Introduction to density-functional theory

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Contents

These notes provide an introduction to ground-state density-functional theory (DFT) of electronic systems. For more intensive coverages of the subject, see e.g. Refs. [1–5].

1 Basic density-functional theory

1.1 The many-body problem

We consider a N-electron system (atom, molecule, or solid) in the Born-Oppenheimer and non-relativistic approximations. The electronic Hamiltonian in the position representation is, in atomic units,

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = -\frac{1}{2}\sum_{i=1}^{N}\nabla_{\mathbf{r}_i}^2 + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\i\neq j}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N}v_{\text{ne}}(\mathbf{r}_i), \tag{1.1}$$

where $v_{\text{ne}}(\mathbf{r}_i) = -\sum_{\alpha} Z_{\alpha}/|\mathbf{r}_i - \mathbf{R}_{\alpha}|$ is the nuclei-electron interaction ($\mathbf{R}_{\alpha}$ and Z_{α} are the positions and charges of the nuclei). The stationary electronic states are determined by the time-independent Schrödinger equation

$$H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N), \tag{1.2}$$

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ is a wave function written with space-spin coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ (with $\mathbf{r}_i \in \mathbb{R}^3$ and $\sigma_i =\uparrow$ or $\downarrow$) which is antisymmetric with respect to the exchange of two coordinates, and E is the associated energy.

Using Dirac notations, the Schrödinger equation (1.2) can be rewritten in a representation-independent formalism

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \tag{1.3}$$

where the Hamiltonian is formally written as

$$\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}, \tag{1.4}$$

with the kinetic-energy operator $\hat{T}$, the electron-electron interaction operator $\hat{W}_{\text{ee}}$, and the nuclei-electron interaction operator $\hat{V}_{\text{ne}}$. These operators can be conveniently expressed in second quantization (see Appendix A).

The quantity of primary interest is the ground-state energy E_0. The variational theorem establishes that E_0 can be obtained by the following minimization

$$\boxed{E_0 = \min_{\Psi}\langle\Psi|\hat{H}|\Psi\rangle,} \tag{1.5}$$

where the search is over all N-electron antisymmetric wave functions Ψ, normalized to unity $\langle\Psi|\Psi\rangle = 1$. DFT is based on a reformulation of the variational theorem in terms of the one-electron density defined as[1]

$$\boxed{n(\mathbf{r}) = N\int\cdots\int|\Psi(\mathbf{x}, \mathbf{x}_2, ..., \mathbf{x}_N)|^2\,\mathrm{d}\sigma\mathrm{d}\mathbf{x}_2...\mathrm{d}\mathbf{x}_N,} \tag{1.6}$$

which is normalized to the electron number, $\int n(\mathbf{r})\mathrm{d}\mathbf{r} = N$.

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[1] In Eq. (1.6), an integration over a spin coordinate σ just means a sum over the two values $\sigma =\uparrow$ and $\sigma =\downarrow$.

1.2 The universal density functional

1.2.1 The Hohenberg-Kohn theorem

Consider an electronic system with an arbitrary external local potential $v(\mathbf{r})$ in place of $v_{\text{ne}}(\mathbf{r})$. A corresponding ground-state wave function Ψ (there can be several of them if the ground state is degenerate) can be obtained by solving the Schrödinger equation, from which the associated ground-state density $n(\mathbf{r})$ can be deduced. Therefore, one has a mapping from the potential $v(\mathbf{r})$ to the considered ground-state density $n(\mathbf{r})$

$$v(\mathbf{r}) \longrightarrow n(\mathbf{r}). \tag{1.7}$$

In 1964, Hohenberg and Kohn [6] showed that this mapping can be inverted, i.e. the ground-state density $n(\mathbf{r})$ determines the potential $v(\mathbf{r})$ up to an arbitrary additive constant

$$\boxed{n(\mathbf{r}) \xrightarrow[\text{Hohenberg-Kohn}]{} v(\mathbf{r}) + \text{const.}} \tag{1.8}$$

Proof: The two-step proof by contradiction proceeds as follows (see, e.g., Ref. [2]).
We consider two local potentials $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ differing by more than an additive constant, $v_1(\mathbf{r}) \neq v_2(\mathbf{r}) + \text{const}$, and we note E_1 and E_2 the ground-state energies of the Hamiltonians $\hat{H}_1 = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_1$ and $\hat{H}_2 = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_2$, respectively.
(1) Assume that $\hat{H}_1$ and $\hat{H}_2$ have the same ground-state wave function Ψ, i.e. $\hat{H}_1|\Psi\rangle = E_1|\Psi\rangle$ and $\hat{H}_2|\Psi\rangle = E_2|\Psi\rangle$. Then, subtracting these two equations gives

$$(\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle, \tag{1.9}$$

or, in position representation,

$$\sum_{i=1}^{N}[v_1(\mathbf{r}_i) - v_2(\mathbf{r}_i)]\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = (E_1 - E_2)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N), \tag{1.10}$$

which implies $v_1(\mathbf{r}) - v_2(\mathbf{r}) = \text{const}$, in contradiction with the initial hypothesis. Note that, to eliminate Ψ in Eq. (1.10), it was assumed that $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \neq 0$ for all spatial coordinates $(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ and at least one fixed set of spin coordinates $(\sigma_1, \sigma_2, ..., \sigma_N)$. This in fact true "almost everywhere" for "reasonably well behaved" potentials. In this case, we thus conclude that two local potentials differing by more than an additive constant cannot share the same ground-state wave function.
(2) Let then Ψ_1 and Ψ_2 be (necessarily different) ground-state wave functions of $\hat{H}_1$ and $\hat{H}_2$, respectively, and assume that Ψ_1 and Ψ_2 have the same ground-state density $n(\mathbf{r})$. The variational theorem leads to the following inequality

$$E_1 = \langle\Psi_1|\hat{H}_1|\Psi_1\rangle < \langle\Psi_2|\hat{H}_1|\Psi_2\rangle = \langle\Psi_2|\hat{H}_2 + \hat{V}_1 - \hat{V}_2|\Psi_2\rangle = E_2 + \int [v_1(\mathbf{r}) - v_2(\mathbf{r})]\, n(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{1.11}$$

where the strict inequality comes from the fact that Ψ_2 cannot be a ground-state wave function of $\hat{H}_1$, as shown in the first step of the proof. Symmetrically, by exchanging the role of systems 1 and 2, we have the strict inequality

$$E_2 < E_1 + \int [v_2(\mathbf{r}) - v_1(\mathbf{r})]\, n(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{1.12}$$

Adding Eqs. (1.11) and (1.12) gives the inconsistent result

$$E_1 + E_2 < E_1 + E_2, \tag{1.13}$$

which finally leads to the conclusion that there cannot exist two local potentials differing by more than an additive constant which have the same ground-state density. Note that this proof does not assume non-degenerate ground states (contrary to the original Hohenberg-Kohn proof). ∎

So, the ground-state density $n(\mathbf{r})$ determines the potential $v(\mathbf{r})$, which in turn determines the Hamiltonian, and thus everything about the many-body problem. In other words, the potential v is a unique (up to an additive constant) functional of the ground-state density n, and all other properties as well. The ground-state wave function Ψ for the potential $v(\mathbf{r})$ is itself a functional of n, denoted by $\Psi[n]$, which was exploited by Hohenberg and Kohn to define the universal (i.e., independent from the external potential) density functional

$$\boxed{F[n] = \langle \Psi[n]|\hat{T} + \hat{W}_{\text{ee}}|\Psi[n]\rangle,} \tag{1.14}$$

which can be used to define the total electronic energy functional

$$E[n] = F[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{1.15}$$

for the specific external potential $v_{\text{ne}}(\mathbf{r})$ of the system considered. Note that, for degenerate ground states, $\Psi[n]$ is not unique but stands for any degenerate ground-state wave function. However, all $\Psi[n]$ give the same $F[n]$, which is thus a unique functional of n.

Hohenberg and Kohn further showed that the density functional $E[n]$ satisfies a variational property: the ground-state energy E_0 of the system considered is obtained by minimizing this functional with respect to N-electron densities n that are ground-state densities associated with some local potential (referred to as v-representable densities)

$$\boxed{E_0 = \min_n \left\{ F[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} \right\},} \tag{1.16}$$

the minimum being reached for a ground-state density $n_0(\mathbf{r})$ corresponding to the potential $v_{\text{ne}}(\mathbf{r})$.

The existence of a mapping from a ground-state density to a local potential, the existence of the universal density functional, and the variational property with respect to the density constitutes the *Hohenberg-Kohn theorem*.

Exercise 1 : For the special case of Coulombic potentials $v_{\text{ne}}(\mathbf{r})$ there is a simple argument due to E. Bright Wilson showing that the ground-state density $n_0(\mathbf{r})$ fully determines $v_{\text{ne}}(\mathbf{r})$. Can you find it yourself?

Exercise 2 : Prove the variational property [Eq. (1.16)] of the density functional $E[n]$.

1.2.2 Levy's constrained-search formulation

In 1979 Levy [7, 8], and later Lieb [9], proposed to redefine the universal density functional $F[n]$ using a *constrained-search formulation*

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle = \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle, \tag{1.17}$$

where $\Psi \to n$ means that the minimization is done over normalized antisymmetric wave functions Ψ which yield the fixed density n [via Eq. (1.6)]. For a given density n, the minimizing wave function is denoted by $\Psi[n]$ (possibly non unique in case of degeneracy). This definition of $F[n]$ is more straightforward than the Hohenberg-Kohn definition. It does not require the existence of a local potential associated to the density: it is defined on the larger set of N-electron densities coming from an antisymmetric wave function (referred to as N-representable densities).

The variational property of the total electronic energy functional can easily be demonstrated using the constrained-search formulation. One starts from the usual variational theorem and decomposes the minimization over Ψ in two steps: a constrained minimization over Ψ giving a fixed density n, followed by a minimization over n,

$$
\begin{aligned}
E_0 &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} | \Psi \rangle \\
&= \min_{n} \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} | \Psi \rangle \\
&= \min_{n} \left\{ \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}\mathbf{r} \right\} \\
&= \min_{n} \left\{ F[n] + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}\mathbf{r} \right\},
\end{aligned}
\tag{1.18}
$$

and again the minimum is reached for a ground-state density $n_0(\mathbf{r})$ corresponding to the potential $v_{\mathrm{ne}}(\mathbf{r})$.

The ground-state energy and density can then be in principle obtained by minimizing over the density $n(\mathbf{r})$, i.e. a simple function of 3 variables, which is a tremendous simplification compared to the minimization over a complicated many-body wave function Ψ. However, the explicit expression of $F[n]$ in terms of the density is not known, and the direct approximations for $F[n]$ that have been tried so far turn out not to be accurate enough, especially for the kinetic energy part $T[n]$ included in $F[n]$

$$F[n] = T[n] + W_{\mathrm{ee}}[n], \tag{1.19}$$

where $T[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle$ and $W_{\mathrm{ee}}[n] = \langle \Psi[n] | \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle$.

1.3 The Kohn-Sham method

1.3.1 Decomposition of the universal functional

Faced with the difficulty of approximating directly $F[n]$, Kohn and Sham (KS) [10] proposed to decompose $F[n]$ as

$$F[n] = T_{\mathrm{s}}[n] + E_{\mathrm{Hxc}}[n], \tag{1.20}$$

where $T_{\mathrm{s}}[n]$ is the non-interacting kinetic-energy functional which can be defined with a constrained-search formulation

$$T_{\mathrm{s}}[n] = \min_{\Phi \to n} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle, \tag{1.21}$$

where $\Phi \to n$ means that the minimization is done over normalized *single-determinant* wave functions Φ which yield the fixed density n. For a given density n, the (non necessarily unique) minimizing single-determinant wave function is called the *KS wave function* and is denoted by $\Phi[n]$. The remaining functional $E_{\mathrm{Hxc}}[n]$ in Eq. (1.20) is called the Hartree-exchange-correlation functional. The idea of the KS method is then to use the exact expression of $T_{\mathrm{s}}[n]$ by reformulating the variational property of $F[n]$ in terms of single-determinant wave functions Φ

$$
\begin{aligned}
E_0 &= \min_{n} \left\{ F[n] + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}\mathbf{r} \right\}, \\
&= \min_{n} \left\{ \min_{\Phi \to n} \langle \Phi | \hat{T} | \Phi \rangle + E_{\mathrm{Hxc}}[n] + \int v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}\mathbf{r} \right\} \\
&= \min_{n} \min_{\Phi \to n} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hxc}}[n_\Phi] \right\} \\
&= \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hxc}}[n_\Phi] \right\},
\end{aligned}
\tag{1.22}
$$

the minimizing single-determinant KS wave function giving the exact ground-state density $n_0(\mathbf{r})$. Thus, the exact ground-state energy and density can in principle be obtained by minimizing over single-determinant wave functions only. Even though a wave function has been reintroduced compared to Eq. (1.18), it is only a single-determinant wave function Φ and therefore it still represents a tremendous simplification over the usual variational theorem involving a multi-determinant wave function Ψ. The advantage of Eq. (1.22) over Eq. (1.18) is that a major part of the kinetic energy can be treated explicitly with the single-determinant wave function Φ, and only $E_{\mathrm{Hxc}}[n]$ needs to be approximated as a functional of the density.

In practice, $E_{\mathrm{Hxc}}[n]$ is written as

$$
E_{\mathrm{Hxc}}[n] = E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n],
\tag{1.23}
$$

where $E_{\mathrm{H}}[n]$ is the Hartree energy functional

$$
E_{\mathrm{H}}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2,
\tag{1.24}
$$

representing the classical electrostatic repulsion energy for the charge distribution $n(\mathbf{r})$, and $E_{\mathrm{xc}}[n]$ is the exchange-correlation energy functional that remains to approximate. This functional is often decomposed as

$$
E_{\mathrm{xc}}[n] = E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n],
\tag{1.25}
$$

where $E_{\mathrm{x}}[n]$ is the exchange energy functional

$$
E_{\mathrm{x}}[n] = \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle - E_{\mathrm{H}}[n],
\tag{1.26}
$$

and $E_{\mathrm{c}}[n]$ is the correlation energy functional

$$
E_{\mathrm{c}}[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle = T_{\mathrm{c}}[n] + U_{\mathrm{c}}[n],
\tag{1.27}
$$

which contains a kinetic contribution $T_{\mathrm{c}}[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} | \Phi[n] \rangle$ and a potential contribution $U_{\mathrm{c}}[n] = \langle \Psi[n] | \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle - \langle \Phi[n] | \hat{W}_{\mathrm{ee}} | \Phi[n] \rangle$.

1.3.2 The Kohn-Sham equations

The single-determinant wave function Φ is constructed from a set of N orthonormal occupied spin-orbitals $\{\psi_i(\mathbf{x})\}_{i=1,\dots,N}$. To enforce $\hat{S}_z$ symmetry, each spin-orbital is factorized as $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\chi_{\sigma_i}(\sigma)$ where $\phi_i(\mathbf{r})$ is a spatial orbital and $\chi_{\sigma_i}(\sigma) = \delta_{\sigma_i,\sigma}$ is a spin function (σ_i is the spin of the spin-orbital i). Alternatively, when this is convenient, we will sometimes reindex the spatial orbitals, $\{\phi_i(\mathbf{r})\} \rightarrow \{\phi_{i\sigma}(\mathbf{r})\}$, including explicitly the spin σ in the index. Writing the total electronic energy in Eq. (1.22) in terms of spin-orbitals and integrating over the spin variables, we obtain

$$E[\{\phi_i\}] = \sum_{i=1}^{N} \int \phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\mathbf{r}) \right) \phi_i(\mathbf{r})\mathrm{d}\mathbf{r} + E_{\mathrm{Hxc}}[n], \tag{1.28}$$

where the density is expressed in terms of the orbitals as

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 . \tag{1.29}$$

The minimization over Φ can then be recast into a minimization of $E[\{\phi_i\}]$ with respect to the spatial orbitals $\phi_i(\mathbf{r})$ with the constraint of keeping the orbitals orthonormalized. Using the method of Lagrange multipliers, we introduce the following Lagrangian

$$\mathcal{L}[\{\phi_i\}] \;=\; E[\{\phi_i\}] - \sum_{i=1}^{N} \varepsilon_i \left(\int \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})\mathrm{d}\mathbf{r} - 1 \right), \tag{1.30}$$

where ε_i is the Lagrange multiplier associated to the normalization condition of $\phi_i(\mathbf{r})^2$. The Lagrangian should then be stationary with respect to variations of the orbitals $\phi_i(\mathbf{r})$[3]

$$\frac{\delta\mathcal{L}}{\delta\phi_i^*(\mathbf{r})} = 0, \tag{1.31}$$

where $\delta\mathcal{L}/\delta\phi_i^*(\mathbf{r})$ is the functional derivative of $\mathcal{L}$ with respect to $\phi_i^*(\mathbf{r})$. Calculating this functional derivative gives (see Appendix B for an introduction to functional calculus)

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta\phi_i^*(\mathbf{r})} = \varepsilon_i\phi_i(\mathbf{r}), \tag{1.32}$$

where the term $\delta E_{\mathrm{Hxc}}[n]/\delta\phi_i^*(\mathbf{r})$ can be expressed as, using the chain rule,

$$\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta\phi_i^*(\mathbf{r})} = \int \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta\phi_i^*(\mathbf{r})}\mathrm{d}\mathbf{r}'. \tag{1.33}$$

Noting that $\delta n(\mathbf{r}')/\delta\phi_i^*(\mathbf{r}) = \phi_i(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')$ [from Eq. (1.29)], and defining the Hartree-exchange-correlation potential $v_{\mathrm{Hxc}}(\mathbf{r})$ as the functional derivative of $E_{\mathrm{Hxc}}[n]$ with respect to $n(\mathbf{r})$

$$v_{\mathrm{Hxc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}, \tag{1.34}$$

---

[2]It turns out that it is not necessary to include the orthogonalization conditions $\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\mathrm{d}\mathbf{r} = 0$ for $i \neq j$ in Eq. (1.30). Indeed, we will find that the minimizing orbitals $\phi_i(\mathbf{r})$ are eigenfunctions of a self-adjoint operator, which implies that we can always find an orthogonal set of orbitals

[3]Here, the orbitals are assumed to take complex values, so that $\phi_i(\mathbf{r})$ and $\phi_i^*(\mathbf{r})$ can be taken as independent functions. We then write the stationary equation for variations with respect to $\phi_i^*(\mathbf{r})$ only, the second stationary equation for variations with respect to $\phi_i(\mathbf{r})$ is just the complex conjugate of the first one.

which is itself a functional of the density, we then arrive at the KS equations

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \tag{1.35}$$

The orbitals satisfying Eq. (1.35) are called the KS orbitals. They are the eigenfunctions of the KS one-electron Hamiltonian

$$h_{\text{s}}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{\text{s}}(\mathbf{r}), \tag{1.36}$$

where

$$v_{\text{s}}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}), \tag{1.37}$$

is the KS potential, and ε_i are then the KS orbital energies. Note that Eq. (1.35) constitutes a set of coupled self-consistent equations since the potential $v_{\text{Hxc}}(\mathbf{r})$ depends on all the occupied orbitals $\{\phi_i(\mathbf{r})\}_{i=1,\ldots,N}$ through the density [Eq. (1.29)]. At convergence, the orbitals obtained by solving Eq. (1.35) must be the same as the orbitals used to construct $v_{\text{Hxc}}(\mathbf{r})$. The operator $h_{\text{s}}(\mathbf{r})$ defines the KS system which is a system of N non-interacting electrons in an effective external potential $v_{\text{s}}(\mathbf{r})$ ensuring that its ground-state density $n(\mathbf{r})$ is the same as the exact ground-state density $n_0(\mathbf{r})$ of the physical system of N interacting electrons. The exact ground-state energy E_0 is then obtained by injecting the KS orbitals in Eq. (1.28). Note that Eq. (1.35) also permits to define virtual KS orbitals $\{\phi_a(\mathbf{r})\}_{a=N+1,\ldots,\infty}$ which together with the occupied KS orbitals form a complete basis since $h_{\text{s}}(\mathbf{r})$ is a self-adjoint operator.

Note that the existence of the functional derivative in Eq. (1.34) has been assumed. This is in fact not true for all densities but only for v_{s}-representable densities, i.e. densities that are the ground-state densities of a non-interacting system with some local potential. Also, note that the KS potential in Eq. (1.37) is defined only up to an additive constant. For finite systems, we choose the constant so that the potential vanishes at infinity, $v_{\text{s}}(\infty) = 0$.

Following the decomposition of $E_{\text{Hxc}}[n]$ in Eq. (1.23), the potential $v_{\text{Hxc}}(\mathbf{r})$ is decomposed as

$$v_{\text{Hxc}}(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}), \tag{1.38}$$

where $v_{\text{H}}(\mathbf{r}) = \delta E_{\text{H}}[n]/\delta n(\mathbf{r})$ is the Hartree potential and $v_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}}[n]/\delta n(\mathbf{r})$ is the exchange-correlation potential. Likewise, following the decomposition of $E_{\text{xc}}[n]$ in Eq. (1.25), the potential $v_{\text{xc}}(\mathbf{r})$ can be decomposed as

$$v_{\text{xc}}(\mathbf{r}) = v_{\text{x}}(\mathbf{r}) + v_{\text{c}}(\mathbf{r}), \tag{1.39}$$

where $v_{\text{x}}(\mathbf{r}) = \delta E_{\text{x}}[n]/\delta n(\mathbf{r})$ is the exchange potential and $v_{\text{c}}(\mathbf{r}) = \delta E_{\text{c}}[n]/\delta n(\mathbf{r})$ is the correlation potential. Thus, the Kohn-Sham equations are similar to the Hartree-Fock equations, with the difference that they involve a local exchange potential $v_{\text{x}}(\mathbf{r})$ instead of a nonlocal one, and an additional correlation potential.

Exercise 3 : Show that the expression of the Hartree potential is

$$v_{\text{H}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}'. \tag{1.40}$$

1.3.3 Practical calculations in an atomic basis

In practical calculations for molecular systems, we usually work in a basis of M atomic functions $\{\chi_\nu(\mathbf{r})\}$, e.g. Gaussian-type basis functions centered on the nuclei. We then expand the orbitals as

$$\phi_i(\mathbf{r}) = \sum_{\nu=1}^{M} c_{\nu i}\, \chi_\nu(\mathbf{r}), \tag{1.41}$$

and thus calculating the orbitals amounts to calculating the orbital coefficients $c_{\nu i}$. Inserting Eq. (1.41) into the KS equations

$$h_\mathrm{s}(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \tag{1.42}$$

multiplying on the left by $\chi_\mu^*(\mathbf{r})$ and integrating over $\mathbf{r}$, we arrive at

$$\sum_{\nu=1}^{M} F_{\mu\nu}\, c_{\nu i} = \varepsilon_i \sum_{\nu=1}^{M} S_{\mu\nu}\, c_{\nu i}, \tag{1.43}$$

where $F_{\mu\nu} = \int \chi_\mu^*(\mathbf{r})h_\mathrm{s}(\mathbf{r})\chi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}$ are the elements of the KS Fock matrix and $S_{\mu\nu} = \int \chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}$ are the elements of the overlap matrix of the basis functions.

