

An introduction to reduced density matrix
functional theory
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In these notes we introduce the basic concepts of Reduced Density-Matrix Functional Theory (RDMFT). We discuss the Hohenberg-Kohn theorem for local and non-local external potentials, which states that there exists a one-to-one mapping between the (non-degenerate) ground-state wavefunction of the system and the corresponding one-body reduced density matrix (1-RDM). As a consequence of this theorem all the ground-state properties of a physical system are functionals of the ground-state 1-RDM. We discuss the variational principle which allows us to determine the 1-RDM. In practice, however, approximations to the exchange-correlation energy are needed. We will discuss some of them.

0.1 Preliminaries

Let us consider a stationary system of N interacting electrons. The quantum mechanical behavior is completely described by the Schrödinger equation

$$\hat{H} |\Psi\rangle = E |\Psi\rangle. \quad (1)$$

where $|\Psi\rangle$ is an eigenstate and E the corresponding eigenenergy of the N -particle system. Here \hat{H} is the Hamiltonian operator of the system and is given by

$$\hat{H} = \hat{T} + \hat{V} + \hat{W},$$

where \hat{T} , \hat{V} and \hat{W} are the operators corresponding to the kinetic energy, the external potential and the two-particle interaction, respectively. In second quantization they are explicitly given by

$$\begin{aligned} \hat{T} &= \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \hat{\psi}(\mathbf{x}), \\ \hat{V} &= \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}') v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \hat{\psi}(\mathbf{x}), \\ \hat{W} &= \frac{1}{2} \int d\mathbf{x}' d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}), \end{aligned}$$

where \mathbf{x} is a combined space-spin coordinate $\mathbf{x} \equiv (\mathbf{r}, s)$ and $\int d\mathbf{x} = \sum_s \int d\mathbf{r}$. $\hat{\psi}(\mathbf{x})$ and $\hat{\psi}^\dagger(\mathbf{x})$ are the field operators in the Schrödinger picture and we assumed that particles interact via the Coulomb potential $v_c(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$. We note that atomic units are used throughout this work. Here we consider a non-local external potential $v_{\text{ext}}(\mathbf{x}, \mathbf{x}')$ as it will be useful for the following discussion. Non-local potentials are encountered if one wants to deal, for example, with spin-dependent potentials, magnetic fields or if one wants to study valence electrons using a pseudopotential to treat nuclei and core electrons.

The density matrix $\Gamma^{(N)}$ for a pure state of N electrons is defined, in second quantization, as

$$\Gamma^{(N)}(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{x}'_1, \dots, \mathbf{x}'_N) \equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_N) \dots \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \dots \hat{\psi}(\mathbf{x}_N) | \Psi \rangle.$$

This is equivalent to

$$\Gamma^{(N)}(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{x}'_1, \dots, \mathbf{x}'_N) \equiv N! \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N),$$

where $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \langle \mathbf{x}_1, \dots, \mathbf{x}_N | \Psi \rangle$ is the wavefunction corresponding to $|\Psi\rangle$. The n -body reduced density matrix (n -RDM) is defined as

$$\begin{aligned} \Gamma^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n; \mathbf{x}'_1, \dots, \mathbf{x}'_n) &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_n) \dots \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \dots \hat{\psi}(\mathbf{x}_n) | \Psi \rangle \\ &= \frac{N!}{(N-n)!} \int d\mathbf{x}_{n+1} \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_n, \mathbf{x}_{n+1}, \dots, \mathbf{x}_N) \\ &\quad \times \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N). \end{aligned} \quad (2)$$

In particular for the two-body reduced density matrix (2-RDM) and the one-body reduced density matrix (1-RDM) $\gamma \equiv \Gamma^{(1)}$, definition (2) reduces respectively to

$$\begin{aligned} \Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_2) | \Psi \rangle \\ &= N(N-1) \int d\mathbf{x}_3 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N), \end{aligned} \quad (3)$$

and

$$\begin{aligned} \gamma(\mathbf{x}, \mathbf{x}') &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) | \Psi \rangle \\ &= N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}', \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N). \end{aligned} \quad (4)$$

According to these definitions the 1-RDM normalizes to the total number of electrons

$$\text{Tr } \gamma(\mathbf{x}, \mathbf{x}') \equiv \int d\mathbf{x} \gamma(\mathbf{x}, \mathbf{x}) = N.$$

From the definition (2) one can see that the n -body and the $(n-1)$ -body reduced density matrices are related *via*

$$\begin{aligned} \Gamma^{(n-1)}(\mathbf{x}_1, \dots, \mathbf{x}_{n-1}; \mathbf{x}'_1, \dots, \mathbf{x}'_{n-1}) &= \frac{1}{N-n+1} \\ &\quad \times \int d\mathbf{x}_n \Gamma^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_{n-1}, \mathbf{x}_n; \mathbf{x}'_1, \dots, \mathbf{x}'_{n-1}, \mathbf{x}_n). \end{aligned}$$

In particular for $n = 2$

$$\gamma(\mathbf{x}, \mathbf{x}') = \frac{1}{N-1} \int d\mathbf{x}_2 \Gamma^{(2)}(\mathbf{x}, \mathbf{x}_2; \mathbf{x}', \mathbf{x}_2). \quad (5)$$

It is also worth noting that

$$\rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x}) = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (6)$$

i.e., the diagonal of the 1-RDM gives the electron density ρ .

We can now express the total energy of the system, $E = \langle \Psi | \hat{H} | \Psi \rangle$, in terms of reduced density matrices. It reads as

$$E = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}'), \quad (7)$$

where we used Eqs (3) and (4). This means that the total energy of the system is completely determined by the 1-RDM and the diagonal of the 2-RDM.

Using Eq. (5) the total energy can be rewritten as a functional of the 2-RDM alone. One might think to minimize this functional with respect to the 2-RDM to obtain the ground-state total energy. However there is a major obstacle in following this direction. The trial 2-RDMs must correspond to some antisymmetric wavefunction, *i.e.*, they must be N -representables. Varying the 2-RDM without imposing sufficient constraints can lead to a lower energy than the ground-state energy. The complete set of conditions for 2-RDM to be N -representable have been formulated by Mazziotti (2012) [18]. However, they are not practical.

The set of necessary and sufficient conditions for the 1-RDM to be N -representable is, instead, known and it turns out to be extremely simple as it will be discussed in the next section. One can, thus, use the 1-RDM as fundamental variable and express the total energy (7) and the ground-state expectation value of any operator as a functional of the 1-RDM. This is justified by a theorem, similar to the Hohenberg-Kohn theorem [12] of Density Functional Theory (DFT), which guarantees a one-to-one mapping between the 1-RDM γ and the ground-state wavefunction Ψ_0 .

0.2 Hohenberg-Kohn theorems

Before proving the map $\gamma \leftrightarrow \Psi_0$ in the general case of a nonlocal external potential $v_{\text{ext}}(\mathbf{r}, \mathbf{r}')$, it is instructive to review the case of a local external potential $v_{\text{ext}}(\mathbf{r}, \mathbf{r}') = v_{\text{ext}}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$.

