\mathbf{T}^{(3)} + \mathbf{T}^{(3)}\Delta\epsilon + \mathbf{K}\mathbf{T}^{(2)} + \mathbf{T}^{(2)}\mathbf{K} + \mathbf{T}^{(1)}\mathbf{K}\mathbf{T}^{(1)} = \mathbf{0} \quad (3.3.23)$$

$$\lambda^4 : \Delta\epsilon\mathbf{T}^{(4)} + \mathbf{T}^{(4)}\Delta\epsilon + \mathbf{K}\mathbf{T}^{(3)} + \mathbf{T}^{(3)}\mathbf{K} + \mathbf{T}^{(1)}\mathbf{K}\mathbf{T}^{(2)} + \mathbf{T}^{(2)}\mathbf{K}\mathbf{T}^{(1)} = \mathbf{0} \quad (3.3.24)$$

For instance, multiplication of the first order Riccati equation by  $\mathbf{T}^{(2)}$  and taking the trace leads to

$$\text{tr}\{\mathbf{K}\mathbf{T}^{(2)}\} = -2\text{tr}\{\Delta\epsilon\mathbf{T}^{(1)}\mathbf{T}^{(2)}\} \quad (3.3.25)$$

and multiplication of the second order Riccati by  $\mathbf{T}^{(1)}$

$$2\text{tr}\{\mathbf{K}(\mathbf{T}^{(1)})^2\} = -2\text{tr}\{\Delta\epsilon\mathbf{T}^{(2)}\mathbf{T}^{(1)}\} \quad (3.3.26)$$

we have used the cyclic invariance of the trace and obtain that

$$\frac{1}{2}\text{tr}\{\mathbf{K}\mathbf{T}^{(2)}\} = \text{tr}\{\mathbf{K}(\mathbf{T}^{(1)})^2\} \quad (3.3.27)$$

The third order energy contribution of the AC-dRPA-I energy is equal to the third order of the drCCD result:

$$\frac{4}{6}\text{tr}\{\mathbf{K}\mathbf{T}^{(2)}\} + \frac{2}{6}\text{tr}\{\mathbf{K}\mathbf{T}^{(2)}\} = \text{tr}\{\mathbf{K}\mathbf{T}^{(2)}\} \quad (3.3.28)$$

In a similar manner one can prove in each order the equivalence of the two energy expressions.

### 3.4 Approximate RPA schemes with exchange

As it has been stressed, the DFT definition of RPA is the neglect the exchange-correlation kernel. Exchange effects can be re-introduced at different levels: roughly speaking either in the density matrix (via the calculation of the response function) or in the amplitudes (via the Riccati equations). In the following a few examples, falling in one of these categories, will be discussed.

#### SOSEX

The *second order screened exchange* RPA method, introduced in this name by Kresse and Grüneis, is based on the drCCD amplitudes but uses antisymmetrized two-electron integrals in the correlation energy. This method has been first described by Freeman in a study of the correlation energy of the homogeneous electron gas. The significant improvement with respect to the dRPA-I method is related to the fact that SOSEX correction effectively removes the self-correlation error for a one-electron system. The SOSEX method in the coupled cluster formulation is thus defined by the energy expression (in spinorbitals):

$$E_c^{\text{SOSEX}} = \frac{1}{2} \text{tr}\{\mathbf{B}\mathbf{T}^{\text{drCCD}}\} \quad (3.4.1)$$

**Exercise #:** Show that the first approximation of the amplitudes substituted in the SOSEX energy expression yields the MP2 result.

We note that SOSEX-like approximations can also be derived in response function based RPA formulations as well. Following the philosophy of SOSEX, first we have to calculate the response at the dRPA level and contract the correlation density matrix, obtained from analytical (or numerical) frequency integration, with antisymmetrized two-electron integrals. This “AC-SOSEX” variant, called in our previous works also as dRPA-IIa is the density-matrix analog of the SOSEX energy expression:

$$E_c^{\text{dRPA-IIa}} = \frac{1}{2} \text{tr}\{\mathbf{B}\bar{\mathbf{P}}_c^{\text{dRPA}}\} \quad (3.4.2)$$

It can be shown analytically by a perturbation analysis that these two SOSEX variants are not strictly equivalent, but our numerical experience shows that the differences are usually very small.

The main advantage of SOSEX is in the calculation of total correlation energies. For weakly bound intermolecular complexes (London dispersion forces) the difference between dRPA-I and SOSEX is very small.

#### Hesselmann’s RPAX2 method

The dRPA Riccati equations

$$\boldsymbol{\varepsilon}\mathbf{T} + \mathbf{T}\boldsymbol{\varepsilon} + (\mathbf{I} + \mathbf{T})\mathbf{K}(\mathbf{I} + \mathbf{T}) = \mathbf{0} \quad (3.4.3)$$

can be quite efficiently solved by density fitting or Cholesky decomposition methods. The usual update formula is

$$\mathbf{T}^{(n+1)} = -\Delta \circ (\mathbf{K} + \mathbf{K}\mathbf{T}^{(n)} + \mathbf{T}^{(n)}\mathbf{K} + \mathbf{T}^{(n)}\mathbf{K}\mathbf{T}^{(n)}) \quad (3.4.4)$$

with  $\Delta_{ia,jb} = 1/(\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j)$  and  $\circ$  means an entrywise matrix product. By taking the decomposition of the two-electron integrals and of the energy denominator

$$\mathbf{K} = \mathbf{L}\mathbf{L}^T \quad \Delta = \sum_{\zeta} \mathbf{e}_{\zeta}\mathbf{e}_{\zeta}^T \quad (3.4.5)$$

the update

$$\mathbf{T}^{(n+1)} = -\sum_{\zeta} \mathbf{e}_{\zeta} \cdot (\mathbf{L} + \mathbf{T}^{(n)}\mathbf{L})(\mathbf{L} + \mathbf{T}^{(n)}\mathbf{L})^T \cdot \mathbf{e}_{\zeta}^T = -\sum_{\zeta} \mathbf{e}_{\zeta} \cdot \mathbf{U}\mathbf{U}^T \cdot \mathbf{e}_{\zeta}^T \quad (3.4.6)$$

Since  $\mathbf{U}$  has smaller dimensions as the occ/virt products, the resulting algorithm is considerably lighter.