The Fock matrix is calculated as

$$F_{\mu\nu} = h_{\mu\nu} + J_{\mu\nu} + V_{\mathrm{xc},\mu\nu}, \tag{1.44}$$

where $h_{\mu\nu}$ are the one-electron integrals

$$h_{\mu\nu} = \int \chi_\mu^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_\mathrm{ne}(\mathbf{r}) \right) \chi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{1.45}$$

$J_{\mu\nu}$ is the Hartree potential contribution

$$J_{\mu\nu} = \int \chi_\mu^*(\mathbf{r})v_\mathrm{H}(\mathbf{r})\chi_\nu(\mathbf{r})\mathrm{d}\mathbf{r} = \sum_{\lambda=1}^{M}\sum_{\gamma=1}^{M} P_{\gamma\lambda}(\chi_\mu\chi_\nu|\chi_\lambda\chi_\gamma), \tag{1.46}$$

with the density matrix

$$P_{\gamma\lambda} = \sum_{i=1}^{N} c_{\gamma i}c_{\lambda i}^*, \tag{1.47}$$

and the two-electron integrals (in chemists' notation)

$$(\chi_\mu\chi_\nu|\chi_\lambda\chi_\gamma) = \iint \frac{\chi_\mu^*(\mathbf{r}_1)\chi_\nu(\mathbf{r}_1)\chi_\lambda^*(\mathbf{r}_2)\chi_\gamma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{1.48}$$

and $V_{\mathrm{xc},\mu\nu}$ is the exchange-correlation potential contribution

$$V_{\mathrm{xc},\mu\nu} = \int \chi_\mu^*(\mathbf{r})v_\mathrm{xc}(\mathbf{r})\chi_\nu(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{1.49}$$

In Eq. (1.49), the exchange-correlation potential $v_\mathrm{xc}(\mathbf{r})$ is evaluated at the density calculated as

$$n(\mathbf{r}) = \sum_{\gamma=1}^{M}\sum_{\lambda=1}^{M} P_{\gamma\lambda}\chi_\gamma(\mathbf{r})\chi_\lambda^*(\mathbf{r}). \tag{1.50}$$

Eq. (1.43) is a self-consistent generalized eigenvalue equation that must be solved iteratively for finding the KS orbital coefficients and KS orbital energies. The converged density matrix can then be used to obtain the total electronic energy

$$E = \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\nu\mu} h_{\mu\nu} + \frac{1}{2} \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\nu\mu} J_{\mu\nu} + E_{\text{xc}}, \tag{1.51}$$

where E_{xc} is calculated with the density in Eq. (1.50).

In the simplest approximations (see Section 3), the exchange-correlation energy functional has a local form

$$E_{\text{xc}}^{\text{local}} = \int f(n(\mathbf{r})) \mathrm{d}\mathbf{r}, \tag{1.52}$$

where $f(n(\mathbf{r}))$ has a complicated nonlinear dependence on the density $n(\mathbf{r})$. For example, in the local-density approximation (LDA) (see Section 3.1), the exchange energy is

$$E_{\text{x}}^{\text{LDA}} = c_{\text{x}} \int n(\mathbf{r})^{4/3} \mathrm{d}\mathbf{r}, \tag{1.53}$$

where c_{x} is a constant, and the exchange potential is

$$v_{\text{x}}^{\text{LDA}}(\mathbf{r}) = \frac{4}{3} c_{\text{x}} n(\mathbf{r})^{1/3}. \tag{1.54}$$

Therefore, the integrals in Eq. (1.49) and Eq. (1.52) cannot be calculated analytically, but are instead evaluated by numerical integration

$$V_{\text{xc},\mu\nu} \approx \sum_{k} w_k \, \chi_\mu^*(\mathbf{r}_k) v_{\text{xc}}(\mathbf{r}_k) \chi_\nu(\mathbf{r}_k), \tag{1.55}$$

and

$$E_{\text{xc}}^{\text{local}} \approx \sum_{k} w_k \, f(n(\mathbf{r}_k)), \tag{1.56}$$

where $\mathbf{r}_k$ and w_k are quadrature points and weights. For example, for polyatomic molecules, the multicenter numerical integration scheme of Becke [11] is generally used.

1.3.4 Extension to spin density-functional theory

For dealing with an external magnetic field, DFT has been extended from the total density to spin-resolved densities [12, 13]. Without external magnetic fields, this spin density-functional theory is in principle not necessary, even for open-shell systems. In practice, however, the dependence on the spin densities allows one to construct approximate exchange-correlation functionals that are more accurate, and is therefore almost always used for open-shell systems.

The universal density functional is now defined as [14]

$$F[n_\uparrow, n_\downarrow] = \min_{\Psi \to n_\uparrow, n_\downarrow} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle, \tag{1.57}$$

where the search is over normalized antisymmetric wave functions Ψ which yield fixed spin densities

$$n_\uparrow(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r} \uparrow, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \, \mathrm{d}\mathbf{x}_2 ... \mathrm{d}\mathbf{x}_N, \tag{1.58a}$$

$$n_\downarrow(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r}\downarrow, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \, \mathrm{d}\mathbf{x}_2 ... \mathrm{d}\mathbf{x}_N, \tag{1.58b}$$

which integrate respectively to the numbers of $\uparrow$- and $\downarrow$-spin electrons, $N_\uparrow$ and $N_\downarrow$, i.e. $\int n_\uparrow(\mathbf{r})\mathrm{d}\mathbf{r} = N_\uparrow$ and $\int n_\downarrow(\mathbf{r})\mathrm{d}\mathbf{r} = N_\downarrow$. A KS method is obtained by decomposing $F[n_\uparrow, n_\downarrow]$ as

$$F[n_\uparrow, n_\downarrow] = T_\mathrm{s}[n_\uparrow, n_\downarrow] + E_\mathrm{H}[n] + E_\mathrm{xc}[n_\uparrow, n_\downarrow], \tag{1.59}$$

where $T_\mathrm{s}[n_\uparrow, n_\downarrow]$ is defined with a constrained search over spin-unrestricted Slater determinants Φ

$$T_\mathrm{s}[n_\uparrow, n_\downarrow] = \min_{\Phi \to n_\uparrow, n_\downarrow} \langle \Phi | \hat{T} | \Phi \rangle, \tag{1.60}$$

and $E_\mathrm{H}[n]$ is the Hartree energy which is a functional of the total density $n = n_\uparrow + n_\downarrow$ only [Eq. (1.24)], and $E_\mathrm{xc}[n_\uparrow, n_\downarrow]$ is the spin-resolved exchange-correlation energy functional. Writing the spatial orbitals of the spin-unrestricted determinant as $\phi_{i\uparrow}(\mathbf{r})$ and $\phi_{i\downarrow}(\mathbf{r})$ (with indices explicitly including spin now for clarity), we have now the spin-dependent KS equations

$$\left(-\frac{1}{2}\nabla^2 + v_\mathrm{ne}(\mathbf{r}) + v_\mathrm{H}(\mathbf{r}) + v_{\mathrm{xc},\uparrow}(\mathbf{r}) \right) \phi_{i\uparrow}(\mathbf{r}) = \varepsilon_{i\uparrow} \phi_{i\uparrow}(\mathbf{r}), \tag{1.61a}$$

$$\left(-\frac{1}{2}\nabla^2 + v_\mathrm{ne}(\mathbf{r}) + v_\mathrm{H}(\mathbf{r}) + v_{\mathrm{xc},\downarrow}(\mathbf{r}) \right) \phi_{i\downarrow}(\mathbf{r}) = \varepsilon_{i\downarrow} \phi_{i\downarrow}(\mathbf{r}), \tag{1.61b}$$

with the spin-dependent exchange-correlation potentials

$$v_{\mathrm{xc},\uparrow}(\mathbf{r}) = \frac{\delta E_\mathrm{xc}[n_\uparrow, n_\downarrow]}{\delta n_\uparrow(\mathbf{r})}, \quad \text{and} \quad v_{\mathrm{xc},\downarrow}(\mathbf{r}) = \frac{\delta E_\mathrm{xc}[n_\uparrow, n_\downarrow]}{\delta n_\downarrow(\mathbf{r})}, \tag{1.62}$$

and the spin densities

$$n_\uparrow(\mathbf{r}) = \sum_{i=1}^{N_\uparrow} |\phi_{i\uparrow}(\mathbf{r})|^2 \quad \text{and} \quad n_\downarrow(\mathbf{r}) = \sum_{i=1}^{N_\downarrow} |\phi_{i\downarrow}(\mathbf{r})|^2 . \tag{1.63}$$

It turns out that the spin-dependent exchange functional $E_\mathrm{x}[n_\uparrow, n_\downarrow]$ can be exactly expressed in terms of the spin-independent exchange functional $E_\mathrm{x}[n]$ [15]

$$E_\mathrm{x}[n_\uparrow, n_\downarrow] = \frac{1}{2} \left(E_\mathrm{x}[2n_\uparrow] + E_\mathrm{x}[2n_\downarrow] \right), \tag{1.64}$$

which is known as the *spin-scaling relation* and stems directly from the fact the $\uparrow$- and $\downarrow$-spin electrons are uncoupled in the exchange energy. Therefore, any approximation for the spin-independent exchange functional $E_\mathrm{x}[n]$ can be easily extended to an approximation for the spin-dependent exchange functional $E_\mathrm{x}[n_\uparrow, n_\downarrow]$. Unfortunately, there is no such relation for the correlation functional.

Exercise 5 : Prove the spin-scaling relation of Eq. (1.64).

Obviously, in the spin-unpolarized case, i.e. $n_\uparrow = n_\downarrow = n/2$, this spin-dependent formalism reduces to the spin-independent one.

2   More advanced topics in density-functional theory

2.1   The exchange and correlation functionals in terms of the exchange and correlation holes

2.1.1   The exchange and correlation holes

Let us consider the pair density associated with the wave function $\Psi[n]$ defined in Eq. (1.17)

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \cdots \int |\Psi[n](\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \, \mathrm{d}\sigma_1 \mathrm{d}\sigma_2 \mathrm{d}\mathbf{x}_3...\mathrm{d}\mathbf{x}_N, \tag{2.1}$$

which is a functional of the density, and is normalized to the number of electron pairs, $\iint n_2(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = N(N-1)$. It is proportional to the probability density of finding two electrons at positions $(\mathbf{r}_1, \mathbf{r}_2)$ with all the other electrons anywhere. The pair density is useful to express the expectation of the electron-electron interaction operator

$$\langle \Psi[n] | \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle = \frac{1}{2} \iint \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2. \tag{2.2}$$

Mirroring the decomposition of the Hartree-exchange-correlation energy performed in the KS method [Eq. (1.23)], the pair density can be decomposed as

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2) + n_{2,\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2). \tag{2.3}$$

The product of the densities $n(\mathbf{r}_1)n(\mathbf{r}_2)$ corresponds to the case of independent electrons and the exchange-correlation pair density $n_{2,\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2)$ represents the modification of the pair density due to exchange and correlation effects between the electrons. It can be further written as

$$n_{2,\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n_{\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2), \tag{2.4}$$

where $n_{\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2)$ is the *exchange-correlation hole*. It can be interpreted as the modification due to exchange and correlation effects of the conditional probability of finding an electron at $\mathbf{r}_2$ knowing that one has been found at $\mathbf{r}_1$. The positivity of $n_2(\mathbf{r}_1, \mathbf{r}_2)$ implies that

$$n_{\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2) \geq -n(\mathbf{r}_2). \tag{2.5}$$

Moreover, we have the following sum rule

$$\int n_{\mathrm{xc}}(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1. \tag{2.6}$$

Exercise 6 : Prove the sum rule of Eq. (2.6).

We can separate the exchange and correlation contributions in the exchange-correlation hole. For this, consider the pair density $n_{2,\mathrm{KS}}(\mathbf{r}_1, \mathbf{r}_2)$ associated with the KS single-determinant wave function $\Phi[n]$ defined in Eq. (1.21). It can be decomposed as

$$n_{2,\mathrm{KS}}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2) + n_{2,\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2), \tag{2.7}$$

where $n_{2,\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)$ is the exchange pair density, which is further written as

$$n_{2,\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2), \tag{2.8}$$

where $n_\text{x}(\mathbf{r}_1, \mathbf{r}_2)$ is the *exchange hole*. Just like the exchange-correlation hole, the exchange hole satisfies the conditions

$$n_\text{x}(\mathbf{r}_1, \mathbf{r}_2) \geq -n(\mathbf{r}_2), \tag{2.9}$$

and

$$\int n_\text{x}(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -1. \tag{2.10}$$

Moreover, by writing the exchange hole in terms of the KS orbitals[4], one can show that it is always negative

$$n_\text{x}(\mathbf{r}_1, \mathbf{r}_2) \leq 0. \tag{2.11}$$

From Eqs. (1.26), (2.2), (2.7), and (2.8), it can be seen that the exchange energy functional can be written in terms of the exchange hole

$$E_\text{x}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n_\text{x}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{2.12}$$

leading to the interpretation of E_x as the electrostatic interaction energy of an electron and its exchange hole. It is also useful to write the exchange energy functional as

$$E_\text{x}[n] = \int n(\mathbf{r}_1)\varepsilon_\text{x}[n](\mathbf{r}_1)\mathrm{d}\mathbf{r}_1, \tag{2.13}$$

where $\varepsilon_\text{x}[n](\mathbf{r}_1)$ is the exchange energy per particle

$$\varepsilon_\text{x}[n](\mathbf{r}_1) = \frac{1}{2} \int \frac{n_\text{x}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2, \tag{2.14}$$

which is itself a functional of the density. In approximate exchange density functionals, the quantity $\varepsilon_\text{x}[n](\mathbf{r}_1)$ is usually what is approximated.

Exercise 7 : Show that, for finite systems, $\varepsilon_\text{x}[n](\mathbf{r}) \underset{r\to+\infty}{\sim} -1/(2r)$.

The *correlation hole* is defined as the difference

$$n_\text{c}(\mathbf{r}_1, \mathbf{r}_2) = n_\text{xc}(\mathbf{r}_1, \mathbf{r}_2) - n_\text{x}(\mathbf{r}_1, \mathbf{r}_2), \tag{2.15}$$

and, from Eqs. (2.6) and (2.10), satisfies the sum rule

$$\int n_\text{c}(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = 0, \tag{2.16}$$

which implies that the correlation hole has negative and positive contributions[5]. The potential contribution to the correlation energy can be written in terms of the correlation hole

$$U_\text{c}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n_\text{c}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2. \tag{2.17}$$

In order to express the total correlation energy $E_\text{c}[n] = T_\text{c}[n] + U_\text{c}[n]$ in a form similar to Eq. (2.17), we need to introduce the adiabatic-connection formalism.

---

[4]The exchange hole can be written as $n_\text{x}(\mathbf{r}_1, \mathbf{r}_2) = -\sum_{\sigma=\uparrow,\downarrow} |n_{1,\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2/n(\mathbf{r}_1)$ with the one-electron KS density matrix $n_{1,\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j=1}^{N_\sigma} \phi_{j\sigma}^*(\mathbf{r}_2)\phi_{j\sigma}(\mathbf{r}_1)$.

[5]Therefore, the correlation hole is really a "hole" only in some region of space, and a "bump" in other regions.

2.1.2 The adiabatic connection

The idea of the *adiabatic connection* is to have a continuous path between the non-interacting KS system and the physical system while keeping the ground-state density constant. An infinity of such paths are possible, but the one most often considered consists in switching on the electron-electron interaction linearly with a coupling constant λ. The Hamiltonian along this adiabatic connection is

$$\hat{H}^\lambda = \hat{T} + \lambda\hat{W}_{\mathrm{ee}} + \hat{V}^\lambda, \tag{2.18}$$

where $\hat{V}^\lambda$ is the external local potential operator imposing that the ground-state density is the same as the ground-state density of the physical system for all λ. The Hamiltonian (2.18) reduces to the KS non-interacting Hamiltonian for $\lambda = 0$ and to the physical Hamiltonian for $\lambda = 1$.

Just as for the physical system, it is possible to define a universal functional associated with the system of Eq. (2.18) for each value of the parameter λ

$$F^\lambda[n] \quad = \quad \min_{\Psi \to n}\langle\Psi|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Psi\rangle = \langle\Psi^\lambda[n]|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Psi^\lambda[n]\rangle, \tag{2.19}$$

the minimizing wave function being denoted by $\Psi^\lambda[n]$. This functional can be decomposed as

$$F^\lambda[n] = T_{\mathrm{s}}[n] + E_{\mathrm{H}}^\lambda[n] + E_{\mathrm{xc}}^\lambda[n], \tag{2.20}$$

where $E_{\mathrm{H}}^\lambda[n]$ is the Hartree energy functional associated with the interaction $\lambda\hat{W}_{\mathrm{ee}}$ and is simply linear in λ

$$E_{\mathrm{H}}^\lambda[n] = \frac{1}{2}\iint n(\mathbf{r}_1)n(\mathbf{r}_2)\frac{\lambda}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = \lambda E_{\mathrm{H}}[n], \tag{2.21}$$

and $E_{\mathrm{xc}}^\lambda[n]$ is a remaining exchange-correlation functional. It can be decomposed as a sum of an exchange contribution, which is also linear in λ,

$$E_{\mathrm{x}}^\lambda[n] = \langle\Phi[n]|\lambda\hat{W}_{\mathrm{ee}}|\Phi[n]\rangle - E_{\mathrm{H}}^\lambda[n] = \lambda E_{\mathrm{x}}[n], \tag{2.22}$$

and a correlation contribution, which is nonlinear in λ,

$$E_{\mathrm{c}}^\lambda[n] = \langle\Psi^\lambda[n]|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Psi^\lambda[n]\rangle - \langle\Phi[n]|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Phi[n]\rangle. \tag{2.23}$$

Taking the derivative of Eq. (2.23) with respect to λ and using the Hellmann-Feynman theorem for the wave function $\Psi^\lambda[n]$[6], we obtain

$$\frac{\partial E_{\mathrm{c}}^\lambda[n]}{\partial\lambda} \quad = \quad \langle\Psi^\lambda[n]|\hat{W}_{\mathrm{ee}}|\Psi^\lambda[n]\rangle - \langle\Phi[n]|\hat{W}_{\mathrm{ee}}|\Phi[n]\rangle, \tag{2.24}$$

Integrating over λ from 0 to 1, and using $E_{\mathrm{c}}^{\lambda=1}[n] = E_{\mathrm{c}}[n]$ and $E_{\mathrm{c}}^{\lambda=0}[n] = 0$, we arrive at the *adiabatic-connection formula* for the correlation energy functional of the physical system

$$\boxed{E_{\mathrm{c}}[n] = \int_0^1 \mathrm{d}\lambda \, \langle\Psi^\lambda[n]|\hat{W}_{\mathrm{ee}}|\Psi^\lambda[n]\rangle - \langle\Phi[n]|\hat{W}_{\mathrm{ee}}|\Phi[n]\rangle.} \tag{2.25}$$

---

[6]In this context, the Hellmann-Feynman theorem states that in the derivative $\frac{\partial F^\lambda[n]}{\partial\lambda} = \langle\frac{\partial\Psi^\lambda[n]}{\partial\lambda}|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\Psi^\lambda[n]\rangle + \langle\Psi^\lambda[n]|\hat{W}_{\mathrm{ee}}|\Psi^\lambda[n]\rangle + \langle\Psi^\lambda[n]|\hat{T} + \lambda\hat{W}_{\mathrm{ee}}|\frac{\partial\Psi^\lambda[n]}{\partial\lambda}\rangle$ the first and third terms involving the derivative of $\Psi^\lambda[n]$ vanish. This is due to the fact that $\Psi^\lambda[n]$ is obtained via the minimization of Eq. (2.19) and thus any variation of $\Psi^\lambda[n]$ which keeps the density constant (which is the case for a variation with respect to λ) gives a vanishing variation of $F^\lambda[n]$.

By introducing the correlation hole $n_\mathrm{c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)$ associated to the wave function $\Psi^\lambda[n]$, the adiabatic-connection formula for the correlation energy can also be written as

$$E_\mathrm{c}[n] = \frac{1}{2} \int_0^1 \mathrm{d}\lambda \iint \frac{n(\mathbf{r}_1) n_\mathrm{c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \tag{2.26}$$

or, noting that $n_\mathrm{c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)$ is the only quantity that depends on λ in Eq. (2.26), in a more compact way,

$$\boxed{E_\mathrm{c}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1) \bar{n}_\mathrm{c}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2,} \tag{2.27}$$

where $\bar{n}_\mathrm{c}(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 \mathrm{d}\lambda \, n_\mathrm{c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)$ is the coupling-constant-integrated correlation hole. It leads to the interpretation of E_c as the electrostatic interaction energy of an electron with its coupling-constant-integrated correlation hole. As for the exchange energy, the correlation energy functional can be written as

$$E_\mathrm{c}[n] = \int n(\mathbf{r}_1) \varepsilon_\mathrm{c}[n](\mathbf{r}_1) \mathrm{d}\mathbf{r}_1, \tag{2.28}$$

where $\varepsilon_\mathrm{c}[n](\mathbf{r}_1)$ is the correlation energy per particle

$$\varepsilon_\mathrm{c}[n](\mathbf{r}_1) = \frac{1}{2} \int \frac{\bar{n}_\mathrm{c}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_2, \tag{2.29}$$

which is a functional of the density that needs to be approximated.

2.2 Fractional electron numbers and frontier orbital energies

In 1982, Perdew, Parr, Levy, and Balduz [16] extended DFT to fractional electron numbers. Although systems with a noninteger number of electrons may appear as unphysical, such systems in fact naturally arise in quantum mechanics, e.g. as fragments from a molecular dissociation in entangled quantum states. One important result of this extension is that the frontier KS orbital energies can be seen as derivatives of the total energy with respect to the electron number.