0.2.1 Local potentials

In the case of external local potentials the first Hohenberg-Kohn theorem states that there exists a one-to-one mapping $\rho \leftrightarrow v_{\text{ext}}$ (in case of a non-degenerate ground state). The proof is as follows. First we notice that the map $v_{\text{ext}} \rightarrow \rho$ is provided by the time-independent Schrödinger equation (1) and Eq. (6). The external potential, indeed, determines the ground state Ψ_0 , from which ρ is calculated through Eq. (6).

The inverse map $\rho \rightarrow v_{\text{ext}}$ can be proven by *reductio ad absurdum*. First we show that two potentials v_{ext} and v'_{ext} differing by more than a constant, will not lead to

the same wavefunction ($\Psi_0 \rightarrow v_{\text{ext}}$). Let us assume that both potentials give the same ground state Ψ_0 . The Schrödinger equations are

$$\hat{H}\Psi_0 = E_0\Psi_0, \quad (8)$$

$$\hat{H}'\Psi_0 = E'_0\Psi_0, \quad (9)$$

where \hat{H} and \hat{H}' contain the potentials v_{ext} and v'_{ext} , respectively. Subtracting Eq. (9) from Eq. (8) we get

$$(\hat{H} - \hat{H}')\Psi_0 = (E_0 - E'_0)\Psi_0,$$

from which it follows that

$$(\hat{V} - \hat{V}')\Psi_0 = (E_0 - E'_0)\Psi_0. \quad (10)$$

Since \hat{V} and \hat{V}' are multiplicative operators (because we look at local potentials), we see from Eq. (10) that if in some region $v_{\text{ext}} \neq v'_{\text{ext}} + \text{const.}$ then Ψ_0 must vanish in that region for the above equation to hold. The wavefunction Ψ_0 cannot vanish on a set with nonzero measure [16], so we can divide by Ψ_0 arriving at the contradiction $\hat{V} - \hat{V}' = \text{const.}$ Therefore, local potentials that give the same ground-state wavefunction cannot differ by more than a constant.

We now need to prove the map $\rho \rightarrow \Psi_0$. Let v_{ext} and v'_{ext} be two potentials that differ by more than a constant. Since the corresponding wavefunctions Ψ and Ψ' are different by the previous theorem, we have

$$\begin{aligned} E &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle \\ &= \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \int d\mathbf{r} [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] \rho'(\mathbf{r}) \\ &= E' + \int d\mathbf{r} [v_{\text{ext}}(\mathbf{r}) - v'_{\text{ext}}(\mathbf{r})] \rho'(\mathbf{r}). \end{aligned}$$

Interchanging the roles of v_{ext} and v'_{ext} , we have

$$E' < E + \int d\mathbf{r} [v'_{\text{ext}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})] \rho(\mathbf{r}).$$

Adding the two inequalities we obtain

$$\int d\mathbf{r} [v'_{\text{ext}}(\mathbf{r}) - v_{\text{ext}}(\mathbf{r})] [\rho'(\mathbf{r}) - \rho(\mathbf{r})] < 0.$$

If the two ground-state densities were the same, we would have the contradiction $0 < 0$; therefore different ground states must have different ground-state densities. This defines the map $\rho (\rightarrow \Psi_0) \rightarrow v_{\text{ext}}$, and thus the one-to-one map $\rho \leftrightarrow v_{\text{ext}}$ is constructed.

This theorem has an important consequence: the ground-state wavefunction can be written as a functional of the density, $\Psi_0[\rho]$. As a consequence, the ground-state expectation values of any operator \hat{O} is also a functional of the density

$$O[\rho] \equiv \langle \Psi_0[\rho] | \hat{O} | \Psi_0[\rho] \rangle.$$

In particular, the total energy functional can be written as

$$\begin{aligned} E[\rho] &= \langle \Psi_0[\rho] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\rho] \rangle \\ &= \langle \Psi_0[\rho] | \hat{T} + \hat{W} | \Psi_0[\rho] \rangle + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \\ &= F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}), \end{aligned}$$

where $F[\rho]$ is defined independently of the external potential and, thus, it is a universal functional of the density.

Let ρ_0 be the ground-state density corresponding to the potential v_{ext} , then thanks to the variational principle we have for an arbitrary ρ

$$\begin{aligned} E[\rho] &= \langle \Psi_0[\rho] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi_0[\rho] \rangle \\ &\geq \langle \Psi_0[\rho_0] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi_0[\rho_0] \rangle = E[\rho_0]. \end{aligned}$$

This proves the second Hohenberg-Kohn theorem, which states that the exact density minimizes the ground-state energy functional:

$$E_0 = \inf_{\rho} \left\{ \langle \Psi_0[\rho] | \hat{T} + \hat{W} | \Psi_0[\rho] \rangle + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\},$$

where the infimum should be restricted to all pure-state v -representable densities ρ . A density is said to be pure-state v -representable if it is the density associated with the antisymmetric ground-state wavefunction of a Hamiltonian with some external local potential $v_{\text{ext}}(\mathbf{r})$. The conditions for a density to be v -representable are unknown. However DFT can be formulated in a way that only requires the density to be N -representable (see, *e.g.*, Ref. [21]). A density is N -representable if it can be obtained through Eq. (6) from some antisymmetric wavefunction. The conditions for a density ρ to be N -representable are [9]

$$\rho(\mathbf{r}) \geq 0, \quad \int d\mathbf{r} \rho(\mathbf{r}) = N, \quad \text{and} \quad \int d\mathbf{r} |\nabla \rho(\mathbf{r})|^{1/2} < \infty.$$

0.2.2 Non-local potentials

Gilbert [9] provided a generalization of the Hohenberg-Kohn theorem to the case of nonlocal potentials. The first difficulty one encounters is that it is not possible to show the existence of a one-to-one mapping between the external potential and the

ground-state wavefunction. This is a consequence of the fact that the potential is not a multiplicative operator [9]. However one can show that the map between Ψ_0 and γ is one-to-one, which is sufficient to justify a Reduced Density-Matrix Functional Theory. The proof follows the same line of argument as for the case of local potentials. First, Ψ_0 determines γ through the definition of the latter (see Eq. (4)). This is the $\Psi_0 \rightarrow \gamma$ map. The inverse map $\gamma \rightarrow \Psi_0$ is demonstrated by *reductio ad absurdum*.

Let v_{ext} and v'_{ext} be two potentials that generate two distinct ground-states Ψ_0 and Ψ'_0 , respectively. By the variational principle we have

$$\begin{aligned} E &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle \\ &= \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \int d\mathbf{x} d\mathbf{x}' [v_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v'_{\text{ext}}(\mathbf{x}, \mathbf{x}')] \gamma'(\mathbf{x}, \mathbf{x}') \\ &= E' + \int d\mathbf{x} d\mathbf{x}' [v_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v'_{\text{ext}}(\mathbf{x}, \mathbf{x}')] \gamma'(\mathbf{x}, \mathbf{x}'). \end{aligned}$$

Interchanging the roles of v_{ext} and v'_{ext} , we have

$$E' < E + \int d\mathbf{x} d\mathbf{x}' [v'_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v_{\text{ext}}(\mathbf{x}, \mathbf{x}')] \gamma(\mathbf{x}, \mathbf{x}').$$

Adding the two inequalities we obtain

$$\int d\mathbf{x} d\mathbf{x}' [v'_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v_{\text{ext}}(\mathbf{x}, \mathbf{x}')] [\gamma'(\mathbf{x}, \mathbf{x}') - \gamma(\mathbf{x}, \mathbf{x}')] < 0.$$

If the two ground-state 1-RDMs were the same, we would have the contradiction $0 < 0$. Therefore different ground states must have different 1-RDMs. This concludes the proof that the relation between the ground-state wavefunction and the ground-state 1-RDM is one-to-one ($\Psi_0 \leftrightarrow \gamma$).