The rCCD Riccati equation cannot be simplified the above manner, because we have both  $\mathbf{B}$  and  $\mathbf{A}'$  matrices, but the favorable mathematical form can be recovered if one replaces  $\mathbf{A}'$  by  $\mathbf{B}$ . Interestingly, it turned out by the diagrammatic analysis of this method the RPAX behaves better (the various diagrams have the good prefactor) in cases where RPAX fails. Hesselmann justified also the usage of  $\mathbf{B}$  also by the fact that for 2-electron systems the exact-exchange EXX (OEP) Kohn-Sham gives identical formula.

## Other rCCD-based approximations

Szabo and Ostlund proposed alternative rCCD-based energy expressions as possible approximations to self-consistent RPA schemes. One of these approximations (RPAX-SO1) seems to be the only one, which is able to produce a correct asymptotic behavior of vdW complexes in the sense that RPA calculations of the intermolecular interaction energies lead to a  $C_6$  coefficient which is equal to the  $C_6$  calculated from the response equations at the same level (Casimir-Polder consistency).

$$E_{c,\text{RPAX-SO1}} = \frac{1}{2} \text{tr} \{ {}^1\mathbf{B} ({}^1\mathbf{T}^{\text{RPAX}} - {}^3\mathbf{T}^{\text{RPAX}}) \}. \quad (3.4.7)$$

This formula combines the singlet and triplet amplitudes and has the drawback that it is more susceptible to fail due to the triplet instabilities.

The another formula, having a structure reminiscent to the RPAX-I AC expression, is not affected by the triplet instability, but the asymptotic behavior of the van der Waals interaction energy is only approximately Casimir-Polder consistent:

$$E_{c,\text{RPAX-SO2}} = \frac{1}{2} \text{tr} \{ {}^1\mathbf{K} {}^1\mathbf{T}^{\text{RPAX}} \}. \quad (3.4.8)$$

According to our numerical experience the SO1 and SO2 methods produce very good results in a range-separated context.

## Bibliography

- [1] A. Hesselmann (Springer, Berlin, Heidelberg, 2014).
- [2] X. Ren, P. Rinke, C. Joas, and M. Scheffler, *J. Mater. Sci.* **47**, 7447 (2012).
- [3] A. Hesselmann, *Phys. Rev. A* **85**, 012517 (2012).
- [4] J. Paier, X. Ren, P. Rinke, G. E. Scuseria, A. Grüneis, G. Kresse, and M. Scheffler, *New J. Phys.* **14**, 043002 (2012).
- [5] H. Eshuis, J. E. Bates, and F. Furche, *Theoret. Chem. Acc.* **131**, 1 (2012).
- [6] A. Hesselmann and A. Görling, *Mol. Phys.* **109**, 2473 (2011).
- [7] D. Bohm and D. Pines, *Phys. Rev. B* **82**, 625 (1951).
- [8] D. Pines and D. Bohm, *Phys. Rev. B* **85**, 338 (1952).
- [9] D. Bohm and D. Pines, *Phys. Rev. B* **92**, 609 (1953).
- [10] P. Ring and P. Schuck, *The nuclear many-body problem* (Springer, New York, 1980).
- [11] A. D. McLachlan and M. A. Ball, *Rev. Mod. Phys.* **36**, 844 (1964).
- [12] A. Szabo and N. Ostlund, *J. Chem. Phys.* **67**, 4351 (1977).
- [13] J. Oddershede, *Adv. Quantum Chem.* **11**, 275 (1978).
- [14] D. C. Langreth and J. C. Perdew, *Solid State Commun.* **17**, 1425 (1975).
- [15] J. Harris and R. O. Jones, *J. Phys. F : Metal Phys.* **4**, 1170 (1974).
- [16] F. Furche, *Phys. Rev. B* **64**, 195120 (2001).
- [17] M. Fuchs and X. Gonze, *Phys. Rev. B* **65**, 235109 (2002).
- [18] T. Miyake, F. Aryasetiawan, T. Kotani, M. van Schilfgaarde, M. Usuda, and K. Terakura, *Phys. Rev. B* **66**, 245103 (2002).
- [19] F. Aryasetiawan, T. Miyake, and K. Terakura, *Phys. Rev. Lett.* **88**, 166401 (2002).
- [20] J. Harl and G. Kresse, *Phys. Rev. Lett.* **103**, 056401 (2009).
- [21] H.-V. Nguyen and S. de Gironcoli, *Phys. Rev. B* **79**, 205114 (2009).
- [22] F. Furche, *J. Chem. Phys.* **129**, 114105 (2008).
- [23] X. Ren, P. Rinke, and M. Scheffler, *Phys. Rev. B* **80**, 045402 (2009).
- [24] H. Eshuis, J. Yarkony, and F. Furche, *J. Chem. Phys.* **132**, 234114 (2010).

- [25] W. Yang, J. Chem. Phys. **109**, 10107 (1998).
- [26] J. G. Ángyán, R.-F. Liu, J. Toulouse, and G. Jansen, J. Chem. Theory Comput. **7**, 3116 (2011).
- [27] G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, J. Chem. Phys. **129**, 231101 (2008).