2.2.1 Quantum mechanics with fractional electron numbers

The ground-state energy of a system with a fixed fractional number of electrons $\mathcal{N} = N-1+f$ (where N is an integer and $0 \leq f \leq 1$) can be defined in an ensemble formalism as

$$E_0^{N-1+f} = \min_{\hat{\Gamma}} \mathrm{Tr} \left[\hat{\Gamma} \left(\hat{T} + \hat{W}_\mathrm{ee} + \hat{V}_\mathrm{ne} \right) \right], \tag{2.30}$$

where Tr denotes the trace[7] (in Fock space) and the minimization is over ensemble density matrices $\hat{\Gamma}$ of the form

$$\hat{\Gamma} = (1-f)|\Psi^{N-1}\rangle\langle\Psi^{N-1}| + f|\Psi^N\rangle\langle\Psi^N|, \tag{2.31}$$

where f is fixed, and Ψ^{N-1} and Ψ^N are $(N-1)$- and N-electron normalized antisymmetric wave functions that must be varied. This form of $\hat{\Gamma}$ in Eq. (2.31) ensures an average electron number of $N - 1 + f$.[8] The minimizing ensemble density matrix is

$$\hat{\Gamma}_0 = (1-f)|\Psi_0^{N-1}\rangle\langle\Psi_0^{N-1}| + f|\Psi_0^N\rangle\langle\Psi_0^N|, \tag{2.32}$$

---

[7] The trace of an operator $\hat{A}$ is defined as $\mathrm{Tr}[\hat{A}] = \sum_n \langle\Psi_n|\hat{A}|\Psi_n\rangle$ where $\{\Psi_n\}$ is an orthonormal basis of states.

[8] In fact, with the assumption that the ground-state energy for integer electron numbers in a fixed external potential is a convex function, $E^N \leq (E^{N+1} + E^{N-1})/2$, which is true for any known realistic system, the minimization in Eq. (2.30) can be done over ensemble density matrices $\hat{\Gamma}$ constructed from wave functions with any number of electrons with the only constraint that $\hat{\Gamma}$ gives an average electron number of $N - 1 + f$.

where Ψ_0^{N-1} and Ψ_0^N are the ground-state wave functions of the $(N-1)$- and N-electron systems, respectively.

The fact that the minimizing ensemble density matrix is linear in f implies that the ground-state energy is also linear in f between the integer electron numbers $N-1$ and N

$$E_0^{N-1+f} = (1-f)E_0^{N-1} + f E_0^N, \tag{2.33}$$

where E_0^{N-1} and E_0^N are the ground-state energies of the $(N-1)$- and N-electron systems, respectively. Similarly, between the integer electron numbers N and $N+1$, we have

$$E_0^{N+f} = (1-f)E_0^N + f E_0^{N+1}. \tag{2.34}$$

Thus, the ground-state energy is a *continuous piecewise linear function* of the fractional electron number $\mathcal{N}$.

Exercise 8 : Prove that the minimizing ensemble density matrix is indeed given by Eq. (2.32) and the ground-state energy by Eq. (2.33).

The derivative of $E_0^{\mathcal{N}}$ with respect to $\mathcal{N}$ defines the *electronic chemical potential* [9]

$$\mu = \frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}}, \tag{2.35}$$

and is obtained as the derivative with respect to f of Eq. (2.33) for $N-1 < \mathcal{N} < N$

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N-1<\mathcal{N}<N} = E_0^N - E_0^{N-1} = -I_N, \tag{2.36}$$

where I_N is the ionization energy of the N electron system (I_N is always strictly positive), and similarly from Eq. (2.34) for $N < \mathcal{N} < N+1$

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N<\mathcal{N}<N+1} = E_0^{N+1} - E_0^N = -A_N, \tag{2.37}$$

where A_N is the electron affinity of the N electron system (with this definition, A_N is strictly positive if the $(N+1)$-electron system is bound, otherwise it is zero). The electronic chemical potential μ has thus a discontinuity at the integer electron number N. So, the plot of $E_0^{\mathcal{N}}$ with respect to $\mathcal{N}$ is made of a series of straight lines between integer electron numbers, with derivative discontinuities at each integer.

2.2.2 Density-functional theory with fractional electron numbers

The universal density functional $F[n]$ is extended to densities integrating to a fractional electron number, $\int n(\mathbf{r})\mathrm{d}\mathbf{r} = \mathcal{N} = N - 1 + f$, as

$$F[n] = \min_{\hat{\Gamma} \to n} \mathrm{Tr} \left[\hat{\Gamma} \left(\hat{T} + \hat{W}_{\mathrm{ee}} \right) \right], \tag{2.38}$$

---

[9] The electronic chemical potential is an important quantity in the field of *conceptual DFT*. The electronegativity of a system can be defined as the opposite of the electronic chemical potential

where the minimization is performed over ensemble density matrices $\hat{\Gamma}$ of the form written in Eq. (2.31) and yielding the density n. As usual, to set up a KS method, $F[n]$ is decomposed as

$$F[n] = T_{\mathrm{s}}[n] + E_{\mathrm{Hxc}}[n], \tag{2.39}$$

where $T_{\mathrm{s}}[n] = \min_{\hat{\Gamma}_{\mathrm{s}} \to n} \mathrm{Tr}[\hat{\Gamma}_{\mathrm{s}}\hat{T}]$ is the KS non-interacting kinetic-energy functional and $E_{\mathrm{Hxc}}[n]$ is the remaining Hartree-exchange-correlation functional. The exact ground-state energy can then be expressed as

$$E_0^{N-1+f} = \min_{\hat{\Gamma}_{\mathrm{s}}} \left\{ \mathrm{Tr}\left[\hat{\Gamma}_{\mathrm{s}}\left(\hat{T} + \hat{V}_{\mathrm{ne}}\right)\right] + E_{\mathrm{Hxc}}[n_{\hat{\Gamma}_{\mathrm{s}}}]\right\}, \tag{2.40}$$

where the minimization is over ensemble non-interacting density matrices $\hat{\Gamma}_{\mathrm{s}}$ of the form

$$\hat{\Gamma}_{\mathrm{s}} = (1-f)|\Phi^{N-1,f}\rangle\langle\Phi^{N-1,f}| + f|\Phi^{N,f}\rangle\langle\Phi^{N,f}|, \tag{2.41}$$

where $\Phi^{N-1,f}$ and $\Phi^{N,f}$ are $(N-1)$- and N-electron single-determinant wave functions, respectively, constructed from a common set of orbitals $\{\phi_i\}$ depending on the fixed f. In Eq. (2.40), E_{Hxc} is evaluated at $n_{\hat{\Gamma}_{\mathrm{s}}}$, i.e. the density of $\hat{\Gamma}_{\mathrm{s}}$. The total electronic energy can then be written in terms of these orbitals and occupation numbers n_i

$$E = \sum_{i=1}^{N} n_i \int \phi_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\mathbf{r})\right)\phi_i(\mathbf{r})\mathrm{d}\mathbf{r} + E_{\mathrm{Hxc}}[n], \tag{2.42}$$

with the density

$$n(\mathbf{r}) = \sum_{i=1}^{N} n_i |\phi_i(\mathbf{r})|^2, \tag{2.43}$$

where $n_i = 1$ for $i \leq N-1$ and $n_N = f$ for the highest occupied molecular orbital (HOMO) which is assumed here to be nondegenerate for simplicity. As in the standard KS method, the variation of Eq. (2.42) with respect to the orthonormal orbitals but with fixed occupation numbers leads to the self-consistent KS equations

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \tag{2.44}$$

where $v_{\mathrm{s}}(\mathbf{r})$ is the KS potential

$$v_{\mathrm{s}}(\mathbf{r}) = v_{\mathrm{ne}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}. \tag{2.45}$$

Thus, the KS equations for fractional electron numbers look identical (with the caveat of a fractional occupation number for the HOMO) to the standard KS equations for integer electron numbers. There is however one important difference. In the standard KS equations, the functional derivative of $E_{\mathrm{Hxc}}[n]$ is taken with respect to density variations $\delta n(\mathbf{r})$ keeping the number of electrons constant, i.e. $\int \delta n(\mathbf{r})\mathrm{d}\mathbf{r} = 0$. As a consequence, the functional derivative is defined only up to an additive constant, which can be seen from its definition

$$\delta E_{\mathrm{Hxc}}[n] = \int \left(\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})} + \mathrm{const}\right)\delta n(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{2.46}$$

In the present extension to fractional electron numbers, since the functional $E_{\mathrm{Hxc}}[n]$ is now defined for densities having any noninteger electron numbers, its functional derivative can now be generally taken with respect to density variations which can change the number of electrons, i.e.

$\int \delta n(\mathbf{r}) \mathrm{d}\mathbf{r} \neq 0$. Consequently, the constant in Eq. (2.46) is now determined. This unambiguously fixes the values of the KS orbital energies.

Eqs. (2.42)-(2.45) constitutes a general KS method with fractional occupation numbers. A useful result is that, after optimizing the orbitals with fixed occupation numbers, the derivative of the total energy with respect to the occupation number n_i of an occupied orbital equals the energy ε_i of this orbital,

$$\frac{\partial E}{\partial n_i} = \varepsilon_i, \tag{2.47}$$

which is known as *Janak's theorem* [17].

Exercise 9 : Prove Janak's theorem.

For clarity in the discussion, we will now explicitly indicate the dependence on the electron number $\mathcal{N}$ in the density $n^{\mathcal{N}}(\mathbf{r})$, the KS potential $v_{\mathrm{s}}^{\mathcal{N}}(\mathbf{r})$, the KS orbitals $\phi_i^{\mathcal{N}}(\mathbf{r})$, and the KS orbital energies $\varepsilon_i^{\mathcal{N}}$.

2.2.3 The HOMO energy and the ionization energy

Applying Janak's theorem for the case of the HOMO for a fractional electron number $\mathcal{N} = N - \delta$ where $\delta \to 0^+$ (the limit will be always tacitly assumed) gives

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N-\delta} = \varepsilon_{\mathrm{H}}^{N-\delta} = \varepsilon_{\mathrm{H}}^N, \tag{2.48}$$

where $\varepsilon_{\mathrm{H}}^N$ is the HOMO energy of the N-electron system (here, the HOMO is the Nth orbital). Notice that, since $\partial E_0^{\mathcal{N}} / \partial \mathcal{N}$ has a discontinuity at the integer electron number N, it is important to specify that $\varepsilon_{\mathrm{H}}^N$ is defined as the limit when N is approached from the left (electron-deficient) side. Combining this result with Eq. (2.36) leads to

$$\boxed{\varepsilon_{\mathrm{H}}^N = -I_N,} \tag{2.49}$$

i.e., the energy of the HOMO KS orbital is the opposite of the exact ionization energy.

This can be used, together with the asymptotic behavior of the density, to determine the constant in the KS potential. Indeed, for finite systems, it can be shown that the exact ground-state density of the N-electron system decays exponentially for $r = |\mathbf{r}| \to +\infty$ with an exponent related to the ionization energy I_N [18]

$$n^N(\mathbf{r}) \underset{r \to +\infty}{\sim} e^{-2\sqrt{2I_N}\, r}. \tag{2.50}$$

Besides, each occupied KS orbitals of the N-electron system has the following asymptotic behavior (see Exercise 10)

$$\phi_i^N(\mathbf{r}) \underset{r \to +\infty}{\sim} e^{-\sqrt{-2(\varepsilon_i^N - v_{\mathrm{s}}^N(\infty))}\, r}, \tag{2.51}$$

where $v_{\mathrm{s}}^N(\infty) = v_{\mathrm{s}}^{N-\delta}(\infty)$ is the asymptotic value of the KS potential (defined as the limit from the left side) which is for now unknown but fixed since the additive constant in the KS potential is determined now according to the discussion after Eq. (2.46). Consequently, the HOMO KS orbital $\phi_{\mathrm{H}}^N(\mathbf{r})$ is the slowest decaying orbital and dominates the asymptotic decay of the KS density [via Eq. (2.43)]

$$n^N(\mathbf{r}) \underset{r \to +\infty}{\sim} e^{-2\sqrt{-2(\varepsilon_{\mathrm{H}}^N - v_{\mathrm{s}}^N(\infty))}\, r}. \tag{2.52}$$

Since the KS density is the exact density, Eqs. (2.50) and (2.52) must agree, and since we have already shown that $\varepsilon_{\mathrm{H}}^N = -I_N$, we thus find

$$v_{\mathrm{s}}^N(\infty) = 0, \tag{2.53}$$

in accordance with the choice usually made in the standard KS method for integer electron numbers.

Exercise 10 : Check that the asymptotic decay of the KS orbitals is indeed given by Eq. (2.51). For this, use Eq. (2.44) and the asymptotic behavior of the KS potential $v_{\mathrm{s}}^N(\mathbf{r}) \underset{r \to +\infty}{\sim} v_{\mathrm{s}}^N(\infty) + (Q-1)/r$ where Q is the total charge of the system.

2.2.4 The LUMO energy, the electron affinity, and the derivative discontinuity

Applying Janak's theorem for the HOMO but now for a fractional electron number $\mathcal{N} = N + \delta$ where $\delta \to 0^+$ gives

$$\left(\frac{\partial E_0^{\mathcal{N}}}{\partial \mathcal{N}} \right)_{N+\delta} = \varepsilon_{\mathrm{H}}^{N+\delta}, \tag{2.54}$$

where $\varepsilon_{\mathrm{H}}^{N+\delta}$ is the HOMO energy from the right (excess-electron) side of the discontinuity (here, the HOMO is the $(N+1)^{\mathrm{th}}$ orbital). Since the derivative is in fact the same for all $N < \mathcal{N} < N+1$, it is also the HOMO energy of the $(N+1)$-electron system, $\varepsilon_{\mathrm{H}}^{N+\delta} = \varepsilon_{\mathrm{H}}^{N+1-\delta} = \varepsilon_{\mathrm{H}}^{N+1}$. Combining Eq. (2.54) with Eq. (2.37) leads to

$$\varepsilon_{\mathrm{H}}^{N+\delta} = -A_N. \tag{2.55}$$

Naively, one may think that $\varepsilon_{\mathrm{H}}^{N+\delta}$ is equal to the LUMO energy of the N-electron system $\varepsilon_{\mathrm{L}}^N$ (again defined as the limit from the left side, $\varepsilon_{\mathrm{L}}^N = \varepsilon_{\mathrm{L}}^{N-\delta}$, i.e. the $(N+1)^{\mathrm{th}}$ orbital), and therefore that the LUMO KS energy equals to the opposite of the electron affinity. However, this is not as simple. Let us compare $\varepsilon_{\mathrm{H}}^{N+\delta}$ that we can write as

$$\varepsilon_{\mathrm{H}}^{N+\delta} = \int \phi_{\mathrm{H}}^{N+\delta}(\mathbf{r})^* \left(-\frac{1}{2} \nabla^2 + v_{\mathrm{s}}^{N+\delta}(\mathbf{r}) \right) \phi_{\mathrm{H}}^{N+\delta}(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{2.56}$$

with $\varepsilon_{\mathrm{L}}^{N-\delta}$ that we can write as

$$\varepsilon_{\mathrm{L}}^{N-\delta} = \int \phi_{\mathrm{L}}^{N-\delta}(\mathbf{r})^* \left(-\frac{1}{2} \nabla^2 + v_{\mathrm{s}}^{N-\delta}(\mathbf{r}) \right) \phi_{\mathrm{L}}^{N-\delta}(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{2.57}$$

The problem is that there is nothing preventing the KS potential to have a discontinuity $v_{\mathrm{s}}^{N+\delta}(\mathbf{r}) \neq v_{\mathrm{s}}^{N-\delta}(\mathbf{r})$. Indeed, the continuity of the density implies that $n^{N+\delta}(\mathbf{r}) = n^{N-\delta}(\mathbf{r})$,[10] but this only imposes that $v_{\mathrm{s}}^{N+\delta}(\mathbf{r})$ and $v_{\mathrm{s}}^{N-\delta}(\mathbf{r})$ be equal up to an additive spatial constant (according to the Hohenberg-Kohn theorem). So we can have:

$$v_{\mathrm{s}}^{N+\delta}(\mathbf{r}) - v_{\mathrm{s}}^{N-\delta}(\mathbf{r}) = \Delta_{\mathrm{xc}}^N, \tag{2.58}$$

where Δ_{xc}^N is independent from $\mathbf{r}$. Since the two potentials just differ by an additive constant, the orbitals are continuous at the integer N, and in particular $\phi_{\mathrm{H}}^{N+\delta}(\mathbf{r}) = \phi_{\mathrm{L}}^{N-\delta}(\mathbf{r})$. Using this fact and Eq. (2.58), we find

$$\begin{aligned} \varepsilon_{\mathrm{H}}^{N+\delta} &= \int \phi_{\mathrm{L}}^{N-\delta}(\mathbf{r})^* \left(-\frac{1}{2} \nabla^2 + v_{\mathrm{s}}^{N-\delta}(\mathbf{r}) \right) \phi_{\mathrm{L}}^{N-\delta}(\mathbf{r}) \mathrm{d}\mathbf{r} + \Delta_{\mathrm{xc}}^N \\ &= \varepsilon_{\mathrm{L}}^{N-\delta} + \Delta_{\mathrm{xc}}^N. \end{aligned} \tag{2.59}$$

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[10]From the linearity of the minimizing ensemble density matrix in Eq. (2.32), the exact ground-state density is a continuous piecewise linear function of $\mathcal{N}$: $n^{N-1+f}(\mathbf{r}) = (1-f)n^{N-1}(\mathbf{r}) + fn^N(\mathbf{r})$ and $n^{N+f}(\mathbf{r}) = (1-f)n^N(\mathbf{r}) + fn^{N+1}(\mathbf{r})$, just like the total ground-state energy.

In conclusion, the LUMO energy of the N-electron system is not the opposite of the exact electron affinity

$$\varepsilon_{\text{L}}^N = -A_N - \Delta_{\text{xc}}^N, \tag{2.60}$$

due to the possible discontinuity Δ_{xc}^N in the KS potential.

Such a discontinuity can only come from the exchange-correlation part of the potential $v_{\text{xc}}^{\mathcal{N}}(\mathbf{r})$ since $v_{\text{ne}}(\mathbf{r})$ is independent from $\mathcal{N}$ and the Hartree potential $v_{\text{H}}^{\mathcal{N}}(\mathbf{r}) = \int n^{\mathcal{N}}(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}'$ is a continuous function of $\mathcal{N}$. So, we have

$$\Delta_{\text{xc}}^N = v_{\text{xc}}^{N+\delta}(\mathbf{r}) - v_{\text{xc}}^{N-\delta}(\mathbf{r}) = \left(\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right)_{N+\delta} - \left(\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right)_{N-\delta}, \tag{2.61}$$

i.e. Δ_{xc}^N is the *derivative discontinuity* in the exchange-correlation energy functional $E_{\text{xc}}[n]$. Theoretical and numerical examples show that this derivative discontinuity does exist [19–21].

2.2.5 Fundamental gap

The fundamental gap of the N-electron system is defined as

$$E_{\text{gap}}^N = I_N - A_N. \tag{2.62}$$

Using Eqs. (2.49) and (2.60), it can be expressed as

$$E_{\text{gap}}^N = \varepsilon_{\text{L}}^N - \varepsilon_{\text{H}}^N + \Delta_{\text{xc}}^N, \tag{2.63}$$

i.e., the difference between the LUMO and HOMO energies which defines the KS gap, $E_{\text{gap}}^{\text{KS},N} = \varepsilon_{\text{L}}^N - \varepsilon_{\text{H}}^N$, is not equal to the exact fundamental gap of the system. The difference comes from the derivative discontinuity Δ_{xc}^N. In practice, this last term can represent an important contribution to the fundamental gap. In the special case of open-shell systems, we have $\varepsilon_{\text{L}}^N = \varepsilon_{\text{H}}^N$, and thus if the fundamental gap of an open-shell system is not zero (Mott insulator), it is entirely given by Δ_{xc}^N.

3 Usual approximations for the exchange-correlation energy

We review here the main classes of usual approximations for the exchange-correlation energy. These classes are roughly ordered from the simplest to the most sophisticated ones. The discussion is focus on the contents of the approximations, not their performance in practical calculations. On average, more sophisticated approximations are usually more accurate than simpler ones, even though many exceptions can be found. For a recent very intensive benchmark of approximate functionals, see Ref. [22]. The more complicated case of the so-called orbital-dependent exchange-correlation functionals such as exact exchange and the random-phase approximation, beyond usual hybrid or double-hybrid approximations, is treated separately in Section 4.

3.1 The local-density approximation

In the *local-density approximation* (LDA), introduced by Kohn and Sham [10], the exchange-correlation functional is approximated as

$$E_{\text{xc}}^{\text{LDA}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}^{\text{unif}}(n(\mathbf{r})) \text{d}\mathbf{r}, \tag{3.1}$$

where $\varepsilon_{\text{xc}}^{\text{unif}}(n)$ is the exchange-correlation energy per particle of the infinite *uniform electron gas* with the density n. The uniform electron gas represents a family of systems of interacting electrons with an arbitrary spatially constant density n that acts a parameter. Thus, in the LDA, the exchange-correlation energy per particle of an inhomogeneous system at a spatial point of density $n(\mathbf{r})$ is approximated as the exchange-correlation energy per particle of the uniform electron gas of the same density.

The function $\varepsilon_{\text{xc}}^{\text{unif}}(n)$ is a sum of exchange and correlation contributions, $\varepsilon_{\text{xc}}^{\text{unif}}(n) = \varepsilon_{\text{x}}^{\text{unif}}(n) + \varepsilon_{\text{c}}^{\text{unif}}(n)$. The exchange energy per particle of the uniform electron gas can be calculated analytically

$$\varepsilon_{\text{x}}^{\text{unif}}(n) = c_{\text{x}} \, n^{1/3}, \tag{3.2}$$

where $c_{\text{x}} = -(3/4)(3/\pi)^{1/3}$. The LDA exchange functional is associated with the names of Dirac [23] and Slater [24].

Exercise 11 : The exchange energy of the uniform electron gas can be obtained by starting from the exact exchange energy expression for closed-shell systems [Eq. (3.18) or (4.1) with $\phi_{i\uparrow}(\mathbf{r}) = \phi_{i\downarrow}(\mathbf{r}) = \phi_i(\mathbf{r})$]

$$E_{\text{x}} = -\sum_{i=1}^{N/2} \sum_{j=1}^{N/2} \iint \frac{\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \text{d}\mathbf{r}_1 \text{d}\mathbf{r}_2, \tag{3.3}$$

and by making the replacements $\phi_i(\mathbf{r}) \to (1/V)^{1/2} e^{\imath \mathbf{k}\cdot\mathbf{r}}$ and $\sum_{i=1}^{N/2} \to V/(2\pi)^3 \int_{\Omega_{k_{\text{F}}}} \text{d}\mathbf{k}$ where $\Omega_{k_{\text{F}}}$ is the sphere of radius equal to the Fermi momentum $k_{\text{F}} = (3\pi^2 n)^{1/3}$ with the density $n = N/V$, and doing the spatial integrations on a large box of volume V ($N \to \infty$ and $V \to \infty$ such that $n = N/V$ remains finite). Show that this gives

$$E_{\text{x}}^{\text{unif}} = -\frac{V}{(2\pi)^6} \int_{\Omega_{k_{\text{F}}}} \text{d}\mathbf{k}_1 \int_{\Omega_{k_{\text{F}}}} \text{d}\mathbf{k}_2 \, \frac{4\pi}{|\mathbf{k}_1 - \mathbf{k}_2|^2}. \tag{3.4}$$

Calculate this integral to finally obtain the exchange energy per particle $\varepsilon_{\mathrm{x}}^{\mathrm{unif}} = E_{\mathrm{x}}^{\mathrm{unif}}/N$.