This theorem implies that the ground-state wavefunction can be expressed as a functional of the 1-RDM, $\Psi_0[\gamma]$. Therefore the expectation values of any ground-state operator can be written as a functional of the 1-RDM

$$O[\gamma] \equiv \langle \Psi_0[\gamma] | \hat{O} | \Psi_0[\gamma] \rangle.$$

In particular the total energy functional is given by

$$\begin{aligned} E[\gamma] &= \langle \Psi_0[\gamma] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\gamma] \rangle \\ &= \int d\mathbf{x} d\mathbf{x}' h(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') + \underbrace{\langle \Psi_0[\gamma] | \hat{W} | \Psi_0[\gamma] \rangle}_{W_{HK}[\gamma]}, \end{aligned} \quad (11)$$

where

$$h(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}') \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) + v_{\text{ext}}(\mathbf{x}, \mathbf{x}')$$

is the one-body part of the Hamiltonian. Here it is evident the advantage of using the 1-RDM instead of the density ρ as a basic variable: the kinetic energy term is a well-known functional of the 1-RDM. This is not the case in DFT.

Let us now suppose that γ is the ground-state 1-RDM corresponding to the external potential v_{ext} and γ' the ground-state 1-RDM corresponding to a different v'_{ext} . Using the variational principle, we have

$$\begin{aligned} E[\gamma'] &= \int d\mathbf{x}d\mathbf{x}' h(\mathbf{x}, \mathbf{x}') \gamma'(\mathbf{x}, \mathbf{x}') + \langle \Psi_0[\gamma'] | \hat{W} | \Psi_0[\gamma'] \rangle \\ &= \langle \Psi_0[\gamma'] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\gamma'] \rangle \\ &\geq \langle \Psi_0[\gamma] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\gamma] \rangle = E[\gamma]. \end{aligned}$$

The exact 1-RDM, thus, minimizes the total energy functional. The ground state energy can be found as

$$E_0 = \inf_{\gamma} \left\{ \langle \Psi_0[\gamma] | \hat{W} | \Psi_0[\gamma] \rangle + \int d\mathbf{x}d\mathbf{x}' h(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') \right\}. \quad (12)$$

Note that the energy functional (11) is defined only for pure state v -representable 1-RDM, thus the infimum should be restricted to this class of 1-RDMs. However the conditions for a 1-RDM to be v -representable are unknown.

The problem is solved by minimizing the functional (12) over a larger set of 1-RDM, *i.e.*, the ensemble N -representable 1-RDMs. This is the 1-RDMFT version of the Lieb functional of DFT. Note that in this case, not only we know the sufficient and necessary conditions for ensemble N -representable density matrices but also the domain of the Lieb functional is convex (unlike the HK and Levy-Lieb (over N -representable density matrices) functionals.) By definition, a 1-RDM γ is said to be ensemble N -representable if a set of pure states $|\Psi_i\rangle$ and weights w_i , with $\sum_i w_i = 1$, exists such that

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_i w_i \langle \Psi_i | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) | \Psi_i \rangle.$$

The states $|\Psi_i\rangle$ form a mixed state characterized by the density matrix operator $\hat{\Gamma}^{(N)} = \sum_i w_i |\Psi_i\rangle \langle \Psi_i|$ with $\gamma(\mathbf{x}, \mathbf{x}') = \text{Tr} [\hat{\Gamma}^{(N)} \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x})]$.

For ensemble N -representable 1-RDM the functional $W[\gamma]$ can be defined as

$$W[\gamma] \equiv \inf_{\hat{\Gamma}^{(N)} \rightarrow \gamma} \text{Tr} [\hat{\Gamma}^{(N)} \hat{W}], \quad (13)$$

where now the infimum goes over all the ensemble density matrices which yield the given 1-RDM γ . If the ground-state is non-degenerate, the minimum of (13) corresponds to a pure state. In case the ground-state is degenerate, the minimization will give a linear combination of the 1-RDMs with the lowest energy [9].

The advantage of this extension is that the necessary and sufficient ensemble N -representability conditions for the 1-RDM are known and they turn out to be particularly simple [5, 17]: given the spectral representation of γ in terms of its eigenvalues

n_i (occupation numbers) and eigenfunction ϕ_i (natural spin orbitals, or for simplicity natural orbitals)

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_i n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}'),$$

the 1-RDM is ensemble N -representable if

$$0 \leq n_i \leq 1 \quad (14)$$

and

$$\sum_i n_i = N. \quad (15)$$

Condition (14) is related to the fact that an orbital cannot be occupied by more than one electron, according to Pauli principle. While condition (15) simply reflects the fact that the total number of electrons is equal to N .

Unlike DFT in which the density and the local potential are conjugate variables in the sense of the Legendre transform ($\delta F_{HK}/\delta \rho = -v^{loc}$), in RDMFT this is not the case since we have not managed to demonstrate the one-to-one mapping between 1RDM and non-local potentials up to a constant. Therefore it is not guaranteed that the derivative of the functional $W_{HK}[\gamma]$ can be uniquely defined. Nevertheless in the following I will assume that this is the case.

0.3 Energy as functional of the 1-RDM

As discussed in the previous section, the total energy can be expressed as a functional of the 1-RDM

$$E[\gamma] = E_{\text{kin}}[\gamma] + E_{\text{ext}}[\gamma] + E_{\text{int}}[\gamma],$$

where E_{kin} , E_{ext} and E_{int} are respectively the kinetic, external and interaction energies. The kinetic and external energies have a simple functional dependence in terms of the 1-RDM. The main advantage of RDMFT over DFT is that the kinetic energy is known exactly as a functional of γ

$$E_{\text{kin}}[\gamma] = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}').$$

The energy due to the external potential can also be expressed in a simple way in terms of the 1-RDM

$$E_{\text{ext}}[\gamma] = \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}').$$

Only the interaction part cannot be easily expressed in term of the 1-RDM. We can rewrite the interaction energy as a sum of the following contributions

$$E_{\text{int}}[\gamma] = E_H[\gamma] + E_x[\gamma] + E_c[\gamma].$$

The first term is the Hartree energy and reads as

$$E_H[\gamma] = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{x}, \mathbf{x}) \gamma(\mathbf{x}', \mathbf{x}'). \quad (16)$$

It is referred usually as the classical part of the interaction, in fact it can be regarded as the potential energy associated to a charge distribution $\rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x})$. The exchange energy also can be expressed easily in terms of the 1-RDM and reads as

$$E_x[\gamma] = -\frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}', \mathbf{x}). \quad (17)$$

Only the remaining correlation energy $E_c[\gamma]$ needs to be approximated.