Exercise 12 : Show that the expression of the LDA exchange potential is (see Appendix B for an introduction to functional calculus)

$$v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}) = \frac{\delta E_{\mathrm{x}}^{\mathrm{LDA}}[n]}{\delta n(\mathbf{r})} = \frac{4}{3}c_{\mathrm{x}}\, n(\mathbf{r})^{1/3}. \tag{3.5}$$

Does it satisfy the asymptotic behavior,

$$v_{\mathrm{x}}(\mathbf{r}) \underset{r \to +\infty}{\sim} -\frac{1}{r}, \tag{3.6}$$

of the exact exchange potential?

The correlation energy per particle $\varepsilon_{\mathrm{c}}^{\mathrm{unif}}(n)$ of the uniform electron gas cannot be calculated analytically. This quantity has been obtained numerically for a number of densities n using accurate quantum Monte Carlo calculations [25], and fitted to a parametrized function of n satisfying the known high- and low-density expansions. Expressed in terms of the Wigner-Seitz radius $r_{\mathrm{s}} = (3/(4\pi n))^{1/3}$, the first terms of the high-density expansion ($r_{\mathrm{s}} \to 0$) have the form

$$\varepsilon_{\mathrm{c}}^{\mathrm{unif}} = A\ln r_{\mathrm{s}} + B + Cr_{\mathrm{s}}\ln r_{\mathrm{s}} + O(r_{\mathrm{s}}), \tag{3.7}$$

and the first terms of the low-density expansion ($r_{\mathrm{s}} \to +\infty$) have the form

$$\varepsilon_{\mathrm{c}}^{\mathrm{unif}} = \frac{a}{r_{\mathrm{s}}} + \frac{b}{r_{\mathrm{s}}^{3/2}} + O\left(\frac{1}{r_{\mathrm{s}}^2}\right), \tag{3.8}$$

where A, B, C, a, and b are constants. The two most used parametrizations are the ones of Vosko, Wilk, and Nusair (VWN) [26] and the one of Perdew and Wang (PW92) [27]. Their forms are too complicated to be given here. These parametrizations also include the generalization to spin densities, $\varepsilon_{\mathrm{c}}^{\mathrm{unif}}(n_\uparrow, n_\downarrow)$ differing from $\varepsilon_{\mathrm{c}}^{\mathrm{unif}}(n)$ for spin-polarized systems ($n_\uparrow \neq n_\downarrow$), which is sometimes specifically referred to as local-spin-density (LSD) approximation. For a recent review on the calculations of the exchange and correlation energies of the uniform electron gas, see Ref. [28].

Exercise 13 : The Wigner correlation functional is a simple functional derived from the low-density limit of the uniform electron gas

$$E_{\mathrm{c}}^{\mathrm{W}}[n] = \int n(\mathbf{r})\frac{c}{d + r_{\mathrm{s}}(\mathbf{r})}\mathrm{d}\mathbf{r}, \tag{3.9}$$

where $r_{\mathrm{s}}(\mathbf{r}) = (3/(4\pi n(\mathbf{r})))^{1/3}$, and c and d are two constants. Calculate the corresponding correlation potential $v_{\mathrm{c}}^{\mathrm{W}}(\mathbf{r})$.

3.2 Generalized-gradient approximations

The next logical step beyond the LDA is the *gradient-expansion approximation* (GEA), initiated by Kohn and Sham [10]. One way of deriving the GEA is to start from the uniform electron

gas, introduce a weak and slowly-varying external potential $v(\mathbf{r})$, and expand the exchange-correlation energy in terms of the gradients of the density. At second order, one obtains a functional of the form

$$E_{\text{xc}}^{\text{GEA}}[n] = E_{\text{xc}}^{\text{LDA}}[n] + \int C_{\text{xc}}(n(\mathbf{r})) \, n(\mathbf{r})^{4/3} \left(\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})^{4/3}} \right)^2 \, \mathrm{d}\mathbf{r}, \qquad (3.10)$$

where $C_{\text{xc}}(n) = C_{\text{x}} + C_{\text{c}}(n)$ is the sum of the exchange and correlation coefficients of the second-order gradient expansion. Note that the gradient expansion is most naturally written in terms of the reduced density gradient $|\nabla n|/n^{4/3}$ which is a dimensionless quantity. The GEA should improve over the LDA provided that the reduced density gradient is small. Unfortunately, for real systems, the reduced density gradient can be large in some regions of space, and the GEA turns out to be a worse approximation than the LDA.

The failure of the GEA lead to the development of *generalized-gradient approximations* (GGAs), which really started in the 1980s, of the generic form

$$\boxed{E_{\text{xc}}^{\text{GGA}}[n] = \int f(n(\mathbf{r}), \nabla n(\mathbf{r}))\mathrm{d}\mathbf{r},} \qquad (3.11)$$

where f is some function. The GGAs are *semilocal* approximations in the sense that f does not only use the local value of the density $n(\mathbf{r})$ but also its gradient $\nabla n(\mathbf{r})$[11]. For simplicity, we consider here only the spin-independent form, but in practice GGA functionals are more generally formulated in terms of spin densities $(n_\uparrow, n_\downarrow)$ and their gradients $(\nabla n_\uparrow, \nabla n_\downarrow)$[12].

Exercise 14 : Show that the potential of a GGA functional has the following form

$$v_{\text{xc}}^{\text{GGA}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}^{\text{GGA}}[n]}{\delta n(\mathbf{r})} = \frac{\partial f}{\partial n}(n(\mathbf{r}), \nabla n(\mathbf{r})) - \nabla \cdot \frac{\partial f}{\partial \nabla n}(n(\mathbf{r}), \nabla n(\mathbf{r})), \qquad (3.12)$$

which is a 3-dimensional generalization of Eq. (B.13). Give then a practical expression for the contribution $V_{\text{xc},\mu\nu}^{\text{GGA}}$ of this potential to the KS Fock matrix [Eq. (1.49)].

Many GGA functionals have been proposed. We very briefly review here some of the most widely used ones.

B88 exchange functional

The Becke 88 (B88 or B) [29] exchange functional is formulated as an additive correction to LDA. It consists in a compact function of n and $|\nabla n|/n^{4/3}$ chosen so as to satisfy the exact asymptotic behavior of the exchange energy per particle for finite systems (see Exercise 7), and with an empirical parameter fitted to Hartree-Fock exchange energies of rare-gas atoms.

LYP correlation functional

The Lee-Yang-Parr (LYP) [30] correlation functional is one of the rare functionals which have not been constructed starting from LDA. It originates from the Colle-Salvetti [31] correlation-energy approximation depending on the Hartree-Fock pair density and containing four parameters fitted to Helium data. By making a further reasonable approximation, LYP turned the

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[11]For generally and simplicity, we consider here that the GGAs depend on the density gradient $\nabla n(\mathbf{r})$, but in practice GGAs depend only on the module of the density gradient $|\nabla n(\mathbf{r})|$, or equivalently on its square $(\nabla n(\mathbf{r}))^2$, and not on its direction.

[12]Again, in practice, the spin-dependent GGAs do not actually depend on the gradients $\nabla n_\uparrow$ and $\nabla n_\downarrow$ but on the scalar quantities $(\nabla n_\uparrow)^2$, $(\nabla n_\downarrow)^2$, and $\nabla n_\uparrow \cdot \nabla n_\downarrow$

Colle-Salvetti expression into a density functional depending on the density n, the square of the density gradient $(\nabla n)^2$, and the Laplacian of the density $\nabla^2 n$. The dependence on the Laplacian can be exactly eliminated by an integration by parts [32].

PW91 exchange-correlation functional

The Perdew-Wang 91 (PW91) (see Refs. [33–35]) exchange-correlation functional is based on a model of the exchange hole $n_x(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (2.14) and of the coupling-constant-integrated correlation hole in Eq. (2.29). The idea is to start from the GEA model of these holes given as gradient expansions and remove the unrealistic long-range parts of these holes to restore important conditions satisfied by the LDA. Specifically, the spurious positive parts of the GEA exchange hole are removed to enforce the negativity condition of Eq. (2.11) and a cutoff in $|\mathbf{r}_1 - \mathbf{r}_2|$ is applied to enforce the normalization condition of Eq. (2.10). Similarly, a cutoff is applied on the GEA correlation hole to enforce the condition that the hole integrates to zero [Eq. (2.16)]. The exchange and correlation energies per particle calculated from these numerical holes are then fitted to functions of n and $|\nabla n|$ chosen to satisfy a number of exact conditions.

PBE exchange-correlation functional

The Perdew-Burke-Ernzerhof (PBE) [36] exchange-correlation functional is a simplification of the PW91 functional. The exchange and correlation energies per particle are expressed as simpler functions of n and $|\nabla n|$ enforcing less exact conditions and with no fitted parameters. Specifically, the function used for correlation enforces the second-order small-gradient expansion in the high-density limit, the vanishing of correlation in the large-gradient limit, and removes the logarithm divergence of the LDA in the high-density limit [see Eq. (3.7)]. The function used for exchange is chosen to cancel out the second-order small-gradient expansion of correlation and enforces the Lieb-Oxford bound in the large-gradient limit.

3.3 Meta-generalized-gradient approximations

The *meta-generalized-gradient approximations* (meta-GGAs or mGGAs) are of the generic form

$$E_{xc}^{mGGA} = \int f(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r})) d\mathbf{r}, \qquad (3.13)$$

i.e., they use more ingredients than the GGAs, namely the Laplacian of the density $\nabla^2 n(\mathbf{r})$ and/or the non-interacting positive kinetic energy density $\tau(\mathbf{r})$

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i(\mathbf{r})|^2, \qquad (3.14)$$

where $\phi_i(\mathbf{r})$ are the KS orbitals. Note that meta-GGAs are only implicit functionals of the density since $\tau(\mathbf{r})$ is itself an implicit functional of the density through the orbitals. To avoid complications for calculating the functional derivative, they are usually considered as functionals of n and τ taken as independent variables, $E_{xc}^{mGGA}[n, \tau]$. This tacitly implies a slight extension of the usual KS method[13]. The meta-GGAs are considered part of the family of semilocal approximations, in the sense that $\tau(\mathbf{r})$ depends only the gradient of the orbitals at point $\mathbf{r}$. Again, we consider here only the spin-independent form, but meta-GGAs are more generally formulated in terms of spin-resolved quantities ($n_\uparrow$, $n_\downarrow$, $\nabla n_\uparrow$, $\nabla n_\downarrow$, $\nabla^2 n_\uparrow$, $\nabla^2 n_\downarrow$, $\tau_\uparrow$, $\tau_\downarrow$).

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[13]Specifically, for meta-GGA approximations, the equation giving the ground-state energy, Eq. (1.22), now becomes: $E_0 = \min_\Phi \left\{ \langle \Phi | \hat{T} + \hat{V}_{ne} | \Phi \rangle + E_H[n_\Phi] + E_{xc}[n_\Phi, \tau_\Phi] \right\}$ where n_Φ and τ_Φ are the density and positive kinetic energy density of the single determinant Φ.

One motivation for the introduction of the variable $\tau(\mathbf{r})$ is that it appears in the short-range expansion of the exchange hole [37], which for the case of a closed-shell system is

$$n_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') = -\frac{n(\mathbf{r})}{2} - \frac{1}{3}\left(\nabla^2 n(\mathbf{r}) - 4\tau(\mathbf{r}) + \frac{|\nabla n(\mathbf{r})|^2}{2n(\mathbf{r})}\right)|\mathbf{r} - \mathbf{r}'|^2 + \cdots . \tag{3.15}$$

Another important motivation is that $\tau(\mathbf{r})$ can be used to make the correlation energy per particle $\varepsilon_{\mathrm{c}}(\mathbf{r})$ correctly vanish in spatial regions where the density has a one-electron character. This is done by comparing $\tau(\mathbf{r})$ with the von Weizsäcker kinetic energy density

$$\tau^{\mathrm{W}}(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})}, \tag{3.16}$$

which is exact for one-electron systems, e.g. by introducing the ratio $\tau(\mathbf{r})/\tau^{\mathrm{W}}(\mathbf{r})$.

Exercise 15 : Show that the von Weizsäcker kinetic energy density in Eq. (3.16) is indeed exact for one-electron systems.

One the most used meta-GGA approximation is the Tao-Perdew-Staroverov-Scuseria (TPSS) [38] exchange-correlation functional. A more recently developed meta-GGA approximation is the SCAN exchange-correlation functional [39] which satisfies 17 known exact constraints and contains 7 parameters determined by fitting to a few simple systems.

3.4 Hybrid approximations

Based on arguments relying on the adiabatic-connection formalism, in 1993 Becke [40] proposed to mix a fraction of the exact or Hartree-Fock (HF) exchange energy $E_{\mathrm{x}}^{\mathrm{HF}}$ with GGA functionals. In particular, he proposed a three-parameter hybrid (3H) approximation [41] of the form

$$E_{\mathrm{xc}}^{\mathrm{3H}} = a\, E_{\mathrm{x}}^{\mathrm{HF}} + b\, E_{\mathrm{x}}^{\mathrm{GGA}} + (1 - a - b)\, E_{\mathrm{x}}^{\mathrm{LDA}} + c\, E_{\mathrm{c}}^{\mathrm{GGA}} + (1 - c)\, E_{\mathrm{c}}^{\mathrm{LDA}}, \tag{3.17}$$

where the three parameters a, b, and c are determined by fitting to experimental data. Note that $E_{\mathrm{x}}^{\mathrm{HF}}$ depends on the occupied orbitals and has the expression

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_\sigma}\iint\frac{\phi_{i\sigma}^*(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2. \tag{3.18}$$

The HF exchange energy has exactly the same form as the exact-exchange energy given in Eq. (4.1). The notation "HF" is there to specify that the orbitals in such hybrid approximations are optimized in the HF way and not in the OEP way (see Section 4.1), i.e. with a nonlocal HF exchange potential instead of a local one (see Exercise 16). This constitutes a slight extension of the usual KS method[14], sometimes referred to as *generalized Kohn-Sham* [42].[15] The main benefit of adding a fraction of HF exchange is to decrease the *self-interaction error* in the exchange functional which tends to favor too much delocalized electron densities over localized

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[14]In fact, the possibility of combining a nonlocal Hartree-Fock potential with a local correlation potential was mentioned already in 1965 in the paper by Kohn and Sham [10].

[15]Specifically, for hybrid approximations, the equation giving the ground-state energy, Eq. (1.22), now becomes: $E_0 = \min_\Phi\left\{\langle\Phi|\hat{T} + \hat{V}_{\mathrm{ne}}|\Phi\rangle + E_{\mathrm{H}}[n_\Phi] + aE_{\mathrm{x}}^{\mathrm{HF}}[\Phi] + \Delta E_{\mathrm{xc}}^{\mathrm{DFA}}[n_\Phi]\right\}$ where $E_{\mathrm{x}}^{\mathrm{HF}}[\Phi]$ is the HF exchange energy viewed as a functional of Φ and $\Delta E_{\mathrm{xc}}^{\mathrm{DFA}}[n]$ is the remaining (semilocal) exchange-correlation density-functional approximation.

electron densities. The most famous and widely used three-parameter hybrid approximation is B3LYP [43], which uses the B88 exchange functional and the LYP correlation functional, and the parameters $a = 0.20$, $b = 0.72$, and $c = 0.81$.

In 1996, Becke proposed a simpler one-parameter hybrid (1H) approximation [44]

$$E_{\text{xc}}^{\text{1H}} = a\, E_{\text{x}}^{\text{HF}} + (1 - a)\, E_{\text{x}}^{\text{DFA}} + E_{\text{c}}^{\text{DFA}}, \tag{3.19}$$

where $E_{\text{x}}^{\text{DFA}}$ and $E_{\text{c}}^{\text{DFA}}$ can be any (semilocal) density-functional approximations (DFA), and the fraction a of HF exchange has to be determined. The fraction of HF exchange should be small enough to keep the compensation of errors usually occurring between the approximate semilocal exchange functional $E_{\text{x}}^{\text{DFA}}$ and the approximate semilocal correlation functional $E_{\text{c}}^{\text{DFA}}$. Fits to experimental data often give an optimal parameter a around 0.25. A rationale has also been proposed in favor of this value [45]. For example, PBE0 [46, 47] is a popular one-parameter hybrid approximation which uses $a = 0.25$ and the PBE exchange and correlation functionals.

A strategy that has been sometimes used to construct approximations of the form of Eq. (3.19) is to employ parameterized flexible functions for $E_{\text{x}}^{\text{DFA}}$ and $E_{\text{c}}^{\text{DFA}}$, and systematically optimize all the parameters (including the fraction a of HF exchange) on large sets of physicochemical properties of molecular systems. For example, the Becke 97 (B97) exchange-correlation functional [48] is a hybrid GGA approximation containing 13 parameters optimized on atomic exchange and correlation energies, atomization energies, ionization potentials, and proton affinities. Another example is the so-called family of "Minnesota" functionals, and in particular the M06 exchange-correlation functional [49] which is a hybrid meta-GGA approximation containing 36 parameters optimized on a very large set of diverse physicochemical properties concerning main-group thermochemistry, reaction barrier heights, noncovalent interactions, electronic spectroscopy, and transition metal bonding.

Exercise 16 : Show that the functional derivative of E_{x}^{HF} with respect to $\phi_{i\sigma}^*(\mathbf{r})$ gives

$$\frac{\delta E_{\text{x}}^{\text{HF}}}{\delta \phi_{i\sigma}^*(\mathbf{r})} = \int v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}, \mathbf{r}')\phi_{i\sigma}(\mathbf{r}')\mathrm{d}\mathbf{r}', \tag{3.20}$$

where $v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}, \mathbf{r}')$ is the nonlocal HF exchange potential

$$v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}, \mathbf{r}') = -\sum_{j=1}^{N_\sigma} \frac{\phi_{j\sigma}(\mathbf{r})\phi_{j\sigma}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{3.21}$$

Show also that Eq. (3.20) can be reformulated in terms of a local HF exchange potential $v_{\text{x},i\sigma}^{\text{HF}}(\mathbf{r})$ depending on each orbital it acts on.

3.5 Double-hybrid approximations

In 2006, Grimme [50] introduced a two-parameter double-hybrid (2DH) approximation

$$E_{\text{xc}}^{\text{2DH}} = a_{\text{x}}\, E_{\text{x}}^{\text{HF}} + (1 - a_{\text{x}})\, E_{\text{x}}^{\text{DFA}} + (1 - a_{\text{c}})E_{\text{c}}^{\text{DFA}} + a_{\text{c}}E_{\text{c}}^{\text{MP2}}, \tag{3.22}$$

mixing a fraction a_{x} of the HF exchange energy with a semilocal exchange DFA, and a fraction a_{c} of the second-order Møller-Plesset (MP2) correlation energy $E_{\text{c}}^{\text{MP2}}$ with a semilocal correlation

DFA. In Eq. (3.22), the first three terms are first calculated in self-consistent manner, and then the last term $E_{\rm c}^{\rm MP2}$ is added perturbatively using the orbitals determined in the first step. The expression of $E_{\rm c}^{\rm MP2}$ is

$$E_{\rm c}^{\rm MP2} = -\frac{1}{4} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \frac{|\langle \psi_i \psi_j || \psi_a \psi_b \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \tag{3.23}$$

where i, j and a, b run over occupied and virtual spin orbitals, respectively (there is a total of $2M$ spin orbitals for M spatial basis functions), ε_k are spin orbital energies, and $\langle \psi_i \psi_j || \psi_a \psi_b \rangle = \langle \psi_i \psi_j | \psi_a \psi_b \rangle - \langle \psi_i \psi_j | \psi_b \psi_a \rangle$ are antisymmetrized two-electron integrals with (in physicists' notation)

$$\langle \psi_p \psi_q | \psi_r \psi_s \rangle = \iint \frac{\psi_p^*(\mathbf{x}_1) \psi_q^*(\mathbf{x}_2) \psi_r(\mathbf{x}_1) \psi_s(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2. \tag{3.24}$$

The presence of nonlocal MP2 correlation allows one to use a larger fraction of nonlocal HF exchange. For example, Grimme proposed the B2-PLYP approximation which uses the B88 exchange and LYP correlation functionals, and the parameters $a_{\rm x} = 0.53$ and $a_{\rm c} = 0.27$ optimized on experimental heats of formation of a set of molecules.

In 2011, Sharkas, Toulouse, and Savin [51] showed how the double-hybrid approximations can be rigorously reformulated using the adiabatic-connection formalism, which leads to a one-parameter double-hybrid (1DH) approximation

$$E_{\rm xc}^{\rm 1DH} = \lambda\, E_{\rm x}^{\rm HF} + (1-\lambda)\, E_{\rm x}^{\rm DFA} + (1-\lambda^2) E_{\rm c}^{\rm DFA} + \lambda^2 E_{\rm c}^{\rm MP2}, \tag{3.25}$$

where the fraction HF exchange $a_{\rm x} = \lambda$ is now connected to the fraction of MP2 correlation $a_{\rm c} = \lambda^2$. It turns out that using $a_{\rm x} = \lambda = 0.53$ nearly reproduces the parameter $a_{\rm c} = \lambda^2 = 0.28 \approx 0.27$ independently optimized in Eq. (3.22). Likewise, Fromager [52] proposed a rigorous formulation of the two-parameter double-hybrid approximations.

The double-hybrid approximations are examples of correlation functionals depending on virtual orbitals. Another example of a correlation functional depending on virtual orbitals is the random-phase approximation (RPA), which goes beyond second order and has been the subject of intensive developments since the 2000s.

3.6 Range-separated hybrid approximations

Based on earlier ideas of Savin [53], in 2001, Iikura, Tsuneda, Yanai, and Hirao [54] proposed a long-range correction (LC) scheme

$$\boxed{E_{\rm xc}^{\rm LC} = E_{\rm x}^{\rm lr, HF} + E_{\rm x}^{\rm sr, DFA} + E_{\rm c}^{\rm DFA},} \tag{3.26}$$

where $E_{\rm x}^{\rm lr, HF}$ is the HF exchange energy for a long-range electron-electron interaction $w_{\rm ee}^{\rm lr}(r_{12}) = \mathrm{erf}(\mu r_{12})/r_{12}$ (where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectronic distance and erf is the error function, see Exercise 17)

$$E_{\rm x}^{\rm lr, HF} = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \iint \phi_{i\sigma}^*(\mathbf{r}_1) \phi_{j\sigma}(\mathbf{r}_1) \phi_{j\sigma}^*(\mathbf{r}_2) \phi_{i\sigma}(\mathbf{r}_2) w_{\rm ee}^{\rm lr}(r_{12}) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \tag{3.27}$$

and $E_{\rm x}^{\rm sr, DFA}$ is the DFA exchange energy for the complementary short-range interaction $w_{\rm ee}^{\rm sr}(r_{12}) = 1/r_{12} - w_{\rm ee}^{\rm lr}(r_{12})$. Similarly to the hybrid approximations of Section 3.4, the introduction of a

fraction of long-range HF exchange reduces the self-interaction error (see, e.g., Ref. [55]) . In addition, the short-range exchange part is easier to approximate with semilocal DFA. In particular, the $-1/r$ asymptotic behavior of the exchange potential [Eq. (3.6)], which is difficult to satisfy with DFAs, does not apply anymore to the short-range exchange potential. The parameter μ (also sometimes denoted as ω) in the error function controls the range of the separation and must be chosen, e.g. by fitting to experimental data. In practice, a value around $\mu \approx 0.3 - 0.5$ bohr^{-1} is often found to be optimal. A popular example of such LC approximations is LC-ωPBE [56] which uses a short-range version of the PBE exchange functional, as well as the standard PBE correlation functional. Note that the LC scheme has also been referred to as the range-separated hybrid exchange (RSHX) scheme [57].

Exercise 17 : Using the definition of the error function

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \mathrm{d}t, \tag{3.28}$$

show that $\text{erf}(x) \underset{x \to 0}{\sim} (2/\sqrt{\pi})x$ and $\text{erf}(x) \xrightarrow[x \to +\infty]{} 1$. Draw then the form of the long-range interaction $\text{erf}(\mu r)/r$ as a function r for different values of the range-separation parameter: $\mu = 0$, $\mu = 1$, and $\mu \to +\infty$.

In 2004, Yanai, Tew, and Handy [58], introduced a more flexible scheme called the Coulomb-attenuating method (CAM) [58] in which fractions of HF exchange are added at both short and long range

$$E_{\text{xc}}^{\text{CAM}} = a\, E_{\text{x}}^{\text{sr,HF}} + b\, E_{\text{x}}^{\text{lr,HF}} + (1-a)\, E_{\text{x}}^{\text{sr,DFA}} + (1-b)\, E_{\text{x}}^{\text{lr,DFA}} + E_{\text{c}}^{\text{DFA}}, \tag{3.29}$$

where $E_{\text{x}}^{\text{sr,HF}}$ is the HF exchange energy for the short-range interaction $w_{\text{ee}}^{\text{sr}}(r_{12})$ and $E_{\text{x}}^{\text{lr,DFA}}$ is the DFA exchange energy for the long-range interaction $w_{\text{ee}}^{\text{lr}}(r_{12})$. The reintroduction of HF exchange at short range improves thermodynamic properties such as atomization energies. According to this scheme, the authors proposed the CAM-B3LYP approximation which uses short- and long-range versions of the B88 exchange functional, the same correlation functional used in B3LYP (i.e., $0.81\, E_{\text{c}}^{\text{LYP}} + 0.19\, E_{\text{c}}^{\text{LDA}}$), and optimized parameters $a = 0.19$, $b = 0.65$, and $\mu = 0.33$ bohr^{-1}. Another example in this class of approximations is the ωB97X exchange-correlation functional [59] which is based on the B97 exchange-correlation functional with re-optimized parameters, and uses $a = 0.16$, $b = 1$, and $\mu = 0.3$ bohr^{-1}. Another functional that can be considered as part of this class of approximations is the Heyd-Scuseria-Ernzerhof (HSE) exchange-correlation functional [60], which uses the parameters $a = 0.25$, $b = 0$ (i.e. no long-range HF exchange), and $\mu = 0.15$ bohr^{-1}, with a long-range version of the PBE exchange correlation functional and the standard PBE correlation functional. The absence of HF exchange at very long range makes this approximation particularly useful for solids.

In 2005, Ángyán, Gerber, Savin, and Toulouse [61] introduced the range-separated hybrid (RSH) scheme

$$E_{\text{xc}}^{\text{RSH}} = E_{\text{x}}^{\text{lr,HF}} + E_{\text{x}}^{\text{sr,DFA}} + E_{\text{c}}^{\text{sr,DFA}}, \tag{3.30}$$

which is very similar to the LC scheme except that it uses a short-range correlation DFA, $E_{\text{c}}^{\text{sr,DFA}}$, instead of a standard correlation DFA, $E_{\text{c}}^{\text{DFA}}$. The idea is that semilocal DFAs are not good for the long-range correlation energy, and so we may as well drop the long-range part of the correlation DFA. The long-range correlation energy can then be added in a second step, e.g., at the second-order level which defines the RSH+MP2 scheme [61]

$$E_{\text{xc}}^{\text{RSH+MP2}} = E_{\text{x}}^{\text{lr,HF}} + E_{\text{x}}^{\text{sr,DFA}} + E_{\text{c}}^{\text{sr,DFA}} + E_{\text{c}}^{\text{lr,MP2}}, \tag{3.31}$$

where $E_c^{\text{lr,MP2}}$ is the MP2 correlation energy calculated with long-range two-electron integrals and the previously calculated RSH orbitals. The RSH+MP2 scheme is thus similar to the double-hybrid approximations of Section 3.5 but with range separation. One of main advantages of using a long-range MP2 correlation energy is the correct qualitative description of London dispersion interaction energies, while displaying a fast convergence with the basis size [62]. For more accurate results, one can go beyond second order by using long-range coupled-cluster [63] or random-phase approximations [64–66].

3.7 Semiempirical dispersion corrections

To explicitly account for London dispersion interactions, it has been proposed in the 2000s to add to the standard approximate functionals a semiempirical dispersion correction of the form [67–69]

$$E_{\text{disp}} = -s \sum_{\alpha < \beta} f(R_{\alpha\beta}) \frac{C_6^{\alpha\beta}}{R_{\alpha\beta}^6}, \tag{3.32}$$

where $R_{\alpha\beta}$ is the distance between each pair of atoms, $C_6^{\alpha\beta}$ is the dispersion coefficient between these atoms, $f(R_{\alpha\beta})$ is a parametrized damping function which tends to 1 at large $R_{\alpha\beta}$ and tends to zero at small $R_{\alpha\beta}$, and s is a possible scaling parameter that can be adjusted for each approximate functional. The dispersion coefficient $C_6^{\alpha\beta}$ for any pair of atoms is empirically calculated from tabulated same-atom dispersion coefficients $C_6^{\alpha\alpha}$ and/or atomic polarizabilities. This approach was named "DFT-D" by Grimme [69]. The last version of DFT-D (referred to as DFT-D3) also includes $C_8^{\alpha\beta}$ two-body terms and $C_9^{\alpha\beta\gamma}$ three-body terms [70]. There have also been various proposals to make the determination of dispersion coefficients less empirical, such as the scheme of Becke and Johnson [71] based on the exchange-hole dipole moment, the scheme of Tkatchenko and Scheffler [72] based on a Hirshfeld atomic partitioning, or the scheme of Sato and Nakai [73] based on the local-response approximation [74].

4 Some less usual orbital-dependent exchange-correlation functionals

We discuss here some exchange-correlation energy functionals explicitly depending on the KS orbitals. Since the KS orbitals are themselves functionals of the density, these exchange-correlation expressions are thus *implicit* functionals of the density (for notational simplicity, this dependence on the density will not be explicitly indicated). In fact, the hybrid, double-hybrid, and range-separated hybrid approximations of Sections 3.4, 3.5, and 3.6 already belong to this family, with the caveat that the orbitals are usually obtained with a *nonlocal* potential. In this Section, we are concerned with orbital-dependent exchange-correlation energy functionals with orbitals obtained with a local potential. These approximations tend to be more computationally involved than the approximations of the previous Section and are thus much less used.

4.1 Exact exchange

Being defined as an expectation value over a single-determinant wave function [see Eq. (1.26)], the exact exchange (EXX) energy functional can be expressed in terms of the orbitals

$$E_{\mathrm{x}} = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \iint \frac{\phi_{i\sigma}^*(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{4.1}$$

where i and j run over spatial occupied orbitals. The exchange energy in Eq. (4.1) has exactly the same form as the HF exchange [Eq. (3.18)], but the orbitals used in this expression are in general different.

Since the exact exchange energy in Eq. (4.1) is not an explicit functional of the density, the corresponding exchange potential $v_{\mathrm{x}}(\mathbf{r}) = \delta E_x/\delta n(\mathbf{r})$ cannot be calculated directly. We can however find an workable equation for $v_{\mathrm{x}}(\mathbf{r})$ by first considering the functional derivative of E_{x} with respect to the KS potential $v_{\mathrm{s}}(\mathbf{r})$ and then applying the chain rule

$$\frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\mathbf{r})} = \int \frac{\delta E_{\mathrm{x}}}{\delta n(\mathbf{r}')}\frac{\delta n(\mathbf{r}')}{\delta v_{\mathrm{s}}(\mathbf{r})}\mathrm{d}\mathbf{r}'. \tag{4.2}$$

Introducing the non-interacting KS static linear-response function $\chi_0(\mathbf{r}',\mathbf{r}) = \delta n(\mathbf{r}')/\delta v_{\mathrm{s}}(\mathbf{r})$, we can rewrite Eq. (4.2) as

$$\int v_{\mathrm{x}}(\mathbf{r}')\chi_0(\mathbf{r}',\mathbf{r})\mathrm{d}\mathbf{r}' = \frac{\delta E_{\mathrm{x}}}{\delta v_{\mathrm{s}}(\mathbf{r})}, \tag{4.3}$$

which is known as the *optimized-effective-potential* (OEP) equation for the exact-exchange potential. Explicit expressions in terms of the orbitals can be derived for $\delta E_{\mathrm{x}}/\delta v_{\mathrm{s}}(\mathbf{r})$ and $\chi_0(\mathbf{r}',\mathbf{r})$.

Exercise 18 : Using first-order perturbation theory on the KS system, show that

$$\frac{\delta\phi_{i\sigma}(\mathbf{r}')}{\delta v_{\mathrm{s}}(\mathbf{r})} = -\sum_{\substack{p=1 \\ p\neq i}}^{M} \frac{\phi_{p\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}{\varepsilon_{p\sigma} - \varepsilon_{i\sigma}}\phi_{p\sigma}(\mathbf{r}'). \tag{4.4}$$

where the sum is over all spatial orbitals p different from orbital i but of the same spin.

Show then that the expression of $\chi_0(\mathbf{r}', \mathbf{r})$ is

$$\chi_0(\mathbf{r}', \mathbf{r}) = - \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{M} \frac{\phi_{i\sigma}^*(\mathbf{r}')\phi_{a\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r})\phi_{a\sigma}(\mathbf{r}')}{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}} + \text{ c.c. }, \qquad (4.5)$$

where a runs over virtual spatial orbitals and c.c. stands for the complex conjugate. Finally, by using the definition of E_x in terms of the orbitals, show that

$$\frac{\delta E_\text{x}}{\delta v_\text{s}(\mathbf{r})} = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{M} (\phi_{a\sigma}\phi_{j\sigma}|\phi_{j\sigma}\phi_{i\sigma}) \frac{\phi_{a\sigma}(\mathbf{r})\phi_{i\sigma}^*(\mathbf{r})}{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}} + \text{ c.c. }, \qquad (4.6)$$

where $(\phi_{a\sigma}\phi_{j\sigma}|\phi_{j\sigma}\phi_{i\sigma})$ are the two-electron integrals [see Eq. (1.48) for the definition] in the basis of the KS spatial orbitals.

Applying this OEP method with the EXX energy (and no correlation energy functional) is an old idea [75, 76], but reasonable efficient calculations for molecules have been possible only relatively recently [77, 78]. The EXX occupied orbitals turn out to be very similar to the HF occupied orbitals, and thus the EXX ground-state properties are also similar to the HF ones. However, the EXX virtual orbitals tend to be much less diffuse than the HF virtual orbitals, and may be more adapted for calculating excited-state properties.

4.2 Second-order Görling-Levy perturbation theory

In 1993, Görling and Levy [79, 80] developed a perturbation theory in terms of the coupling constant λ of the adiabatic connection (Section 2.1.2) which provides an explicit orbital-dependent second-order approximation for the correlation energy functional. The Hamiltonian along the adiabatic connection [Eq. (2.18)] can be written as

$$\begin{aligned}
\hat{H}^\lambda &= \hat{T} + \lambda\hat{W}_\text{ee} + \hat{V}^\lambda \\
&= \hat{H}_\text{s} + \lambda(\hat{W}_\text{ee} - \hat{V}_\text{Hx}) - \hat{V}_\text{c}^\lambda,
\end{aligned} \qquad (4.7)$$

where $\hat{H}_\text{s} = \hat{H}^{\lambda=0} = \hat{T} + \hat{V}_\text{s}$ is the KS non-interacting reference Hamiltonian (which will be assumed to have a nondegenerate ground state). Equation (4.7) was obtained by decomposing the potential operator keeping the density constant as $\hat{V}^\lambda = \hat{V}_\text{s} - \lambda\hat{V}_\text{Hx} - \hat{V}_\text{c}^\lambda$ where $\hat{V}_\text{s} = \hat{V}^{\lambda=0}$ is the KS potential operator, $\lambda\hat{V}_\text{Hx}$ is the Hartree-exchange potential operator which is linear in λ, and $\hat{V}_\text{c}^\lambda$ is the correlation potential which starts at second order in λ, i.e. $\hat{V}_\text{c}^\lambda = \lambda^2\hat{V}_\text{c}^{(2)} + \cdots$. Using a complete set of orthonormal eigenfunctions Φ_n and eigenvalues $\mathcal{E}_n$ of the KS Hamiltonian, $\hat{H}_\text{s}|\Phi_n\rangle = \mathcal{E}_n|\Phi_n\rangle$, the normalized ground-state wave function of the Hamiltonian $\hat{H}^\lambda$ can be expanded as $\Psi^\lambda = \Phi + \lambda\Psi^{(1)} + \cdots$ where $\Phi = \Phi_0$ is the ground-state KS single-determinant wave function and $\Psi^{(1)}$ is its first-order correction given by

$$|\Psi^{(1)}\rangle = - \sum_{n\neq 0} \frac{\langle\Phi_n|\hat{W}_\text{ee} - \hat{V}_\text{Hx}|\Phi\rangle}{\mathcal{E}_n - \mathcal{E}_0} |\Phi_n\rangle. \qquad (4.8)$$

Using the expression in Eq. (2.23), the correlation energy functional can also be expanded in powers of λ

$$\begin{aligned}
E_\text{c}^\lambda &= \langle\Psi^\lambda|\hat{T} + \lambda\hat{W}_\text{ee}|\Psi^\lambda\rangle - \langle\Phi|\hat{T} + \lambda\hat{W}_\text{ee}|\Phi\rangle. \\
&= E_\text{c}^{(0)} + \lambda E_\text{c}^{(1)} + \lambda^2 E_\text{c}^{(2)} + \cdots.
\end{aligned} \qquad (4.9)$$

Since $\Psi^{\lambda=0} = \Phi$, the zeroth-order term vanishes: $E_c^{(0)} = 0$. Using the expression of the first-order derivative of E_c^λ with respect to λ in Eq. (2.24), i.e. $\partial E_c^\lambda / \partial \lambda = \langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \rangle - \langle \Phi | \hat{W}_{ee} | \Phi \rangle$, we find that the first-order term vanishes as well: $E_c^{(1)} = 0$. The second-order term corresponds to the second-order Görling-Levy (GL2) correlation energy and is given by

$$E_c^{(2)} = E_c^{\mathrm{GL2}} = \langle \Phi | \hat{W}_{ee} | \Psi^{(1)} \rangle = \langle \Phi | \hat{W}_{ee} - \hat{V}_{\mathrm{Hx}} | \Psi^{(1)} \rangle, \tag{4.10}$$

where the second equality comes the fact that $\langle \Phi | \hat{V}_{\mathrm{Hx}} | \Psi^{(1)} \rangle = 0$ since it is the derivative with respect to λ at $\lambda = 0$ of $\langle \Psi^\lambda | \hat{V}_{\mathrm{Hx}} | \Psi^\lambda \rangle = \int v_{\mathrm{Hx}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}\mathbf{r}$ which does not depend on λ by virtue of the fact the density $n(\mathbf{r})$ is constant along the adiabatic connection. Using the last expression in Eq. (4.10) allows one to express the GL2 correlation energy as

$$E_c^{\mathrm{GL2}} = - \sum_{n \neq 0} \frac{|\langle \Phi | \hat{W}_{ee} - \hat{V}_{\mathrm{Hx}} | \Phi_n \rangle|^2}{\mathcal{E}_n - \mathcal{E}_0}. \tag{4.11}$$

It is instructive to decompose the GL2 correlation energy as

$$E_c^{\mathrm{GL2}} = E_c^{\mathrm{MP2}} + E_c^{\mathrm{S}}, \tag{4.12}$$

where E_c^{MP2} is a MP2-like correlation energy evaluated with KS spin orbitals

$$E_c^{\mathrm{MP2}} = -\frac{1}{4} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \frac{|\langle \psi_i \psi_j || \psi_a \psi_b \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \tag{4.13}$$

and E_c^{S} is the contribution coming from the single excitations (which does not vanish here, contrary to HF-based MP2 perturbation theory)

$$E_c^{\mathrm{S}} = - \sum_{i=1}^{N} \sum_{a=N+1}^{2M} \frac{|\langle \psi_i | \hat{V}_x^{\mathrm{HF}} - \hat{V}_x | \psi_a \rangle|^2}{\varepsilon_a - \varepsilon_i}, \tag{4.14}$$

involving the difference between the integrals over the nonlocal HF exchange potential $\langle \psi_i | \hat{V}_x^{\mathrm{HF}} | \psi_a \rangle = -\sum_{j=1}^{N} \langle \psi_i \psi_j | \psi_j \psi_a \rangle$ and over the local KS exchange potential $\langle \psi_i | \hat{V}_x | \psi_a \rangle = \int \psi_i^*(\mathbf{x}) v_x(\mathbf{r}) \psi_a(\mathbf{x}) \mathrm{d}\mathbf{x}$.

Exercise 19 : Derive Eqs. (4.12)-(4.14).

Calculations of the GL2 correlation energy using either a non-self-consistent post-EXX implementation or a more complicated OEP self-consistent procedure have been tested (see, e.g., Refs. [81–83]) but the results are often disappointing. It is preferable to go beyond second order with the random-phase approximation in the adiabatic-connection fluctuation-dissipation approach.

4.3   Adiabatic-connection fluctuation-dissipation approach

4.3.1   Exact adiabatic-connection fluctuation-dissipation expression

Using the *adiabatic-connection* formula of Eq. (2.25), the correlation energy functional can be written as

$$\begin{aligned} E_c &= \int_0^1 \mathrm{d}\lambda \, \langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \rangle - \langle \Phi | \hat{W}_{ee} | \Phi \rangle \\ &= \frac{1}{2} \int_0^1 \mathrm{d}\lambda \iint \frac{n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \end{aligned} \tag{4.15}$$

where $n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = n_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) - n_{2,\mathrm{KS}}(\mathbf{r}_1, \mathbf{r}_2)$ is the correlation part of the pair density along the adiabatic connection. The pair density $n_2^\lambda(\mathbf{r}_1, \mathbf{r}_2)$ can be expressed with the pair-density operator $\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2)$ [Eq. (A.10)]

$$n_2^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \langle \Psi^\lambda | \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) | \Psi^\lambda \rangle = \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle - \delta(\mathbf{r}_1 - \mathbf{r}_2)\langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle, \quad (4.16)$$

where $\hat{n}(\mathbf{r})$ is the density operator [Eq. (A.8)], and the KS pair density $n_{2,\mathrm{KS}}(\mathbf{r}_1, \mathbf{r}_2)$ simply corresponds to the case $\lambda = 0$

$$n_{2,\mathrm{KS}}(\mathbf{r}_1, \mathbf{r}_2) = n_2^{\lambda=0}(\mathbf{r}_1, \mathbf{r}_2) = \langle \Phi | \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) | \Phi \rangle - \delta(\mathbf{r}_1 - \mathbf{r}_2)\langle \Phi | \hat{n}(\mathbf{r}_1) | \Phi \rangle, \quad (4.17)$$

Since the density does not change with λ, i.e. $\langle \Psi^\lambda | \hat{n}(\mathbf{r}) | \Psi^\lambda \rangle = \langle \Phi | \hat{n}(\mathbf{r}) | \Phi \rangle = n(\mathbf{r})$, the correlation pair density needed in Eq. (4.15) can thus be expressed as

$$n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle - \langle \Phi | \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) | \Phi \rangle. \quad (4.18)$$

We would like to calculate $n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)$ without having to calculate the complicated many-body wave function Ψ^λ. For this, we consider the (time-ordered) linear-response function along the adiabatic connection[16]

$$\begin{aligned} i\chi_\lambda(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \langle \Psi^\lambda | T[\hat{n}^\lambda(\mathbf{r}_1 t_1)\hat{n}^\lambda(\mathbf{r}_2 t_2)] | \Psi^\lambda \rangle - \langle \Psi^\lambda | \hat{n}^\lambda(\mathbf{r}_1 t_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}^\lambda(\mathbf{r}_2 t_2) | \Psi^\lambda \rangle \\ &= \langle \Psi^\lambda | T[\hat{n}^\lambda(\mathbf{r}_1 t_1)\hat{n}^\lambda(\mathbf{r}_2 t_2)] | \Psi^\lambda \rangle - \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle, \quad (4.19) \end{aligned}$$

where $\hat{n}^\lambda(\mathbf{r}t) = e^{i\hat{H}^\lambda t}\hat{n}(\mathbf{r})e^{-i\hat{H}^\lambda t}$ is the density operator in the Heisenberg picture, and T is the Wick time-ordering operator which orders the operators with larger times on the left, i.e. $T[\hat{n}^\lambda(\mathbf{r}_1 t_1)\hat{n}^\lambda(\mathbf{r}_2 t_2)] = \theta(t_1 - t_2)\hat{n}^\lambda(\mathbf{r}_1 t_1)\hat{n}^\lambda(\mathbf{r}_2 t_2) + \theta(t_2 - t_1)\hat{n}^\lambda(\mathbf{r}_2 t_2)\hat{n}^\lambda(\mathbf{r}_1 t_1)$ where θ is the Heaviside step function. Due to time translation invariance, the linear-response function depends in fact only on $\tau = t_1 - t_2$. If we set $t_2 = t_1 + 0^+$ where 0^+ is an infinitesimal positive shift, i.e. $\tau = 0^-$, we get

$$i\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau = 0^-) = \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle - \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle, \quad (4.20)$$

and, similarly, for the non-interacting KS linear-response function corresponding to the case $\lambda = 0$

$$i\chi_0(\mathbf{r}_1, \mathbf{r}_2; \tau = 0^-) = \langle \Phi | \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) | \Phi \rangle - \langle \Phi | \hat{n}(\mathbf{r}_1) | \Phi \rangle \langle \Phi | \hat{n}(\mathbf{r}_2) | \Phi \rangle. \quad (4.21)$$

We can thus express $n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)$ as the difference between the zero-time linear-response functions

$$n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = i[\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau = 0^-) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; \tau = 0^-)]. \quad (4.22)$$

Alternatively, Eq (4.22) can be rewritten in terms of the Fourier transforms of the linear-response functions, using the definition $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau) = \int_{-\infty}^{+\infty} \mathrm{d}\omega/(2\pi)\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)e^{-i\omega\tau}$,

$$\boxed{n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = -\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{i\omega 0^+} [\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega)],} \quad (4.23)$$

which is known as the (zero-temperature) *fluctuation-dissipation theorem*. This theorem relates ground-state correlations in the time-independent system, $n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2)$, to the linear response of the system due to a time-dependent external perturbation, $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$.