Most of the approximate functionals proposed in literature are implicit functionals of the 1-RDM; they are explicit functional of the occupation numbers n_i and natural orbitals ϕ_i , $E[\{n_i\}, \{\phi_i\}]$. Some of the approximations proposed in literature will be presented in Sec. 0.4.

0.4 Approximations for $E_{xc}[\gamma]$

As discussed in the previous sections the functional dependence of the Hartree and the exchange energies is known exactly in terms of the 1-RDM (see Eqs (16) and (17)). In terms of occupation numbers and natural orbitals the Hartree-Fock energy reads as

$$\begin{aligned} E_{\text{HF}}[\{n_i\}, \{\phi_i\}] &= \frac{1}{2} \sum_{jk} n_j n_k \int d\mathbf{x} d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_k^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_j(\mathbf{x}) \phi_k(\mathbf{x}') \\ &\quad - \frac{1}{2} \sum_{jk} n_j n_k \int d\mathbf{x} d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_k^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{x}) \phi_j(\mathbf{x}'). \end{aligned}$$

The correlation energy functional $E_c[\gamma]$, instead, is not known and thus needs to be approximated. It is important to note that, although the exact E_c is not known, some exact constraints that it should satisfy are known [3]. This knowledge can be used to construct physically meaningful approximations. Most of the approximations combine exchange and correlation parts in simple expressions of the form

$$E_{xc}[\{n_i\}, \{\phi_i\}] = -\frac{1}{2} \sum_{jk} f(n_j, n_k) \int d\mathbf{x} d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_k^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{x}) \phi_j(\mathbf{x}'), \quad (18)$$

i.e., they have the form of the exchange energy modified by the function $f(n_j, n_k)$. This kind of functionals are usually referred to as of J-K type, as they only involve direct Coulomb (J) and exchange (K) integrals over the natural orbitals. In the following we discuss in more detail the J-K type functionals which will be used in the next chapters of the thesis.

0.4.1 Müller functional

Many of the approximations proposed in literature can be traced back to the work of Müller [19]. He proposed the following factorization for the 2-RDM

$$\begin{aligned} \Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &= \gamma(\mathbf{x}_1, \mathbf{x}'_1)\gamma(\mathbf{x}_2, \mathbf{x}'_2) \\ &\quad - \sum_{ij} n_i^{\frac{1}{2}+p} n_j^{\frac{1}{2}-p} \phi_i(\mathbf{x}_1) \phi_i^*(\mathbf{x}'_2) \phi_j(\mathbf{x}_2) \phi_j^*(\mathbf{x}'_1), \end{aligned} \quad (19)$$

with $-1/2 \leq p \leq 1/2$. As shown by Müller, with the form (19), the probability of finding an electron at \mathbf{r} when a second one is at \mathbf{r}' becomes negative in the neighborhood of \mathbf{r}' . This unphysical negative probability is minimal for $p = 0$. In this case, the Müller approximation reduces to

$$\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \gamma(\mathbf{x}_1, \mathbf{x}'_1)\gamma(\mathbf{x}_2, \mathbf{x}'_2) - \gamma^{\frac{1}{2}}(\mathbf{x}_2, \mathbf{x}'_1)\gamma^{\frac{1}{2}}(\mathbf{x}_1, \mathbf{x}'_2),$$

where $\gamma^{1/2}$ can be defined using the spectral representation of the 1-RDM

$$\gamma^{\frac{1}{2}}(\mathbf{x}_1, \mathbf{x}_2) = \sum_i n_i^{\frac{1}{2}} \phi_i(\mathbf{x}_1) \phi_i^*(\mathbf{x}_2).$$

This factorization for the 2-RDM results in an exchange-correlation energy of the form (18) with

$$f^{\text{Müller}}(n_j, n_k) = \sqrt{n_j n_k}. \quad (20)$$

Interestingly Buijse and Baerends arrived at the same functional following a different approach [1]. The Müller functional severely overestimates the correlation energy of all the systems it has been applied to [2, 6, 14]. It provides a lower bound to the total energy as was shown by Frank *et al.* [7].

0.4.2 Goedecker-Umrigar functional

The Müller functional only partially cancels the interaction of the electron with itself in the Hartree energy, due to the square root and the fractional nature of occupation numbers. Goedecker and Umrigar [10] proposed a correction to the Müller functional by explicitly removing all terms with $j = k$, resulting in the formula

$$f^{\text{GU}}(n_j, n_k) = \sqrt{n_j n_k} - \delta_{jk}(n_j - n_j^2).$$

This functional is orbital self-interaction free, *i.e.*, the interaction of an orbital with itself is excluded. However due to the fractional nature of occupation numbers a particular electron can be distributed over several orbitals, thus it is not possible to completely exclude self interaction. However in many practical cases occupation numbers are often close to either zero or one, and, therefore, the orbital self interaction is close to the total self interaction.

For atoms and molecules at equilibrium geometry the GU functional gives much better correlation energies than the Müller functional. But it fails to reproduce the correct dissociation limit of small molecules [25]. When applied to the homogeneous electron gas (HEG), the GU functional, as the Müller functional, leads to rather inaccurate correlation energies [14]; moreover they fail to reproduce the fundamental gap for band as well as Mott insulators [23].

0.4.3 Corrected Hartree-Fock functional

Csányi and Arias [6] derived a functional starting from a tensor product expansion of the 2-RDM. They called their approximation Corrected Hartree-Fock (CHF). It reads as

$$f^{\text{CHF}}(n_j, n_k) = n_j n_k + \sqrt{n_j(1 - n_j)} \sqrt{n_k(1 - n_k)}.$$

When applied to the HEG [6], the CHF functional coincides with the Müller functional in the low density limit. When density increases, however, the CHF severely overestimates correlation and the solution tends quickly to the HF solution. The same is also observed for other systems. For example, for H_2 at equilibrium CHF gives the HF solution [4].

0.4.4 Power functional

Recently Sharma *et al.* [23] proposed a generalization of the Müller functional (20) which reads as

$$f^{\text{Power}}(n_j, n_k) = n_j^\alpha n_k^\alpha,$$

with $1/2 \leq \alpha \leq 1$. This simple form interpolates between the uncorrelated HF limit ($\alpha = 1$) and the overcorrelated Müller ($\alpha = 1/2$), thus α can be considered as a mixing parameter. This functional has been tested both on finite and extended systems [14, 15, 23, 24]. This functional was shown to perform very well in predicting ground-state properties and photoemission spectra for solids. In particular band gaps for semiconductors and insulators, including transition metal oxides, are in good agreement with experiments [23, 24]. A few optimal values of α have been proposed in literature: $\alpha = 0.525$ for stretched H_2 , $\alpha = 0.578$ for molecules at equilibrium, $\alpha = 0.55$ for the HEG, $0.65 \leq \alpha \leq 0.7$ for solids [15, 23]. The optimal value for α thus depends on the kind of system considered.