---

[16]We choose to work with the *time-ordered* linear-response function (or polarization propagator) which is used in many-body Green function theory. In linear-response time-dependent DFT, one normally uses the *retarded* linear-response function $i\chi_\lambda^\mathrm{R}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \theta(t_1 - t_2)\langle \Psi^\lambda | [\hat{n}^\lambda(\mathbf{r}_1 t_1), \hat{n}^\lambda(\mathbf{r}_2 t_2)] | \Psi^\lambda \rangle - \langle \Psi^\lambda | \hat{n}^\lambda(\mathbf{r}_1 t_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}^\lambda(\mathbf{r}_2 t_2) | \Psi^\lambda \rangle$. Their Fourier transforms are related by $\chi_\lambda^\mathrm{R}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$ for $\omega \geq 0$, and $\chi_\lambda^\mathrm{R}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)^*$ for $\omega < 0$. One should be careful to be consistent when switching between these related quantities. For example, the fluctuation-dissipation theorem of Eq. (4.23) takes a slightly different form in terms of $\chi_\lambda^\mathrm{R}(\mathbf{r}_1, \mathbf{r}_2; \omega)$.

Exercise 20 : Show that the linear-response function can be rewritten as

$$
\begin{aligned}
i\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau) = \ & \theta(\tau) \sum_{n \neq 0} \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle e^{-i\omega_n^\lambda \tau} \\
& + \theta(-\tau) \sum_{n \neq 0} \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle e^{i\omega_n^\lambda \tau}, \quad (4.24)
\end{aligned}
$$

where the sums are over all eigenstates Ψ_n^λ of the Hamiltonian $\hat{H}^\lambda$, i.e. $\hat{H}^\lambda | \Psi_n^\lambda \rangle = E_n^\lambda | \Psi_n^\lambda \rangle$, except the ground state $\Psi^\lambda = \Psi_0^\lambda$, and $\omega_n^\lambda = E_n^\lambda - E_0^\lambda$ are the corresponding excitation energies. Show then that the Fourier transform of $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau)$ is

$$
\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{n \neq 0} \frac{\langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle}{\omega - \omega_n^\lambda + i0^+} - \frac{\langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle}{\omega + \omega_n^\lambda - i0^+}, \quad (4.25)
$$

which is called the Lehmann representation of χ_λ. Finally, check directly Eq. (4.23) by performing the integration over ω using the residue theorem.

Combining Eqs. (4.15) and (4.23), we finally arrive the exact *adiabatic-connection fluctuation-dissipation* (ACFD) formula for the correlation energy

$$
E_c = -\frac{1}{2} \int_0^1 \mathrm{d}\lambda \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{i\omega 0^+} \iint \frac{\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2. \quad (4.26)
$$

The usefulness of the ACFD formula is due to the fact there are practical ways of directly calculating $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$ without having to calculate the many-body wave function Ψ^λ. In linear-response time-dependent DFT, one can find a Dyson-like equation for $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$

$$
\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) = \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) + \iint \chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) f_{\mathrm{Hxc}}^\lambda(\mathbf{r}_3, \mathbf{r}_4; \omega) \chi_\lambda(\mathbf{r}_4, \mathbf{r}_2; \omega) \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4, \quad (4.27)
$$

where $f_{\mathrm{Hxc}}^\lambda(\mathbf{r}_3, \mathbf{r}_4; \omega)$ is the *Hartree-exchange-correlation kernel* associated to the Hamiltonian $\hat{H}^\lambda$. Here, Eq. (4.27) will be considered as the definition for f_{Hxc}^λ. In principle, the exact correlation energy can be obtained with Eqs. (4.26) and (4.27). In practice, however, we need to use an approximation for f_{Hxc}^λ.

4.3.2 Direct random-phase approximation

In the *direct random-phase approximation* (dRPA, also just referred to as RPA, or sometimes as time-dependent Hartree), only the Hartree part of the kernel, which is linear in λ and independent from ω, is retained

$$
f_{\mathrm{Hxc}}^\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) \approx f_{\mathrm{H}}^\lambda(\mathbf{r}_1, \mathbf{r}_2) = \lambda w_{\mathrm{ee}}(\mathbf{r}_1, \mathbf{r}_2), \quad (4.28)
$$

where $w_{\mathrm{ee}}(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ is the Coulomb interaction, and the corresponding dRPA linear-response function then satisfies the equation

$$
\chi_\lambda^{\mathrm{dRPA}}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) + \lambda \iint \chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) w_{\mathrm{ee}}(\mathbf{r}_3, \mathbf{r}_4) \chi_\lambda^{\mathrm{dRPA}}(\mathbf{r}_4, \mathbf{r}_2; \omega) \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4. \quad (4.29)
$$

The physical contents of this approximation can be seen by iterating Eq. (4.29) which generates an infinite series

$$\chi_\lambda^{\text{dRPA}}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) + \lambda \iint \chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) w_{\text{ee}}(\mathbf{r}_3, \mathbf{r}_4) \chi_0(\mathbf{r}_4, \mathbf{r}_2; \omega) \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4$$

$$+\lambda^2 \iiiint \chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) w_{\text{ee}}(\mathbf{r}_3, \mathbf{r}_4) \chi_0(\mathbf{r}_4, \mathbf{r}_5; \omega) w_{\text{ee}}(\mathbf{r}_5, \mathbf{r}_6) \chi_0(\mathbf{r}_6, \mathbf{r}_2; \omega) \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 \mathrm{d}\mathbf{r}_5 \mathrm{d}\mathbf{r}_6 + \cdots ,$$
$$(4.30)$$

which, after plugging it into Eq. (4.26), leads to the dRPA correlation energy as the following perturbation expansion

$$E_{\text{c}}^{\text{dRPA}} = -\frac{1}{2} \int_0^1 \mathrm{d}\lambda \int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{i\omega 0^+} \left[\lambda \iiiint \frac{\chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) \chi_0(\mathbf{r}_4, \mathbf{r}_2; \omega)}{|\mathbf{r}_1 - \mathbf{r}_2| \, |\mathbf{r}_3 - \mathbf{r}_4|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 \right.$$

$$\left. +\lambda^2 \iiiiiint \frac{\chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) \chi_0(\mathbf{r}_4, \mathbf{r}_5; \omega) \chi_0(\mathbf{r}_6, \mathbf{r}_2; \omega)}{|\mathbf{r}_1 - \mathbf{r}_2| \, |\mathbf{r}_3 - \mathbf{r}_4| \, |\mathbf{r}_5 - \mathbf{r}_6|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 \mathrm{d}\mathbf{r}_5 \mathrm{d}\mathbf{r}_6 + \cdots \right]. \quad (4.31)$$

Using now the Lehmann representation [Eq. (4.25)] of the KS linear-response function in terms of the KS orbitals and their energies

$$\chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{M} \left[\frac{\phi_{i\sigma}^*(\mathbf{r}_1)\phi_{a\sigma}(\mathbf{r}_1)\phi_{a\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{\omega - (\varepsilon_a - \varepsilon_i) + i0^+} - \frac{\phi_{i\sigma}^*(\mathbf{r}_2)\phi_{a\sigma}(\mathbf{r}_2)\phi_{a\sigma}^*(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_1)}{\omega + (\varepsilon_a - \varepsilon_i) - i0^+} \right],$$
$$(4.32)$$

one can obtain, after quite some work,

$$E_{\text{c}}^{\text{dRPA}} = -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \frac{|\langle \psi_i \psi_j | \psi_a \psi_b \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \sum_{c=N+1}^{2M} \frac{\langle \psi_i \psi_j | \psi_a \psi_b \rangle \langle \psi_j \psi_k | \psi_b \psi_c \rangle \langle \psi_k \psi_i | \psi_c \psi_a \rangle}{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)(\varepsilon_a + \varepsilon_c - \varepsilon_i - \varepsilon_k)} + \cdots .$$
$$(4.33)$$

The dRPA correlation energy is the sum of all the direct terms (i.e., no exchange terms) of the Møller-Plesset or Görling-Levy perturbation expansion. Of course, Eq. (4.33) is not the way to calculate the dRPA correlation energy in practice. To do this, we need to solve the Dyson equation [Eq. (4.29)] without explicitly expanding in powers of λ.

4.3.3 Practical calculation in a spin orbital basis

For solving Eq. (4.29) in a spin orbital basis, it is more convenient to introduce the four-point (time-ordered) linear-response function

$$i\chi_\lambda(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \tau = t_1 - t_2) = \langle \Psi^\lambda | T[\hat{n}_1^\lambda(\mathbf{x}_1, \mathbf{x}_1'; t_1)\hat{n}_1^\lambda(\mathbf{x}_2, \mathbf{x}_2'; t_2)] | \Psi^\lambda \rangle$$
$$-\langle \Psi^\lambda | \hat{n}_1^\lambda(\mathbf{x}_1, \mathbf{x}_1'; t_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}_1^\lambda(\mathbf{x}_2, \mathbf{x}_2'; t_2) | \Psi^\lambda \rangle, \quad (4.34)$$

where $\hat{n}_1^\lambda(\mathbf{x}, \mathbf{x}'; t) = e^{i\hat{H}^\lambda t}\hat{n}_1(\mathbf{x}, \mathbf{x}')e^{-i\hat{H}^\lambda t}$ is the (spin-dependent) one-electron density matrix operator in the Heisenberg picture. The Fourier transform of the linear-response function

$\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$ involved in Eq. (4.26) is just the spin-summed diagonal part of the Fourier transform of the four-point linear-response function

$$\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{\sigma_1=\uparrow,\downarrow} \sum_{\sigma_2=\uparrow,\downarrow} \chi_\lambda(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \omega). \qquad (4.35)$$

In the dRPA approximation, the four-point linear-response function is given by

$$\chi_\lambda^{\text{dRPA}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega) = \chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega)$$
$$+ \iiiint d\mathbf{x}_3 d\mathbf{x}_4 d\mathbf{x}_5 d\mathbf{x}_6 \; \chi_0(\mathbf{x}_1, \mathbf{x}_4; \mathbf{x}_1', \mathbf{x}_3; \omega) f_{\text{H}}^\lambda(\mathbf{x}_3, \mathbf{x}_6; \mathbf{x}_4, \mathbf{x}_5) \chi_\lambda^{\text{dRPA}}(\mathbf{x}_5, \mathbf{x}_2; \mathbf{x}_6, \mathbf{x}_2'; \omega), \quad (4.36)$$

with the four-point Hartree kernel $f_{\text{H}}^\lambda(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = \lambda w_{\text{ee}}(|\mathbf{r}_1 - \mathbf{r}_2|)\delta(\mathbf{x}_1 - \mathbf{x}_1')\delta(\mathbf{x}_2 - \mathbf{x}_2')$, or equivalently in terms of inverses

$$(\chi_\lambda^{\text{dRPA}})^{-1}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega) = \chi_0^{-1}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega) - f_{\text{H}}^\lambda(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'). \qquad (4.37)$$

The non-interacting four-point linear-response function can be explicitly written in terms of the KS spin orbitals and their energies

$$\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega) = \sum_{i=1}^{N} \sum_{a=N+1}^{2M} \left[\frac{\psi_i^*(\mathbf{x}_1')\psi_a(\mathbf{x}_1)\psi_a^*(\mathbf{x}_2')\psi_i(\mathbf{x}_2)}{\omega - (\varepsilon_a - \varepsilon_i) + i0^+} - \frac{\psi_i^*(\mathbf{x}_2')\psi_a(\mathbf{x}_2)\psi_a^*(\mathbf{x}_1')\psi_i(\mathbf{x}_1)}{\omega + (\varepsilon_a - \varepsilon_i) - i0^+} \right],$$
$$(4.38)$$

which can be seen as expanded in a basis, $\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega) = \sum_{p,q}[\chi_0(\omega)]_{p,q} f_p(\mathbf{x}_1, \mathbf{x}_1') f_q^*(\mathbf{x}_2', \mathbf{x}_2)$, where the basis functions are tensor products of two occupied/virtual (ov) $f_{ia}(\mathbf{x}_1, \mathbf{x}_1') = \psi_i^*(\mathbf{x}_1')\psi_a(\mathbf{x}_1)$ or two virtual/occupied (vo) spin orbitals $f_{ai}(\mathbf{x}_1, \mathbf{x}_1') = \psi_a^*(\mathbf{x}_1')\psi_i(\mathbf{x}_1)$, and the matrix of $\chi_0(\omega)$ is in fact diagonal: $[\chi_0(\omega)]_{ia,jb} = \delta_{ij}\delta_{ab}/(\omega - (\varepsilon_a - \varepsilon_i) + i0^+)$, $[\chi_0(\omega)]_{ai,bj} = \delta_{ij}\delta_{ab}/(\omega + (\varepsilon_a - \varepsilon_i) - i0^+)$, and $[\chi_0(\omega)]_{ia,bj} = [\chi_0(\omega)]_{ai,jb} = 0$. The inverse of $\chi_0(\omega)$ in this basis is, written with ov/ov, ov/vo, vo/ov, ov/ov block matrices,

$$\chi_0^{-1}(\omega) = - \left[\begin{pmatrix} \boldsymbol{\Delta\varepsilon} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Delta\varepsilon} \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right], \qquad (4.39)$$

with the diagonal matrix $\Delta\varepsilon_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$. Using Eq. (4.37), the matrix representation of the inverse of $\chi_\lambda^{\text{dRPA}}(\omega)$ can be easily find

$$(\chi_\lambda^{\text{dRPA}})^{-1}(\omega) = - \left[\begin{pmatrix} \mathbf{A}_\lambda & \mathbf{B}_\lambda \\ \mathbf{B}_\lambda^* & \mathbf{A}_\lambda^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right], \qquad (4.40)$$

with the matrices $\mathbf{A}_\lambda$ and $\mathbf{B}_\lambda$ defined by

$$(A_\lambda)_{ia,jb} = \Delta\varepsilon_{ia,jb} + \lambda\langle\psi_a\psi_j|\psi_i\psi_b\rangle, \qquad (4.41a)$$

$$(B_\lambda)_{ia,jb} = \lambda\langle\psi_a\psi_b|\psi_i\psi_j\rangle, \qquad (4.41b)$$

and it can be checked that the matrix $\mathbf{A}_\lambda$ is Hermitian [i.e., $(A_\lambda)_{jb,ia} = (A_\lambda)_{ia,jb}^*$] and the matrix $\mathbf{B}_\lambda$ is symmetric [i.e, $(B_\lambda)_{jb,ia} = (B_\lambda)_{ia,jb}$]. To calculate the inverse of the matrix in the right-hand-side of Eq. (4.40), we then consider the following generalized eigenvalue equation

$$\boxed{\begin{pmatrix} \mathbf{A}_\lambda & \mathbf{B}_\lambda \\ \mathbf{B}_\lambda^* & \mathbf{A}_\lambda^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_{n,\lambda} \\ \mathbf{Y}_{n,\lambda} \end{pmatrix} = \omega_n^\lambda \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_{n,\lambda} \\ \mathbf{Y}_{n,\lambda} \end{pmatrix},} \qquad (4.42)$$

whose solutions come in pairs: if $(\mathbf{X}_{n,\lambda}, \mathbf{Y}_{n,\lambda})$ is an eigenvector with eigenvalue ω_n^λ, then it is easy to check that $(\mathbf{Y}_{n,\lambda}^*, \mathbf{X}_{n,\lambda}^*)$ is also an eigenvector with opposite eigenvalue $-\omega_n^\lambda$. Choosing the normalization of the eigenvectors so that $\mathbf{X}_{n,\lambda}^\dagger \mathbf{X}_{m,\lambda} - \mathbf{Y}_{n,\lambda}^\dagger \mathbf{Y}_{m,\lambda} = \delta_{nm}$, the matrix $\boldsymbol{\chi}_\lambda^{\mathrm{dRPA}}(\omega)$ can be expressed as the following spectral representation

$$
\begin{aligned}
\boldsymbol{\chi}_\lambda^{\mathrm{dRPA}}(\omega) \;=\; & \sum_n \Bigg[\frac{1}{\omega - \omega_n^\lambda + i0^+} \begin{pmatrix} \mathbf{X}_{n,\lambda} \\ \mathbf{Y}_{n,\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{X}_{n,\lambda}^\dagger & \mathbf{Y}_{n,\lambda}^\dagger \end{pmatrix} \\
& - \frac{1}{\omega + \omega_n^\lambda - i0^+} \begin{pmatrix} \mathbf{Y}_{n,\lambda}^* \\ \mathbf{X}_{n,\lambda}^* \end{pmatrix} \begin{pmatrix} \mathbf{Y}_{n,\lambda}^{*\dagger} & \mathbf{X}_{n,\lambda}^{*\dagger} \end{pmatrix} \Bigg],
\end{aligned}
\tag{4.43}
$$

where the sum is over eigenvectors with positive eigenvalues. The fluctuation-dissipation theorem [Eq. (4.23)] leads to the matrix representation of the correlation part of the dRPA two-particle density matrix $\mathbf{n}_{2,\mathrm{c}}^{\lambda,\mathrm{dRPA}}$ (using contour integration in the upper half of the complex plane)

$$
\begin{aligned}
\mathbf{n}_{2,\mathrm{c}}^{\lambda,\mathrm{dRPA}} \;=\; & -\int_{-\infty}^{+\infty} \frac{\mathrm{d}\omega}{2\pi i} e^{i\omega 0^+} [\boldsymbol{\chi}_\lambda(\omega) - \boldsymbol{\chi}_0(\omega)] \\
\;=\; & \sum_n \begin{pmatrix} \mathbf{Y}_{n,\lambda}^* \mathbf{Y}_{n,\lambda}^{*\dagger} & \mathbf{Y}_{n,\lambda}^* \mathbf{X}_{n,\lambda}^{*\dagger} \\ \mathbf{X}_{n,\lambda}^* \mathbf{Y}_{n,\lambda}^{*\dagger} & \mathbf{X}_{n,\lambda}^* \mathbf{X}_{n,\lambda}^{*\dagger} \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix},
\end{aligned}
\tag{4.44}
$$

the simple contribution coming from $\boldsymbol{\chi}_0(\omega)$ resulting from its diagonal form, and the dRPA correlation energy has then the following expression

$$
\begin{aligned}
E_\mathrm{c}^{\mathrm{dRPA}} \;=\; & \frac{1}{2} \int_0^1 \mathrm{d}\lambda \sum_{i=1}^N \sum_{j=1}^N \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \sum_n \Bigg\{ \langle \psi_i \psi_b | \psi_a \psi_j \rangle (Y_{n,\lambda})_{ia}^* (Y_{n,\lambda})_{jb} \\
& + \langle \psi_i \psi_j | \psi_a \psi_b \rangle (Y_{n,\lambda})_{ia}^* (X_{n,\lambda})_{jb} + \langle \psi_a \psi_b | \psi_i \psi_j \rangle (X_{n,\lambda})_{ia}^* (Y_{n,\lambda})_{jb} \\
& + \langle \psi_a \psi_j | \psi_i \psi_b \rangle [(X_{n,\lambda})_{ia}^* (X_{n,\lambda})_{jb} - \delta_{ij}\delta_{ab}] \Bigg\}.
\end{aligned}
\tag{4.45}
$$

For real-valued spin orbitals, the correlation energy can be simplified to

$$
E_\mathrm{c}^{\mathrm{dRPA}} \;=\; \frac{1}{2} \int_0^1 \mathrm{d}\lambda \sum_{i=1}^N \sum_{j=1}^N \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \langle \psi_i \psi_b | \psi_a \psi_j \rangle (P_{\mathrm{c},\lambda})_{ia,jb},
\tag{4.46}
$$

where

$$
(P_{\mathrm{c},\lambda})_{ia,jb} = \sum_n (X_{n,\lambda} + Y_{n,\lambda})_{ia} (X_{n,\lambda} + Y_{n,\lambda})_{jb} - \delta_{ij}\delta_{ab},
\tag{4.47}
$$

or, in matrix form,

$$
\mathbf{P}_{\mathrm{c},\lambda} = \sum_n (\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda}) (\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})^{\mathrm{T}} - \mathbf{1}.
\tag{4.48}
$$

Using the fact that, if $\mathbf{A}_\lambda + \mathbf{B}_\lambda$ and $\mathbf{A}_\lambda - \mathbf{B}_\lambda$ are positive definite, the non-Hermitian eigenvalue equation (4.42) with real spin orbitals can be transformed into the following half-size symmetric eigenvalue equation

$$
\mathbf{M}_\lambda \mathbf{Z}_{n,\lambda} = (\omega_n^\lambda)^2 \mathbf{Z}_{n,\lambda},
\tag{4.49}
$$

where $\mathbf{M}_\lambda = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} (\mathbf{A}_\lambda + \mathbf{B}_\lambda) (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2}$ and with eigenvectors $\mathbf{Z}_{n,\lambda} = \sqrt{\omega_n^\lambda} (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{-1/2} (\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda})$, and using the spectral decomposition $\mathbf{M}_\lambda^{-1/2} =$

$\sum_n (\omega_n^\lambda)^{-1} \mathbf{Z}_{n,\lambda} \mathbf{Z}_{n,\lambda}^{\mathrm{T}}$, the correlation two-particle density matrix $\mathbf{P}_{\mathrm{c},\lambda}$ can be finally expressed as

$$\mathbf{P}_{\mathrm{c},\lambda} = (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} \, \mathbf{M}_\lambda^{-1/2} \, (\mathbf{A}_\lambda - \mathbf{B}_\lambda)^{1/2} - \mathbf{1}. \tag{4.50}$$

In practice, the integration over λ in Eq. (4.46) is done by numerical integration.