0.5 Energy minimization

The total energy functional $E[\{n_i\}, \{\phi_i\}]$ has to be minimized under the constraints that the 1-RDM is ensemble N -representable ($0 \leq n_i \leq 1$, $\sum_i n_i = N$) and under the

orthonormality requirement for the natural orbitals,

$$\langle \phi_i | \phi_j \rangle = \int d\mathbf{x} \phi_i^*(\mathbf{x}) \phi_j(\mathbf{x}) = \delta_{ij}.$$

Bounds on the occupation numbers can be enforced, for example, setting $n_i = \cos^2 \theta_i$ and varying θ_i without constraints. The other two conditions can be taken into account easily using the method of Lagrange multipliers. We can define the auxiliary functional

$$\Omega[\{\theta_i\}, \{\phi_i\}] = E[\{n_i(\theta_i)\}, \{\phi_i\}] - \mu \left(\sum_j \cos^2 \theta_j - N \right) - \sum_{jk} \lambda_{jk} (\langle \phi_j | \phi_k \rangle - \delta_{jk}). \quad (21)$$

The functional (21) has to be stationary with respect to variations in $\{\theta_i\}$, $\{\phi_i(\mathbf{x})\}$, and $\{\phi_i^*(\mathbf{x})\}$

$$\begin{aligned} \delta\Omega = & \sum_i \sin(2\theta_i) \left[\mu - \frac{\partial E}{\partial n_i} \right] \delta\theta_i \\ & + \sum_i \int d\mathbf{x} \left[\frac{\delta E}{\delta \phi_i(\mathbf{x})} - \sum_k \lambda_{ki} \phi_k^*(\mathbf{x}) \right] \delta\phi_i(\mathbf{x}) \\ & + \sum_i \int d\mathbf{x} \delta\phi_i^*(\mathbf{x}) \left[\frac{\delta E}{\delta \phi_i^*(\mathbf{x})} - \sum_k \lambda_{ik} \phi_k(\mathbf{x}) \right] = 0. \end{aligned} \quad (22)$$

The stationarity with respect to θ_i brings to the relation

$$\sin(2\theta_i) \left[\mu - \frac{\partial E}{\partial n_i} \right] = 0, \quad (23)$$

where the partial derivative $\partial E / \partial n_i$ is taken holding the natural orbitals fixed. There are two possible solutions to Eq. (23). The first is

$$\sin(2\theta_i) = 0,$$

which is satisfied by $\theta_i = 0$ or $\theta_i = \pi/2$, which correspond to $n_i = 0$ or $n_i = 1$, respectively. The states corresponding to occupation numbers either 0 or 1 are usually referred as “pinned” states [11]. If an occupation number is equal to one it means that the corresponding natural orbital is present in all the determinants with non-zero coefficient in the full CI expansion. This situation is rather exceptional for the exact wavefunction of a system of interacting particles. However most of the approximate 1-RDM functional known produce occupation numbers equal to one for most of the core states.

The second solution is

$$\frac{\partial E}{\partial n_i} = h_{ii} + \frac{\partial E_{\text{int}}}{\partial n_i} = \mu, \quad (24)$$

where $h_{ii} = \int d\mathbf{x} d\mathbf{x}' \phi_i^*(\mathbf{x}) h(\mathbf{x}, \mathbf{x}') \phi_i(\mathbf{x}')$. Equation (24) is satisfied only by partially occupied orbitals.

For a fixed set of occupation numbers $\{n_i\}$, the equations resulting from the variation with respect to the natural orbitals $\{\phi_i\}$ and their complex conjugates $\{\phi_i^*\}$ are respectively

$$\frac{\delta E}{\delta \phi_i(\mathbf{x})} = n_i \int d\mathbf{x}' \phi_i^*(\mathbf{x}') h(\mathbf{x}', \mathbf{x}) + \frac{\delta E_{\text{int}}}{\delta \phi_i(\mathbf{x})} = \sum_k \lambda_{ki} \phi_k^*(\mathbf{x}) \quad (25)$$

and

$$\frac{\delta E}{\delta \phi_i^*(\mathbf{x})} = n_i \int d\mathbf{x}' h(\mathbf{x}, \mathbf{x}') \phi_i(\mathbf{x}') + \frac{\delta E_{\text{int}}}{\delta \phi_i^*(\mathbf{x})} = \sum_k \lambda_{ik} \phi_k(\mathbf{x}). \quad (26)$$

In principle one has to solve the system of equations consisting of Eqs (24), (25), and (26) combined with the additional constraints for the Lagrange multipliers. This system of equations is nonlinear, so it is a formidable task to solve it in a direct way. In practice the minimum of the functional (22) can be found using a conjugate gradient scheme where the gradient is evaluated using (24), (25), and (26) at each iteration. But in this case particular attention should be paid to the fact that this scheme does not guarantee that the global minimum is reached.

Piris and Ugalde proposed an alternative method for the optimization with respect to the natural orbitals [22]. The optimal natural orbitals are obtained through an iterative diagonalization of an Hermitian matrix derived from the Lagrange multipliers λ_{ij} of Eqs (25) and (26).

0.6 Natural occupation numbers and correlation

Natural occupation numbers are strictly related to the multi-determinant nature of the wavefunction of a physical system. Let us expand the many-body wavefunction in terms of Slater determinants constructed from the eigenvectors of the one-body density matrix $\{\phi_i\}$, $\Psi_0(\mathbf{x}_1 \dots \mathbf{x}_N) = \sum_i C_i \Phi_i(\mathbf{x}_1 \dots \mathbf{x}_N)$. The one-body density-matrix then reads

$$\begin{aligned} \gamma(\mathbf{x}, \mathbf{x}') &= \\ N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \sum_{ij} C_i^* C_j \Phi_i^*(\mathbf{x}', \mathbf{x}_2 \dots \mathbf{x}_N) \Phi_j(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_N) \\ &= \sum_i |C_i|^2 \gamma_i(\mathbf{x}, \mathbf{x}') \end{aligned}$$

where $\gamma_i(\mathbf{x}, \mathbf{x}') = \sum_k \phi_k^i(\mathbf{x}) \phi_k^{i*}(\mathbf{x}')$ is the density matrix associated to the i th Slater determinant. If the wavefunction of the system is described by a single Slater determinant, as in the case of a single (spin-polarized) electron (see Hubbard molecule at 1/4 filling), then the natural occupation numbers are either 1 or 0. If instead more determinants are involved, the natural occupation numbers, in general, take fractional values between 0 and 1. This can be nicely illustrated by considering a two-electron system

with a singlet wavefunction $\Psi_0(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i=1,2} C_i \Phi_i(\mathbf{x}_1, \mathbf{x}_2)$, where $\Phi_1 = |b \uparrow, b \downarrow\rangle$ and $\Phi_2 = |a \uparrow, a \downarrow\rangle$ are Slater determinants constructed from bonding and antibonding orbitals $\{\phi_i\}$, respectively (see Hubbard molecule at 1/2 filling). Note that the bonding/antibonding orbitals in the Hubbard molecule correspond to the natural orbitals. The one-body density matrix reads:

$$\begin{aligned} \gamma(\mathbf{x}, \mathbf{x}') &= |C_1|^2 \sum_{i=b\uparrow, b\downarrow} \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}') \\ &\quad + |C_2|^2 \sum_{i=a\uparrow, a\downarrow} \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}') \\ &= \sum_{i=b\uparrow, b\downarrow, a\uparrow, a\downarrow} n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}') \end{aligned}$$

with $n_{b\uparrow} = n_{b\downarrow} = |C_1|^2$ and $n_{a\uparrow} = n_{a\downarrow} = |C_2|^2$, and $|C_1|^2 + |C_2|^2 = 1$ since the wavefunction Ψ_0 is normalized. In general the relation between C_i and natural occupation numbers is more complicated than in this example, but the fact that fractional occupation numbers reflect the multideterminant nature of the wavefunction, and hence the degree of correlation in a system, remains still valid.