This is the *adiabatic-connection formulation* of dRPA. There also other equivalent formulations of dRPA in which the integration over λ is done analytically: the *plasmon-formula formulation*, the *ring coupled-cluster formulation*, and the *dielectric-matrix formulation*. For more details about all the different formulations, see e.g. Refs. [66, 84–89].

Most dRPA correlation energy (combined with the EXX energy) calculations are done in a non-self-consistent way but self-consistent OEP dRPA calculations have also recently been performed [90, 91]. One of the main advantage of dRPA is that it accounts for van der Waals dispersion interactions, and it can somewhat deals with systems with static correlation. However, it shows large self-interaction errors. To overcome the latter drawback, the exchange contribution to the kernel need to be included.

4.3.4 Random-phase approximation with exchange and beyond

The next logical improvement over dRPA is then to include exchange terms by adding the EXX kernel which is also linear in λ but depends on the frequency

$$f_{\mathrm{Hxc}}^\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) \approx f_{\mathrm{Hx}}^\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lambda w_{\mathrm{ee}}(\mathbf{r}_1, \mathbf{r}_2) + \lambda f_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2; \omega), \tag{4.51}$$

and the corresponding RPAx(EXX) [92–95] linear-response function satisfies the Dyson equation

$$\chi_\lambda^{\mathrm{RPAx(EXX)}}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) + \iint \chi_0(\mathbf{r}_1, \mathbf{r}_3; \omega) f_{\mathrm{Hx}}^\lambda(\mathbf{r}_3, \mathbf{r}_4; \omega) \chi_\lambda^{\mathrm{RPAx(EXX)}}(\mathbf{r}_4, \mathbf{r}_2; \omega) \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4. \tag{4.52}$$

Alternatively, one can define a RPAx(HF) [64, 86] approximation at the level of the four-point linear-response function

$$\chi_\lambda^{\mathrm{RPAx(HF)}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega) = \chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2'; \omega)$$
$$+ \iiiint \mathrm{d}\mathbf{x}_3 \mathrm{d}\mathbf{x}_4 \mathrm{d}\mathbf{x}_5 \mathrm{d}\mathbf{x}_6 \, \chi_0(\mathbf{x}_1, \mathbf{x}_4; \mathbf{x}_1', \mathbf{x}_3; \omega) f_{\mathrm{Hx}}^{\lambda,\mathrm{HF}}(\mathbf{x}_3, \mathbf{x}_6; \mathbf{x}_4, \mathbf{x}_5) \chi_\lambda^{\mathrm{RPAx(HF)}}(\mathbf{x}_5, \mathbf{x}_2; \mathbf{x}_6, \mathbf{x}_2'; \omega), \tag{4.53}$$

with the four-point Hartree-Fock kernel $f_{\mathrm{Hx}}^{\lambda,\mathrm{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = \lambda w_{\mathrm{ee}}(|\mathbf{r}_1 - \mathbf{r}_2|)[\delta(\mathbf{x}_1 - \mathbf{x}_1')\delta(\mathbf{x}_2 - \mathbf{x}_2') - \delta(\mathbf{x}_1 - \mathbf{x}_2')\delta(\mathbf{x}_2 - \mathbf{x}_1')]$ which is linear in λ but independent from the frequency ω. However, contrary to the dRPA case, Eqs. (4.52) and (4.53) do not lead to the same correlation energies. Moreover, several non-equivalent correlation energies can be extracted from Eq. (4.53) [87].

In practice, these diverse RPAx variants does not always improve over dRPA. Going beyond RPAx by also including a correlation kernel is an active area of research (see e.g. Ref. [96]).

Appendices

A The Hamiltonian in second quantization

It is convenient to express the Hamiltonian operator in second quantization. In this formalism, the operators are independent from the number of electrons (i.e., we work in Fock space).

In real-space second quantization, the electronic Hamiltonian operator is written as

$$\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}, \tag{A.1}$$

where $\hat{T}$ is the kinetic-energy operator

$$\hat{T} = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \int \hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla^2 \hat{\psi}_\sigma(\mathbf{r}) \mathrm{d}\mathbf{r}, \tag{A.2}$$

$\hat{W}_{\text{ee}}$ is the electron-electron interaction operator

$$\hat{W}_{\text{ee}} = \frac{1}{2} \sum_{\sigma_1=\uparrow,\downarrow} \sum_{\sigma_2=\uparrow,\downarrow} \iint \hat{\psi}_{\sigma_2}^\dagger(\mathbf{r}_2) \hat{\psi}_{\sigma_1}^\dagger(\mathbf{r}_1) w_{\text{ee}}(\mathbf{r}_1, \mathbf{r}_2) \hat{\psi}_{\sigma_1}(\mathbf{r}_1) \hat{\psi}_{\sigma_2}(\mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \tag{A.3}$$

with $w_{\text{ee}}(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$, and $\hat{V}_{\text{ne}}$ is the nuclei-electron interaction operator

$$\hat{V}_{\text{ne}} = \sum_{\sigma=\uparrow,\downarrow} \int \hat{\psi}_\sigma^\dagger(\mathbf{r}) v_{\text{ne}}(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{A.4}$$

In these expressions, $\hat{\psi}_\sigma^\dagger(\mathbf{r})$ and $\hat{\psi}_\sigma(\mathbf{r})$ are the creation and annihilation field operators, respectively, which obey Fermionic anticommutation rules

$$\left\{ \hat{\psi}_\sigma^\dagger(\mathbf{r}), \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \right\} = 0, \tag{A.5}$$

$$\left\{ \hat{\psi}_\sigma(\mathbf{r}), \hat{\psi}_{\sigma'}(\mathbf{r}') \right\} = 0, \tag{A.6}$$

$$\left\{ \hat{\psi}_\sigma^\dagger(\mathbf{r}), \hat{\psi}_{\sigma'}(\mathbf{r}') \right\} = \delta(\mathbf{r} - \mathbf{r}')\delta_{\sigma\sigma'}. \tag{A.7}$$

It is also convenient to define the density operator

$$\hat{n}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}), \tag{A.8}$$

the one-particle density-matrix operator

$$\hat{n}_1(\mathbf{r}, \mathbf{r}') = \sum_{\sigma=\uparrow,\downarrow} \hat{\psi}_\sigma^\dagger(\mathbf{r}') \hat{\psi}_\sigma(\mathbf{r}), \tag{A.9}$$

and the pair-density operator

$$\begin{aligned}
\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{\sigma_1=\uparrow,\downarrow} \sum_{\sigma_2=\uparrow,\downarrow} \hat{\psi}_{\sigma_2}^\dagger(\mathbf{r}_2) \hat{\psi}_{\sigma_1}^\dagger(\mathbf{r}_1) \hat{\psi}_{\sigma_1}(\mathbf{r}_1) \hat{\psi}_{\sigma_2}(\mathbf{r}_2) \\
&= \hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1) - \hat{n}(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2), \\
&= \hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) - \hat{n}(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2),
\end{aligned} \tag{A.10}$$

so that Eqs. (A.2), (A.3), and (A.4) can be rewritten in a more compact way

$$\hat{T} = -\frac{1}{2} \int \left[\nabla_{\mathbf{r}}^2 \hat{n}_1(\mathbf{r}, \mathbf{r}')\right]_{\mathbf{r}'=\mathbf{r}} \mathrm{d}\mathbf{r}, \tag{A.11}$$

$$\hat{W}_{\mathrm{ee}} = \frac{1}{2} \iint w_{\mathrm{ee}}(\mathbf{r}_1, \mathbf{r}_2) \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \tag{A.12}$$

$$\hat{V}_{\mathrm{ne}} = \int v_{\mathrm{ne}}(\mathbf{r}) \hat{n}(\mathbf{r}) \mathrm{d}\mathbf{r}. \tag{A.13}$$

We can also use the second-quantization formalism in an orthonormal spin-orbital basis $\{\psi_p(\mathbf{x})\}$ where $\mathbf{x} = (\mathbf{r}, \sigma)$. For this, we expand the field operators as

$$\hat{\psi}_\sigma^\dagger(\mathbf{r}) = \sum_p \psi_p^*(\mathbf{x}) \hat{a}_p^\dagger, \tag{A.14}$$

and

$$\hat{\psi}_\sigma(\mathbf{r}) = \sum_p \psi_p(\mathbf{x}) \hat{a}_p, \tag{A.15}$$

where $\hat{a}_p^\dagger$ and $\hat{a}_p$ are the creation and annihilation operators in this basis, which still obey anticommutation rules: $\{\hat{a}_p^\dagger, \hat{a}_q^\dagger\} = \{\hat{a}_p, \hat{a}_q\} = 0$ and $\{\hat{a}_p^\dagger, \hat{a}_q\} = \delta_{pq}$. The expressions of the operators are then

$$\hat{T} = \sum_{pq} t_{pq}\, \hat{a}_p^\dagger \hat{a}_q, \tag{A.16}$$

$$\hat{W}_{\mathrm{ee}} = \frac{1}{2} \sum_{pqrs} \langle \psi_p \psi_q | \psi_r \psi_s \rangle\, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r, \tag{A.17}$$

$$\hat{V}_{\mathrm{ne}} = \sum_{pq} v_{\mathrm{ne},pq}\, \hat{a}_p^\dagger \hat{a}_q, \tag{A.18}$$

where t_{pq} and $v_{\mathrm{ne},pq}$ are the one-electron kinetic and nuclei-electron integrals, respectively, and $\langle \psi_p \psi_q | \psi_r \psi_s \rangle$ are the two-electron integrals.

B A brief introduction to functional calculus

This section is inspired from Appendix A of Ref. [1] to which the reader is referred for more details.

A function f is a mapping from a number x to another number $f(x)$, i.e. $x \to f(x)$. Similarly, a *functional* F is a mapping from a function f to a number $F[f]$, i.e. $f \to F[f]$. In other words, a functional is a function of a function.

The differential of a functional $F[f]$ is $\delta F[f] = F[f + \delta f] - F[f]$, where δf is a infinitesimal variation of f. It represents the infinitesimal variation of $F[f]$ due to an infinitesimal variation of f. The infinitesimal variation $\delta F[f]$ is linear in $\delta f(x)$ at any point x

$$\boxed{\delta F[f] = \int \frac{\delta F[f]}{\delta f(x)} \delta f(x) \mathrm{d}x,} \tag{B.1}$$

which defines the *functional derivative* of $F[f]$ with respect $f(x)$, denoted by $\delta F[f]/\delta f(x)$. The functional derivative generalizes the concept of partial derivative. Indeed, if we consider a function $F(f_1, f_2, ...)$ of several variables f_1, f_2, ..., then the differential of F is $\mathrm{d}F = \sum_i \partial F/\partial f_i \, \mathrm{d}f_i$, which is the analog of Eq. (B.1). Thus, $\delta F[f]/\delta f(x)$ is the analog of $\partial F/\partial f_i$ for the case of an infinitely continuous number of variables.

Functional derivatives shares most of the properties of ordinary derivatives. The functional derivative of a linear combination of functionals $c_1 F[f] + c_2 G[f]$ is

$$\frac{\delta}{\delta f(x)} \left(c_1 F[f] + c_2 G[f] \right) = c_1 \frac{\delta F[f]}{\delta f(x)} + c_2 \frac{\delta G[f]}{\delta f(x)}. \tag{B.2}$$

The functional derivative of a product of two functionals $F[f]G[f]$ is

$$\frac{\delta}{\delta f(x)} \left(F[f]G[f] \right) = \frac{\delta F[f]}{\delta f(x)} G[f] + F[f] \frac{\delta G[f]}{\delta f(x)}. \tag{B.3}$$

A functional $F[f]$ of a function $f[g](x)$ which is itself a functional of a function $g(x)$ has a functional derivative with respect to $g(x)$ given by the chain rule

$$\frac{\delta F[f]}{\delta g(x)} = \int \frac{\delta F[f]}{\delta f(x')} \frac{\delta f(x')}{\delta g(x)} \mathrm{d}x'. \tag{B.4}$$

It is the analog of the chain rule for a function $F(f_1, f_2, ...)$ of several variables $f_i(g_1, g_2, ...)$ which are themselves functions of other variables $g_1, g_2, ...$, i.e. $\partial F/\partial g_i = \sum_j (\partial F/\partial f_j)(\partial f_j/\partial g_i)$.

An important special case is when the functional $F(f(x))$ is just an ordinary function of $f(x)$. The functional derivative of $F(f(x))$ with respect to $f(x')$ is

$$\frac{\delta F(f(x))}{\delta f(x')} = \frac{\mathrm{d}F(f(x))}{\mathrm{d}f} \delta(x - x'), \tag{B.5}$$

where $\mathrm{d}F/\mathrm{d}f$ is the ordinary derivative of the function F and $\delta(x-x')$ is the Dirac delta function. In particular, if $F(f(x)) = f(x)$, we have

$$\frac{\delta f(x)}{\delta f(x')} = \delta(x - x'). \tag{B.6}$$

Also, if $f(x)$ is a functional of $g(x)$, the chain rule (B.4) and Eq. (B.6) give

$$\frac{\delta f(x)}{\delta f(x')} = \int \frac{\delta f(x)}{\delta g(x'')} \frac{\delta g(x'')}{\delta f(x')} \mathrm{d}x'' = \delta(x - x'), \tag{B.7}$$

which permits one to interpret $\delta g / \delta f$ as the inverse of $\delta f / \delta g$. Eq. (B.7) is analogous to the matrix relation: $\sum_k (A)_{ik} (A^{-1})_{kj} = \delta_{ij}$.

Higher-order functional derivatives can also be defined. For example, the second-order functional derivative $\delta^2 F[f]/\delta f(x)\delta f(x')$ is the define as the first-order functional derivative of $\delta F[f]/\delta f(x)$ with respect to $f(x')$. The order of differentiation is usually irrelevant

$$\frac{\delta^2 F[f]}{\delta f(x)\delta f(x')} = \frac{\delta^2 F[f]}{\delta f(x')\delta f(x)}. \tag{B.8}$$

These functional derivatives can be used to expand a functional in a Taylor series

$$F[f + \Delta f] = F[f] + \int \frac{\delta F[f]}{\delta f(x)} \Delta f(x)\mathrm{d}x + \frac{1}{2} \iint \frac{\delta^2 F[f]}{\delta f(x)\delta f(x')} \Delta f(x)\Delta f(x')\mathrm{d}x\mathrm{d}x' + ..., \tag{B.9}$$

where Δf is a finite change in f.

Finally, consider the following frequently occurring semilocal form for the functional $F[f]$ depending on a function $f(x)$ and its first-order derivative $f'(x) = \mathrm{d}f(x)/\mathrm{d}x$

$$F[f] = \int h(f(x), f'(x))\mathrm{d}x, \tag{B.10}$$

where h is some function and $f(x)$ vanishes at the boundary of x. The differential of $F[f]$ can be written as

$$\delta F[f] = \int \delta h(f(x), f'(x))\mathrm{d}x = \int \left[\frac{\partial h(f(x), f'(x))}{\partial f} \delta f(x) + \frac{\partial h(f(x), f'(x))}{\partial f'} \delta f'(x) \right] \mathrm{d}x. \tag{B.11}$$

Using now $\delta f'(x) = \delta[f(x + \varepsilon) - f(x)]/\varepsilon = [\delta f(x + \varepsilon) - \delta f(x)]/\varepsilon = (\delta f(x))'$ (with $\varepsilon \to 0$), and integrating by parts the second term in Eq. (B.11) gives

$$\delta F[f] = \int \left[\frac{\partial h(f(x), f'(x))}{\partial f} \delta f(x) - \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial h(f(x), f'(x))}{\partial f'} \right) \delta f(x) \right] \mathrm{d}x, \tag{B.12}$$

where we have used that $\delta f(x)$ mush vanish on the boundary so that the boundary term of the integration by parts vanishes. Comparing Eq. (B.12) with Eq. (B.1) shows that the functional derivative of $F[f]$ is

$$\frac{\delta F[f]}{\delta f(x)} = \frac{\partial h(f(x), f'(x))}{\partial f} - \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial h(f(x), f'(x))}{\partial f'} \right). \tag{B.13}$$

Exercise 21 : Generalize Eq. (B.13) to a semilocal functional F depending up to on n-order derivatives of f

$$F[f] = \int h(f(x), f'(x), f''(x), ..., f^{(n)}(x))\mathrm{d}x, \tag{B.14}$$

where $f^{(n)}(x) = \mathrm{d}^n f(x)/\mathrm{d}x^n$.

Solutions to the exercises

Exercise 1

For the special case of Coulombic potentials of the form $v_{\text{ne}}(\mathbf{r}) = -\sum_\alpha Z_\alpha/|\mathbf{r} - \mathbf{R}_\alpha|$, it is easy to see that the ground-state density $n_0(\mathbf{r})$ determines the parameters of the potential. Indeed, the locations of the local maxima of $n_0(\mathbf{r})$ give the positions of the nuclei $\mathbf{r}_{\text{max}} = \mathbf{R}_\alpha$, and the electron-nucleus cusp condition at each nucleus, $(\partial \bar{n}_0(r_\alpha)/\partial r_\alpha)_{r_\alpha=0} = -2Z_\alpha \bar{n}_0(0)$ where $\bar{n}_0(r_\alpha)$ is the spherical average of the density around the nucleus α ($r_\alpha = |\mathbf{r} - \mathbf{R}_\alpha|$), gives the nucleus charge Z_α. Moreover, the integral of the density gives the number of electrons, $\int n_0(\mathbf{r})\mathrm{d}\mathbf{r} = N$. It is important to realize however that the Hohenberg-Kohn theorem is much more general than that since it states that the ground-state density determines the potential *for any form of the potential*.

Exercise 2

Let n_0 be a ground-state density associated with the potential $v_{\text{ne}}(\mathbf{r})$ and let $\Psi[n_0]$ be a corresponding ground-state wave function. Let n be a ground-state density associated with another potential $v(\mathbf{r})$ and let $\Psi[n]$ be a corresponding ground-state wave function. The variational property of the Hohenberg-Kohn density functional $E[n]$ directly follows from the variational theorem on wave functions:

$$
\begin{aligned}
E_0 = E[n_0] &= F[n_0] + \int v_{\text{ne}}(\mathbf{r})n_0(\mathbf{r})\mathrm{d}\mathbf{r} \\
&= \langle \Psi[n_0]|\hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}|\Psi[n_0]\rangle \\
&\leq \langle \Psi[n]|\hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}|\Psi[n]\rangle \\
&= F[n] + \int v_{\text{ne}}(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} = E[n],
\end{aligned}
\tag{S.1}
$$

establishing Eq. (1.16).

Exercise 3

Let us consider a variation of the density δn, the induced variation of the Hartree energy functional [Eq. (1.24)] is:

$$
\begin{aligned}
\delta E_{\text{H}}[n] &= \frac{1}{2} \iint \frac{\delta n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + \frac{1}{2} \iint \frac{n(\mathbf{r}_1)\delta n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\
&= \frac{1}{2} \int \left[\int \frac{n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 \right] \delta n(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 + \frac{1}{2} \int \left[\int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_1 \right] \delta n(\mathbf{r}_2)\mathrm{d}\mathbf{r}_2 \\
&= \int \left[\int \frac{n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 \right] \delta n(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1,
\end{aligned}
\tag{S.2}
$$

which, according to Eq. (B.1), allows us to identify the functional derivative of $E_{\text{H}}[n]$

$$
v_{\text{H}}(\mathbf{r}_1) = \frac{\delta E_{\text{H}}[n]}{\delta n(\mathbf{r}_1)} = \int \frac{n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2.
\tag{S.3}
$$

Exercise 4

We start from the expression of the density in Eq. (1.29) and insert the expansion of $\phi_i(\mathbf{r})$ in terms of basis functions [Eq. (1.41)]

$$
\begin{aligned}
n(\mathbf{r}) &= \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 = \sum_{i=1}^{N} \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}) \\
&= \sum_{i=1}^{N} \left(\sum_{\gamma=1}^{M} c_{\gamma i}\, \chi_\gamma(\mathbf{r}) \right) \left(\sum_{\lambda=1}^{M} c_{\lambda i}^*\, \chi_\lambda^*(\mathbf{r}) \right) \\
&= \sum_{\gamma=1}^{M} \sum_{\lambda=1}^{M} P_{\gamma\lambda} \chi_\gamma(\mathbf{r})\chi_\lambda^*(\mathbf{r}),
\end{aligned}
\tag{S.4}
$$

where $P_{\gamma\lambda} = \sum_{i=1}^{N} c_{\gamma i} c_{\lambda i}^*$. The second equality in Eq. (1.46) is then found by inserting the expression of the Hartree potential v_H [Eq. S.3] and using Eq. (S.4)

$$
\begin{aligned}
J_{\mu\nu} &= \int \chi_\mu^*(\mathbf{r}_1) v_H(\mathbf{r}_1) \chi_\nu(\mathbf{r}_1) d\mathbf{r}_1 \\
&= \iint \chi_\mu^*(\mathbf{r}_1) \frac{n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_\nu(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \sum_{\gamma=1}^{M} \sum_{\lambda=1}^{M} P_{\gamma\lambda} \iint \frac{\chi_\mu^*(\mathbf{r}_1)\chi_\gamma(\mathbf{r}_2)\chi_\lambda^*(\mathbf{r}_2)\chi_\nu(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \sum_{\lambda=1}^{M} \sum_{\gamma=1}^{M} P_{\gamma\lambda} (\chi_\mu \chi_\nu | \chi_\lambda \chi_\gamma),
\end{aligned} \tag{S.5}
$$

where $(\chi_\mu\chi_\nu|\chi_\lambda\chi_\gamma)$ are the two-electron integrals defined in Eq. (1.48).

Exercise 5

Since the ↑- and ↓-spin electrons are uncoupled in the exchange energy (in the non-relativistic approximation), the spin-dependent exchange functional can be decomposed as

$$
E_x[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, 0] + E_x[0, n_\downarrow]. \tag{S.6}
$$

Applying this equation with $n_\uparrow = n_\downarrow = n/2$ gives

$$
E_x[n/2, n/2] = E_x[n/2, 0] + E_x[0, n/2] = 2E_x[n/2, 0] = 2E_x[0, n/2], \tag{S.7}
$$

where it has been used that the functional is symmetric in its two arguments. Now, since $E_x[n/2, n/2] = E_x[n]$ where $E_x[n]$ is the spin-independent exchange functional, we thus have

$$
2E_x[n/2, 0] = 2E_x[0, n/2] = E_x[n], \tag{S.8}
$$

or, equivalently,

$$
E_x[n, 0] = E_x[0, n] = \frac{1}{2} E_x[2n]. \tag{S.9}
$$

Since this is true for any density n, it can be applied with arbitrary spin-resolved densities $n_\uparrow$ and $n_\downarrow$, leading to the spin-scaling relation

$$
E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} \left(E_x[2n_\uparrow] + E_x[2n_\downarrow] \right). \tag{S.10}
$$

Exercise 6

Using Eqs. (2.3) and (2.4), we can write the exchange-correlation hole as

$$
n_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)} - n(\mathbf{r}_2), \tag{S.11}
$$

which, after integrating over $\mathbf{r}_2$, leads to

$$
\int n_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \frac{\int n_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2}{n(\mathbf{r}_1)} - \int n(\mathbf{r}_2) d\mathbf{r}_2 = \frac{(N-1)n(\mathbf{r}_1)}{n(\mathbf{r}_1)} - N = -1, \tag{S.12}
$$

where the relation $\int n_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = (N-1)n(\mathbf{r}_1)$ has been used, stemming directly from the definition of $n_2(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (2.1).