0.7 Properties

0.7.1 Ionization potentials and electron affinities

Besides the ground-state total energy, one can also calculate the IP and EA as total energy differences in finite systems. One can get higher IPs by using extended Koopmans' theorem (EKT) as proposed by Pernal and Cioslowski [K. Pernal and J. Cioslowski, Chem. Phys. Lett. 412, 71(2005)]. The method is based on the diagonalization of the Lagrangian matrix :

$$\Lambda_{ij} = \frac{1}{\sqrt{n_i n_j}} \left[n_i h_{0,ji} + 2 \sum_{klm} \Gamma_{iklm}^{(2)} v_{c,jkml} \right]$$

with $h_{0,ji} = \int d\mathbf{x} \phi_j^*(\mathbf{x}) h_0(\mathbf{x}) \phi_i(\mathbf{x})$,

$$\begin{aligned} \Gamma_{iklm}^{(2)} &= \int d\mathbf{x}'_1 d\mathbf{x}'_2 d\mathbf{x}_1 d\mathbf{x}_2 \Gamma^{(2)}(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) \\ &\quad \times \phi_m^*(\mathbf{x}_2) \phi_l^*(\mathbf{x}_1) \phi_k(\mathbf{x}'_2) \phi_i(\mathbf{x}'_1), \end{aligned}$$

and

$$v_{c,jkml} = \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_j^*(\mathbf{x}_1) \phi_k^*(\mathbf{x}_2) v_c(\mathbf{x}_1, \mathbf{x}_2) \phi_m(\mathbf{x}_1) \phi_l(\mathbf{x}_2).$$

The eigenvalues of Λ are the removal energies. The underlying physics of this method is as follows: in the EKT the $N-1$ -electron states are obtained as a linear combination

of states obtained by removing an electron from the ground state of the N -electron system, $|\Psi^{N-1}\rangle = \sum_i B_i c_i |\Psi_0^N\rangle$; the energy of the so obtained $N - 1$ -electron states is minimized with respect to the coefficients B_i . In practice the EKT has only been applied to finite systems. Note that the lowest addition energy can be obtained from the highest removal energy of the $N + 1$ -system (if the latter is stable). Numerical evidence suggests that EKT is exact only for the lowest ionization potential. An alternative approximate method to calculate IPs/EAs, which can be applied also to solids, has been proposed by Sharma et al. [S. Sharma, J. K. Dewhurst, S. Shallcross, and E. K. U. Gross, Phys. Rev. Lett. 110, 116403 (2013)]. The method has been derived in the spirit of Koopmans' theorem, and gives the IPs/EAs as

$$\epsilon_k^- = -\epsilon_k^+ = \epsilon_k = E[\{n_i\}, \{\phi_i\}]|_{n_k=1} - E[\{n_i\}, \{\phi_i\}]|_{n_k=0},$$

where $E[\{n_i\}, \{\phi_i\}]|_{n_k=1}$ ($E[\{n_i\}, \{\phi_i\}]|_{n_k=0}$) is the total energy for the N -particle system with all the occupation numbers fixed at their optimal value (i.e. the value that minimize the energy functional) except for the occupation number n_k which is fixed to 1 (0). Here ϵ_k^- and $-\epsilon_k^+$ denote removal and addition energies, respectively. The total energy difference, Eq. (0.7.1), can be further approximated as

$$E[\{n_i\}, \{\phi_i\}]|_{n_k=1} - E[\{n_i\}, \{\phi_i\}]|_{n_k=0} \approx \left. \frac{\partial E}{\partial n_k} \right|_{n_k=1/2}$$

which is justified if the total energy is linear in the occupation number n_k .

0.7.2 Spectral function

The photoemission spectra can be obtained from the imaginary part of the one-body Green's function (1-GF) $G(12) = \langle \Psi_0 | T[\hat{\psi}_H(1)\hat{\psi}_H^\dagger(1')] | \Psi_0 \rangle$, where 1, 1' stand for combined space-spin-time coordinates, i.e., $1 \equiv (\mathbf{r}_1, s_1, t_1)$, etc.; $|\Psi_0\rangle$ is the ground state of the system in the Heisenberg picture, $\hat{\psi}_H$ and $\hat{\psi}_H^\dagger$ are the field operators in the Heisenberg picture

$$\hat{\psi}_H(1) = e^{i\hat{H}t_1} \hat{\psi}(\mathbf{x}_1) e^{-i\hat{H}t_1}, \quad (28)$$

where $\hat{\psi}(\mathbf{x}_1)$ is the field operator in the Schrödinger picture. T is the Wick time ordering operator, which, when applied to a product of operators, arranges them in a chronological order of their time arguments with a multiplicative factor ± 1 depending on whether the chronological order is an even or odd permutation of the original order. In the following, to simplify the notation, we will assume that $|\Psi_0\rangle$ is normalized, i.e., $\langle \Psi_0 | \Psi_0 \rangle = 1$. Working out the expression for the 1-GF one arrives at the following expression for the spectral function $A_{\lambda\lambda'}(\omega) = 1/\pi \Im[G_{\lambda\lambda'}(\omega)]$

$$\begin{aligned} A_{\lambda\lambda'}(\omega) &= \sum_j \langle \Psi_0^N | c_\lambda | \Psi_j^{N+1} \rangle \langle \Psi_j^{N+1} | c_{\lambda'}^\dagger | \Psi_0^N \rangle \delta(\omega - [E_j^{N+1} - E_0^N]) \\ &= \sum_i \langle \Psi_0^N | c_{\lambda'}^\dagger | \Psi_i^{N-1} \rangle \langle \Psi_i^{N-1} | c_\lambda | \Psi_0^N \rangle \delta(\omega - [E_0^N - E_i^{N-1}]). \end{aligned}$$

Using the basis of natural orbitals and the approximations

$$\begin{aligned} |\Psi_i^{N+1}\rangle &\approx \frac{1}{\sqrt{1-n_i}} c_i^\dagger |\Psi_0^N\rangle \\ |\Psi_i^{N-1}\rangle &\approx \frac{1}{\sqrt{n_i}} c_i |\Psi_0^N\rangle \end{aligned}$$

the spectral function can be approximated as

$$A_{\lambda\lambda'}(\omega) \approx \sum_i [n_i \delta(\omega - \epsilon_i^R) + (1 - n_i) \delta(\omega + \epsilon_i^A)].$$

This approximation has been proposed by Sharma *et al.* [Phys. Rev. Lett. 110, 116403 (2013)], with the energies given by Eq. (0.7.1) or (0.7.1)

Along a different derivation Di Sabatino *et al.* [Phys. Rev. B 94, 155141 (2016)] arrived at the same expression for the spectral function, but with the energies expressed in terms of an effective energy which can be approximated at various level of accuracy by including higher-order density matrices. At the lowest order of approximation these energies correspond to the diagonal of the $\Lambda^{R/A}$ matrices.

0.8 Connection to Green's function

At zero temperature the time-ordered equilibrium n -body Green's function (n -GF) is defined as

$$G^{(n)}(1, 2, \dots, n; 1', 2', \dots, n') \equiv (-i)^n \frac{\langle \Psi_0 | T[\hat{\psi}_H(1) \dots \hat{\psi}_H(n) \hat{\psi}_H^\dagger(n') \dots \hat{\psi}_H^\dagger(1')] | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}, \quad (32)$$

where $1, 2, \dots, n$ stand for combined space-spin-time coordinates, *i.e.*, $1 \equiv (\mathbf{r}_1, s_1, t_1)$, etc.; $|\Psi_0\rangle$ is the ground state of the system in the Heisenberg picture, $\hat{\psi}_H$ and $\hat{\psi}_H^\dagger$ are the field operators in the Heisenberg picture

$$\hat{\psi}_H(1) = e^{i\hat{H}t_1} \hat{\psi}(\mathbf{x}_1) e^{-i\hat{H}t_1}, \quad (33)$$

where $\hat{\psi}(\mathbf{x}_1)$ is the field operator in the Schrödinger picture. T is the Wick time ordering operator, which, when applied to a product of operators, arranges them in a chronological order of their time arguments with a multiplicative factor ± 1 depending on whether the chronological order is an even or odd permutation of the original order. In the following, to simplify the notation, we will assume that $|\Psi_0\rangle$ is normalized, *i.e.*, $\langle \Psi_0 | \Psi_0 \rangle = 1$.

The connection to the n -body density matrix is clear, since one of the time ordering of $G^{(n)}$ corresponds to the n -body density matrix when all the times are equal.

In particular the one-body Green's function (1-GF), according to Eq. (32), is defined as

$$G(1, 1') = -i \langle \Psi_0 | T[\hat{\psi}_H(1) \hat{\psi}_H^\dagger(1')] | \Psi_0 \rangle.$$

The time-ordered product can be written explicitly as

$$T[\hat{\psi}_H(1)\hat{\psi}_H^\dagger(1')] = \begin{cases} \hat{\psi}_H(1)\hat{\psi}_H^\dagger(1') & \text{for } t_1 > t_{1'} \\ -\hat{\psi}_H^\dagger(1')\hat{\psi}_H(1) & \text{for } t_{1'} > t_1, \end{cases}$$

from which

$$\begin{aligned} G(1, 1') &= -i\theta(t_1 - t_{1'}) \langle \Psi_0 | \hat{\psi}_H(1)\hat{\psi}_H^\dagger(1') | \Psi_0 \rangle \\ &\quad + i\theta(t_{1'} - t_1) \langle \Psi_0 | \hat{\psi}_H^\dagger(1')\hat{\psi}_H(1) | \Psi_0 \rangle, \end{aligned} \quad (34)$$

where $\theta(t)$ is the Heaviside step function. Equation (34) suggests a simple interpretation of the 1-GF: it expresses the probability amplitude for an electron (hole) which at time $t_{1'}$ (t_1) is added to the N -electron system (in its ground-state) at position \mathbf{r}'_1 (\mathbf{r}_1) with spin s'_1 (s_1) to be found at position \mathbf{r}_1 (\mathbf{r}'_1) with spin s_1 (s'_1) at time $t_1 > t'_{1'}$ ($t'_{1'} > t_1$).

It now becomes clear that taking $t_{1'} = t_1^+$ we obtain the 1-RDM $\gamma(\mathbf{x}, \mathbf{x}') = -iG(\mathbf{x}, \mathbf{x}'; t_1 - t_1^+)$.

Even if the 1-GF does not contain all the information of the ground-state wavefunction, we can still obtain from it all the observable properties of greatest interest, namely the ground-state expectation value of any one-particle operator, the ground-state total energy, and the one-particle excitation spectrum of the system. Let us discuss these properties in more detail. Given a one-particle operator \hat{O} in second quantization form

$$\hat{O} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) o(\mathbf{x}) \hat{\psi}(\mathbf{x}),$$

where $o(\mathbf{x}_1)$ is the single particle operator in first quantization form,¹ the ground-state expectation value can be evaluated as

$$\begin{aligned} \langle \Psi_0 | \hat{O} | \Psi_0 \rangle &= \int d\mathbf{x} o(\mathbf{x}) \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) | \Psi_0 \rangle \\ &= \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \int d\mathbf{x} o(\mathbf{x}) \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) | \Psi_0 \rangle \\ &= -i \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \lim_{t' \rightarrow t^+} \int d\mathbf{x} o(\mathbf{x}) G(\mathbf{x}t; \mathbf{x}'t'), \end{aligned}$$

where t^+ stands for $t + \delta$, with δ an infinitesimal positive real number. Note that in the last step we used the definitions (33) and (34). Thus the 1-GF allows us to calculate the ground-state expectation value of any one-particle operator. For example, the electron density of the system is the diagonal in space, spin and time of the 1-GF, $n(\mathbf{x}) = -iG(\mathbf{x}t; \mathbf{x}t^+)$, whereas the one-body reduced density matrix (1-RDM) is the diagonal in time of the 1-GF $\gamma(\mathbf{x}, \mathbf{x}') = -iG(\mathbf{x}t, \mathbf{x}'t^+)$.

¹For simplicity we consider here a local operator.

The 1-GF can also be used to calculate the total energy, which in principle contains a two-body operator. The Galitskii-Migdal formula [8] gives the total ground-state energy in terms of the 1-GF, and it reads as

$$E_0 = -\frac{i}{2} \int d\mathbf{x} \lim_{t' \rightarrow t^+} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left[i \frac{\partial}{\partial t} + h(\mathbf{r}) \right] G(\mathbf{x}t, \mathbf{x}'t'), \quad (35)$$

where $h(\mathbf{r}) = -\nabla_{\mathbf{r}}^2/2 + v_{\text{ext}}(\mathbf{r})$ is the one-particle Hamiltonian, with v_{ext} a local external potential.

The relation of the 1-GF with the one-particle excitation spectrum will be discussed in the next subsection, where the Lehmann representation of the 1-GF will be introduced.

0.8.1 Lehmann representation

In the following we will write the 1-GF in such a way to make clear its connection with the excitation energies of the system.

In absence of a time-dependent external potential, due to the homogeneity of time, the 1-GF depends only on the time difference $\tau = t_1 - t'_1$. Introducing, in Eq. (34), the resolution of the identity $\sum_k \sum_M |\Psi_k^M\rangle \langle \Psi_k^M| = \hat{1}$ in the Fock space, where $|\Psi_k^M\rangle$ indicates the k -th eigenstate of the M -electron system, we obtain

$$\begin{aligned} G(\mathbf{x}, \mathbf{x}'; \tau) = & -i\theta(\tau) \sum_m \langle \Psi_0 | \hat{\psi}_H(\mathbf{x}t) | \Psi_m^{N+1} \rangle \langle \Psi_m^{N+1} | \hat{\psi}_H^\dagger(\mathbf{x}'t') | \Psi_0 \rangle \\ & + i\theta(-\tau) \sum_n \langle \Psi_0 | \hat{\psi}_H^\dagger(\mathbf{x}'t') | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \hat{\psi}_H(\mathbf{x}t) | \Psi_0 \rangle, \end{aligned} \quad (36)$$

where we have used the fact that field operators select only states with $N+1$ particles if $\tau > 0$ or with $N-1$ particles if $\tau < 0$. We can explicitly indicate the time dependence of the field operators in Eq. (36) using Eq. (33) and obtain the following expression for the 1-GF

$$\begin{aligned} G(\mathbf{x}, \mathbf{x}'; \tau) = & -i\theta(\tau) \sum_m \langle \Psi_0 | \hat{\psi}(\mathbf{x}) | \Psi_m^{N+1} \rangle \langle \Psi_m^{N+1} | \hat{\psi}^\dagger(\mathbf{x}') | \Psi_0 \rangle e^{i(E_0^N - E_m^{N+1})\tau} \\ & + i\theta(-\tau) \sum_n \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}') | \Psi_n^{N-1} \rangle \langle \Psi_n^{N-1} | \hat{\psi}(\mathbf{x}) | \Psi_0 \rangle e^{-i(E_0^N - E_n^{N-1})\tau}. \end{aligned} \quad (37)$$

The terms

$$f_m(\mathbf{x}) = \langle \Psi_0 | \hat{\psi}(\mathbf{x}) | \Psi_m^{N+1} \rangle,$$

and

$$g_n(\mathbf{x}) = \langle \Psi_n^{N-1} | \hat{\psi}(\mathbf{x}) | \Psi_0 \rangle$$

are generally referred to as the Feynman-Dyson amplitudes. Thus Eq. (37) assumes the more compact form

$$G(\mathbf{x}, \mathbf{x}'; \tau) = -i\theta(\tau) \sum_m f_m(\mathbf{x}) f_m^*(\mathbf{x}') e^{i(E_0^N - E_m^{N+1})\tau} + i\theta(-\tau) \sum_n g_n(\mathbf{x}) g_n^*(\mathbf{x}') e^{-i(E_0^N - E_n^{N-1})\tau}. \quad (38)$$

Note that the amplitudes f_m as well as g_n are, in general, not orthogonal nor linearly independent. One can only prove that the total set is complete:

$$\sum_m f_m(\mathbf{x}) f_m^*(\mathbf{x}') + \sum_n g_n(\mathbf{x}) g_n^*(\mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'). \quad (39)$$

Using the following relation

$$\int_{-\infty}^{\infty} dt [\theta(\pm t) e^{-i\alpha t}] e^{i\omega t} = \lim_{\eta \rightarrow 0^+} \frac{\pm i}{\omega - \alpha \pm i\eta},$$

we can obtain the Fourier transform of Eq. (38). We arrive at the Lehmann representation in frequency space for the 1-GF

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \lim_{\eta \rightarrow 0^+} \left[\sum_m \frac{f_m(\mathbf{x}) f_m^*(\mathbf{x}')}{\omega - (E_m^{N+1} - E_0^N) + i\eta} + \sum_n \frac{g_n(\mathbf{x}) g_n^*(\mathbf{x}')}{\omega - (E_0^N - E_n^{N-1}) - i\eta} \right]. \quad (40)$$

From Eq. (40) it becomes clear that the 1-GF has poles at the electron addition ($E_m^{N+1} - E_0^N$) and removal ($E_0^N - E_n^{N-1}$) energies of the system. The smallest electron removal energy gives the ionization potential $\text{IP} = -(E_0^N - E_0^{N-1})$, while the electron affinity is defined as $\text{EA} = E_0^N - E_0^{N+1}$. If the system under study is a metal, then $\text{IP} = \text{EA}$ is the chemical potential μ . If, instead, the system is insulating, then one can define the band gap ΔE_g as

$$\Delta E_g = \text{IP} - \text{EA} = E_0^{N+1} + E_0^{N-1} - 2E_0^N.$$

In this case, the chemical potential μ lies somewhere inside the band gap.

0.8.2 Spectral function and connection with experiments

It is convenient to define the spectral function in terms of the imaginary part of the 1-GF according to

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\pi} \text{sign}(\mu - \omega) \text{Im} G(\mathbf{x}, \mathbf{x}'; \omega).$$

Using the Lehmann representation for the 1-GF (Eq. (40)), the spectral function reads as

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \sum_m f_m(\mathbf{x}) f_m^*(\mathbf{x}') \delta(\omega - (E_m^{N+1} - E_0^N)) + \sum_n g_n(\mathbf{x}) g_n^*(\mathbf{x}') \delta(\omega - (E_0^N - E_n^{N-1})). \quad (41)$$

The full 1-GF can be obtained back from the spectral function using the relation

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \int_{-\infty}^{\mu} d\omega' \frac{A(\mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' - i\eta} + \int_{\mu}^{\infty} d\omega' \frac{A(\mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\eta}.$$

This means that the spectral function contains the same information as the 1-GF, but it has the main advantage of being a positive real-valued function, while the 1-GF is in general a complex function.

The spectral function satisfies the following normalization condition

$$\int_{-\infty}^{\infty} d\omega A(\mathbf{x}, \mathbf{x}'; \omega) = \delta(\mathbf{x} - \mathbf{x}'), \quad (42)$$

which can be obtained by integrating Eq. (41) with respect to ω and using the completeness relation (39). Several observables have a simple link to the spectral function. For example the ground state electron density $\rho(\mathbf{r})$ can be calculated as

$$\rho(\mathbf{r}) = \int_{-\infty}^{\mu} d\omega A(\mathbf{r}, \mathbf{r}; \omega),$$

while an expression for the ground-state energy in terms of the spectral function can be derived from the Galitskii-Migdal formula (35) and reads as

$$E_0 = \frac{1}{2} \sum_{ij} \int_{-\infty}^{\mu} d\omega [\omega \delta_{ij} + h_{ij}] A_{ji}(\omega),$$

where we introduced a complete set of orthonormal one-electron wavefunctions $\{\phi_i\}$, and defined the matrix elements of the spectral function and the one-particle Hamiltonian as

$$A_{ij}(\omega) = \int d\mathbf{x} d\mathbf{x}' \phi_i^*(\mathbf{x}) A(\mathbf{x}, \mathbf{x}'; \omega) \phi_j(\mathbf{x}'), \quad (43)$$

and

$$h_{ij} = \int d\mathbf{x} \phi_i^*(\mathbf{x}) h(\mathbf{x}) \phi_j(\mathbf{x}),$$

respectively. Using Eq. (43) together with (42) we obtain the sum rule

$$\int_{-\infty}^{\infty} A_{ij}(\omega) d\omega = \delta_{ij}.$$

Moreover, one can obtain from the spectral function the distribution of one-electron states as

$$n_i = \langle \Psi_0 | c_i^\dagger c_i | \Psi_0 \rangle = \int_{-\infty}^{\mu} d\omega A_{ii}(\omega).$$

If for example we choose the states i to be the momentum eigenstates, we obtain the momentum distribution, a key quantity in, *e.g.*, Compton scattering [13, 20].

Finally the spectral function gives information about the photoelectron spectrum of a system.

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