Exercise 7

We start from the definition of the exchange energy per particle of Eq. (2.14) and separate the domain of integration over $\mathbf{r}_2$ into two subdomains

$$
\begin{aligned}
\varepsilon_{\mathrm{x}}[n](\mathbf{r}_1) &= \frac{1}{2}\int \frac{n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 \\
&= \frac{1}{2}\int_{\Omega(r_1)} \frac{n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 + \frac{1}{2}\int_{\bar{\Omega}(r_1)} \frac{n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2,
\end{aligned}
\tag{S.13}
$$

where $\Omega(r_1)$ is the ball centered at $\mathbf{0}$ of radius r_1 and $\bar{\Omega}(r_1)$ is the complement subdomain. In the first subdomain $\Omega(r_1)$, we have $r_2 < r_1$ so we can make a convergent multipole expansion of the Coulomb interaction $1/|\mathbf{r}_1 - \mathbf{r}_2|$ around $\mathbf{r}_2 = \mathbf{0}$

$$
\begin{aligned}
\frac{1}{2}\int_{\Omega(r_1)} \frac{n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 &= \frac{1}{2}\int_{\Omega(r_1)} n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)\left(\frac{1}{r_1} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1^3} + \cdots\right)\mathrm{d}\mathbf{r}_2 \\
&= \frac{1}{2r_1}\int_{\Omega(r_1)} n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_2 + \frac{\mathbf{r}_1}{2r_1^3}\cdot\int_{\Omega(r_1)} n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)\mathbf{r}_2\mathrm{d}\mathbf{r}_2 + \cdots \\
&\underset{r_1 \to +\infty}{\sim} \frac{1}{2r_1}\int n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)\mathrm{d}\mathbf{r}_2 = -\frac{1}{2r_1},
\end{aligned}
\tag{S.14}
$$

where we have used the sum rule on the exchange hole [Eq. (2.10)] and the fact that all the moments of the exchange hole exist for finite systems. As regards now the second contribution to the integral in Eq. (S.13), since for finite systems the exchange hole decays exponentially, $n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2) \underset{|\mathbf{r}_1 - \mathbf{r}_2| \to 0}{\propto} e^{-\alpha|\mathbf{r}_1 - \mathbf{r}_2|}$, this remaining contribution vanishes exponentially for $r_1 \to +\infty$

$$
\frac{1}{2}\int_{\bar{\Omega}(r_1)} \frac{n_{\mathrm{x}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}\mathbf{r}_2 \underset{r_1 \to +\infty}{=} O(e^{-\alpha r_1}).
\tag{S.15}
$$

This thus proves that

$$
\varepsilon_{\mathrm{x}}[n](\mathbf{r}_1) \underset{r \to +\infty}{\sim} -\frac{1}{2r_1}.
\tag{S.16}
$$

Exercise 8

We search the minimizing ensemble density matrices in the form

$$
\hat{\Gamma} = (1 - f)\sum_n w_n^{N-1}|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}| + f\sum_m w_m^N|\Psi_m^N\rangle\langle\Psi_m^N|,
\tag{S.17}
$$

where $\{\Psi_n^{N-1}\}$ and $\{\Psi_m^N\}$ are complete orthonormal basis of fixed eigenstates of the $(N-1)$- and N-electron systems, respectively, and w_n^{N-1} and w_m^N are weights to be optimized with the constraints $0 \le w_n^{N-1} \le 1$ and $\sum_n w_n^{N-1} = 1$, and similarly for w_m^N. The energy corresponding to the ensemble density matrix of Eq. (S.17) is

$$
\begin{aligned}
E^{N-1+f} &= \mathrm{Tr}\left[\hat{\Gamma}\hat{H}\right] \\
&= (1-f)\sum_n w_n^{N-1}\mathrm{Tr}\left[|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|\hat{H}\right] + f\sum_m w_m^N\mathrm{Tr}\left[|\Psi_m^N\rangle\langle\Psi_m^N|\hat{H}\right] \\
&= (1-f)\sum_{n,n'} w_n^{N-1}\langle\Psi_{n'}^{N-1}|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|\hat{H}|\Psi_{n'}^{N-1}\rangle + f\sum_{m,m'} w_m^N\langle\Psi_{m'}^N|\Psi_m^N\rangle\langle\Psi_m^N|\hat{H}|\Psi_{m'}^N\rangle \\
&= (1-f)\sum_n w_n^{N-1}\langle\Psi_n^{N-1}|\hat{H}|\Psi_n^{N-1}\rangle + f\sum_m w_m^N\langle\Psi_m^N|\hat{H}|\Psi_m^N\rangle \\
&= (1-f)\sum_n w_n^{N-1}E_n^{N-1} + f\sum_m w_m^N E_m^N,
\end{aligned}
\tag{S.18}
$$

where $E_n^{N-1} = \langle \Psi_n^{N-1} | \hat{H} | \Psi_n^{N-1} \rangle$ and $E_m^N = \langle \Psi_m^N | \hat{H} | \Psi_m^N \rangle$ are the corresponding eigenenergies for the $(N-1)$- and N-electron systems, respectively. Clearly, the minimum of E^{N-1+f} in Eq. (S.18) is reached when only the ground-state energies E_0^{N-1} and E_0^N of the $(N-1)$- and N-electron systems remain in the sums, i.e. for the weights $w_0^{N-1} = 1$ and $w_{n>0}^{N-1} = 0$, and $w_0^N = 1$ and $w_{m>0}^N = 0$. The minimizing ensemble density matrix is thus indeed given by Eq. (2.32) and the corresponding ground-state energy by Eq. (2.33).

Exercise 9

In the energy expression of Eq. (2.42), the orbitals $\{\phi_j\}$ are optimized in the presence of the orbital occupation numbers $\{n_i\}$. Therefore, the derivative of the energy with respect to n_i contains two contributions, a term corresponding to the explicit dependence on n_i at fixed orbitals $\{\phi_j\}$ and a term coming from the implicit dependence on n_i via the orbitals $\{\phi_j\}$,

$$\frac{\partial E}{\partial n_i} = \left(\frac{\partial E}{\partial n_i} \right)_{\{\phi_j\}} + \left[\sum_{j=1}^N \int \frac{\delta E}{\delta \phi_j^*(\mathbf{r})} \frac{\partial \phi_j^*(\mathbf{r})}{\partial n_i} d\mathbf{r} + \text{c.c.} \right]. \tag{S.19}$$

The first term gives

$$\begin{aligned}
\left(\frac{\partial E}{\partial n_i} \right)_{\{\phi_j\}} &= \int \phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) d\mathbf{r} + \left(\frac{\partial E_{\text{Hxc}}[n]}{\partial n_i} \right)_{\{\phi_j\}} \\
&= \int \phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) d\mathbf{r} + \int \frac{\delta E_{\text{Hxc}}[n]}{\delta n(\mathbf{r})} \left(\frac{\partial n(\mathbf{r})}{\partial n_i} \right)_{\{\phi_j\}} d\mathbf{r} \\
&= \int \phi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}) \right) \phi_i(\mathbf{r}) d\mathbf{r} \\
&= \varepsilon_i, \tag{S.20}
\end{aligned}$$

where the expression of the density in terms of n_i in Eq. (2.43) has been used, and ε_i is the orbital energy introduced in Eq. (2.44). It can be shown that the second term in Eq. (S.19) vanishes

$$\begin{aligned}
\sum_{j=1}^N \int \frac{\delta E}{\delta \phi_j^*(\mathbf{r})} \frac{\partial \phi_j^*(\mathbf{r})}{\partial n_i} d\mathbf{r} + \text{c.c.} &= \sum_{j=1}^N \int \left[n_j \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) \right) \phi_j(\mathbf{r}) + \frac{\delta E_{\text{Hxc}}[n]}{\delta \phi_j^*(\mathbf{r})} \right] \frac{\partial \phi_j^*(\mathbf{r})}{\partial n_i} d\mathbf{r} + \text{c.c.} \\
&= \sum_{j=1}^N \int \left[n_j \left(-\frac{1}{2}\nabla^2 + v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}) \right) \phi_j(\mathbf{r}) \right] \frac{\partial \phi_j^*(\mathbf{r})}{\partial n_i} d\mathbf{r} + \text{c.c.} \\
&= \sum_{j=1}^N \int n_j \varepsilon_j \phi_j(\mathbf{r}) \frac{\partial \phi_j^*(\mathbf{r})}{\partial n_i} d\mathbf{r} + \text{c.c.} \\
&= \sum_{j=1}^N n_j \varepsilon_j \frac{\partial}{\partial n_i} \int |\phi_j(\mathbf{r})|^2 d\mathbf{r} = 0, \tag{S.21}
\end{aligned}$$

since the orbitals are normalized, $\int |\phi_j(\mathbf{r})|^2 d\mathbf{r} = 1$. This proves Janak's theorem [Eq. (2.47)].

Exercise 10

For large r, the KS potential $v_{\text{s}}^N(\mathbf{r}) \underset{r \to +\infty}{\sim} v_{\text{s}}^N(\infty) + (Q-1)/r$ has spherical symmetry, and the KS equations (2.44) for the asymptotic orbitals $\phi_{i,\text{asymp}}^N(r)$ can thus be written as

$$-\frac{1}{2}\left(\frac{d^2 \phi_{i,\text{asymp}}^N(r)}{dr^2} + \frac{2}{r}\frac{d\phi_{i,\text{asymp}}^N(r)}{dr} - \frac{\ell(\ell+1)}{r^2}\phi_{i,\text{asymp}}^N(r) \right) + \left(v_{\text{s}}^N(\infty) + \frac{Q-1}{r} \right) \phi_{i,\text{asymp}}^N(r)$$
$$= \varepsilon_i^N \phi_{i,\text{asymp}}^N(r), \quad \text{(S.22)}$$

where ℓ is the angular momentum. For $r \to +\infty$, the terms in $1/r$ or $1/r^2$ are negligible, so it remains

$$-\frac{1}{2}\frac{d^2 \phi_{i,\text{asymp}}^N(r)}{dr^2} + v_{\text{s}}^N(\infty)\phi_{i,\text{asymp}}^N(r) = \varepsilon_i^N \phi_{i,\text{asymp}}^N(r), \tag{S.23}$$

which has the general solutions

$$\phi_{i,\text{asymp}}^N(r) = c_1 e^{-\sqrt{-2(\varepsilon_i^N - v_{\text{s}}^N(\infty))}\, r} + c_2 e^{+\sqrt{-2(\varepsilon_i^N - v_{\text{s}}^N(\infty))}\, r}, \tag{S.24}$$

for bound states, i.e. $\varepsilon_i^N < v_{\text{s}}^N(\infty)$. Since the second term on the right-hand-side of Eq. (S.24) diverges for $r \to +\infty$, we must have $c_2 = 0$ and therefore the asymptotic behavior of the KS orbitals is

$$\phi_i^N(r) \underset{r \to +\infty}{\sim} e^{-\sqrt{-2(\varepsilon_i^N - v_{\text{s}}^N(\infty))}\, r}. \tag{S.25}$$

Exercise 11

By making the indicated replacements in Eq. (3.3), we arrive at

$$E_{\text{x}}^{\text{unif}} = \frac{1}{(2\pi)^6} \int_{\Omega_{k_{\text{F}}}} d\mathbf{k}_1 \int_{\Omega_{k_{\text{F}}}} d\mathbf{k}_2 \iint \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{i\,(\mathbf{k}_1 - \mathbf{k}_2)\cdot(\mathbf{r}_2 - \mathbf{r}_1)} d\mathbf{r}_1 d\mathbf{r}_2, \tag{S.26}$$

where the spatial integrations are on a box of volume $V \to \infty$. Performing the change of variables $(\mathbf{r}_1, \mathbf{r}_2) \to (\mathbf{r}_1, \mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1)$, we get

$$
\begin{aligned}
E_{\text{x}}^{\text{unif}} &= \frac{1}{(2\pi)^6} \int_{\Omega_{k_{\text{F}}}} d\mathbf{k}_1 \int_{\Omega_{k_{\text{F}}}} d\mathbf{k}_2 \iint \frac{1}{|\mathbf{r}_{12}|} e^{i\,(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_{12} \\
&= -\frac{V}{(2\pi)^6} \int_{\Omega_{k_{\text{F}}}} d\mathbf{k}_1 \int_{\Omega_{k_{\text{F}}}} d\mathbf{k}_2 \frac{4\pi}{|\mathbf{k}_1 - \mathbf{k}_2|^2},
\end{aligned} \tag{S.27}
$$

where it was used that the integration over $\mathbf{r}_{12}$ gives the Fourier transform of the Coulomb interaction $\int (1/|\mathbf{r}_{12}|) e^{i\,(\mathbf{k}_1 - \mathbf{k}_2)\cdot\mathbf{r}_{12}} d\mathbf{r}_{12} = 4\pi/|\mathbf{k}_1 - \mathbf{k}_2|^2$ and the integration over $\mathbf{r}_1$ gives the volume of the box $\int d\mathbf{r}_1 = V$. We can rewrite the integrals over $\mathbf{k}_1$ and $\mathbf{k}_2$ in spherical coordinates choosing as the polar angle θ of $\mathbf{k}_2$ the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$

$$E_{\text{x}}^{\text{unif}} = -\frac{V}{(2\pi)^6} \int_0^{k_{\text{F}}} dk_1 4\pi k_1^2 \int_0^{k_{\text{F}}} dk_2 2\pi k_2^2 \int_0^\pi d\theta \sin\theta \frac{4\pi}{k_1^2 + k_2^2 - 2k_1 k_2 \cos\theta}. \tag{S.28}$$

The integral over θ is easy to calculate

$$
\begin{aligned}
\int_0^\pi d\theta \sin\theta \frac{4\pi}{k_1^2 + k_2^2 - 2k_1 k_2 \cos\theta} &= \int_{-1}^1 dx \frac{4\pi}{k_1^2 + k_2^2 - 2k_1 k_2 x} \\
&= \frac{-2\pi}{k_1 k_2} \left[\ln\left((k_1 - k_2)^2\right) - \ln\left((k_1 + k_2)^2\right) \right],
\end{aligned} \tag{S.29}
$$

and we are left with

$$
\begin{aligned}
E_{\text{x}}^{\text{unif}} &= \frac{2V}{(2\pi)^3} \int_0^{k_{\text{F}}} dk_1 \int_0^{k_{\text{F}}} dk_2\, k_1 k_2 \left[\ln\left((k_1 - k_2)^2\right) - \ln\left((k_1 + k_2)^2\right) \right] \\
&= \frac{2V k_{\text{F}}^4}{(2\pi)^3} \int_0^1 dx_1 \int_0^1 dx_2\, x_1 x_2 \left[\ln\left((x_1 - x_2)^2\right) - \ln\left((x_1 + x_2)^2\right) \right],
\end{aligned} \tag{S.30}
$$

where we have introduced $x_1 = k_1/k_{\text{F}}$ and $x_2 = k_2/k_{\text{F}}$. It can be shown that the last double integral over x_1 and x_2 equals -1, so we get

$$E_{\text{x}}^{\text{unif}} = -\frac{2V k_{\text{F}}^4}{(2\pi)^3}. \tag{S.31}$$

We finally obtain the exchange energy per particle

$$\varepsilon_{\text{x}}^{\text{unif}} = \frac{E_{\text{x}}^{\text{unif}}}{N} = -\frac{2k_{\text{F}}^4}{(2\pi)^3 n} = c_{\text{x}} n^{1/3}, \tag{S.32}$$

where the definition of $k_{\text{F}} = (3\pi^2 n)^{1/3}$ was used and the constant $c_{\text{x}} = -(3/4)(3/\pi)^{1/3}$ was introduced. For an alternative way of calculating the integral in Eq. (S.27) see Fetter and Walecka, page 28 [97].

Exercise 12

The LDA exchange energy functional is

$$E_{\mathrm{x}}^{\mathrm{LDA}}[n] = \int n(\mathbf{r})\varepsilon_{\mathrm{x}}^{\mathrm{unif}}(n(\mathbf{r}))\mathrm{d}\mathbf{r} = \int f(n(\mathbf{r}))\mathrm{d}\mathbf{r}, \tag{S.33}$$

where $f(n) = c_{\mathrm{x}}n^{4/3}$. The variation of $E_{\mathrm{x}}^{\mathrm{LDA}}[n]$ due to a variation of the density can be written as

$$\delta E_{\mathrm{x}}^{\mathrm{LDA}}[n] = \int \delta f(n(\mathbf{r}))\mathrm{d}\mathbf{r} = \int \left(\frac{\mathrm{d}f(n)}{\mathrm{d}n}\right)_{n=n(\mathbf{r})} \delta n(\mathbf{r})\mathrm{d}\mathbf{r}, \tag{S.34}$$

which, according to Eq. (B.1), means that the functional derivative is

$$v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}) = \frac{\delta E_{\mathrm{x}}^{\mathrm{LDA}}[n]}{\delta n(\mathbf{r})} = \left(\frac{\mathrm{d}f(n)}{\mathrm{d}n}\right)_{n=n(\mathbf{r})} = \frac{4}{3}c_{\mathrm{x}}n(\mathbf{r})^{1/3}. \tag{S.35}$$

Since the density $n(\mathbf{r})$ decays exponentially for $r \to +\infty$ [Eq. (2.50)], the LDA exchange potential $v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r})$ also decays exponentially for $r \to +\infty$, i.e. much too fast in comparison to the asymptotic behavior of the exact exchange potential $v_{\mathrm{x}}(\mathbf{r}) \underset{r \to +\infty}{\sim} -1/r$.

Exercise 13

The Wigner correlation energy functional can be written as

$$E_{\mathrm{c}}^{\mathrm{W}}[n] = \int f(n(\mathbf{r}))\mathrm{d}\mathbf{r}, \tag{S.36}$$

with $f(n) = cn/(d+kn^{-1/3})$ where $k = (3/(4\pi))^{1/3}$. Similarly to Exercise 12, the corresponding potential is calculated as

$$\begin{aligned} v_{\mathrm{c}}^{\mathrm{W}}(\mathbf{r}) = \frac{\delta E_{\mathrm{c}}^{\mathrm{W}}[n]}{\delta n(\mathbf{r})} = \left(\frac{\mathrm{d}f(n)}{\mathrm{d}n}\right)_{n=n(\mathbf{r})} &= \frac{c(d + kn(\mathbf{r})^{-1/3}) - cn(\mathbf{r})(-kn(\mathbf{r})^{-4/3}/3)}{(d + kn(\mathbf{r})^{-1/3})^2} \\ &= \frac{cd + (4/3)ckn(\mathbf{r})^{-1/3}}{(d + kn(\mathbf{r})^{-1/3})^2}. \end{aligned} \tag{S.37}$$

Exercise 14

The derivation of the potential of a GGA functional is just a 3D generalization of the 1D case of Eqs. (B.10)-(B.13). The variation of $E_{\mathrm{xc}}^{\mathrm{GGA}}[n]$ induced by a variation of the density $\delta n(\mathbf{r})$ is

$$\delta E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int \delta f(n(\mathbf{r}), \nabla n(\mathbf{r}))\mathrm{d}\mathbf{r} = \int \left[\frac{\partial f(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial n}\delta n(\mathbf{r}) + \frac{\partial f(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n} \cdot \delta \nabla n(\mathbf{r})\right]\mathrm{d}\mathbf{r}, \tag{S.38}$$

where the notation $\partial f/\partial \nabla n$ means the vector containing the derivatives of f with respect to the different components of ∇n. Using $\delta \nabla n(\mathbf{r}) = \nabla \delta n(\mathbf{r})$ (since ∇ is a linear operator) and integrating by parts the second term in Eq. (S.38)

$$\delta E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int \left[\frac{\partial f(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial n}\delta n(\mathbf{r}) - \nabla \cdot \frac{\partial f(n(\mathbf{r}), \nabla n(\mathbf{r}))}{\partial \nabla n}\delta n(\mathbf{r})\right]\mathrm{d}\mathbf{r}, \tag{S.39}$$

where we have used that $\delta n(\mathbf{r})$ mush vanish at infinity so that the boundary term of the integration by parts vanishes. Using the definition of a functional derivative, the potential associated with $E_{\mathrm{xc}}^{\mathrm{GGA}}[n]$ is thus

$$v_{\mathrm{xc}}^{\mathrm{GGA}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}^{\mathrm{GGA}}[n]}{\delta n(\mathbf{r})} = \frac{\partial f}{\partial n}(n(\mathbf{r}), \nabla n(\mathbf{r})) - \nabla \cdot \frac{\partial f}{\partial \nabla n}(n(\mathbf{r}), \nabla n(\mathbf{r})). \tag{S.40}$$

The contribution of $v_{\text{xc}}^{\text{GGA}}(\mathbf{r})$ to the KS Fock matrix [Eq. (1.49)] can then be expressed as

$$
\begin{aligned}
V_{\text{xc},\mu\nu}^{\text{GGA}} &= \int \chi_\mu^*(\mathbf{r}) v_{\text{xc}}^{\text{GGA}}(\mathbf{r}) \chi_\nu(\mathbf{r}) \mathrm{d}\mathbf{r} \\
&= \int \chi_\mu^*(\mathbf{r}) \left[\frac{\partial f}{\partial n}(n(\mathbf{r}), \nabla n(\mathbf{r})) - \nabla \cdot \frac{\partial f}{\partial \nabla n}(n(\mathbf{r}), \nabla n(\mathbf{r})) \right] \chi_\nu(\mathbf{r}) \mathrm{d}\mathbf{r} \\
&= \int \frac{\partial f}{\partial n}(n(\mathbf{r}), \nabla n(\mathbf{r})) \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \mathrm{d}\mathbf{r} + \int \frac{\partial f}{\partial \nabla n}(n(\mathbf{r}), \nabla n(\mathbf{r})) \cdot \nabla \left(\chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \right) \mathrm{d}\mathbf{r}, \quad \text{(S.41)}
\end{aligned}
$$

where an integration by parts has been performed in the second term. Note that, since in practice f depends on $(\nabla n)^2$, the derivative $\partial f / \partial \nabla n$ is calculated as

$$
\frac{\partial f}{\partial \nabla n} = \frac{\partial f}{\partial (\nabla n)^2} \frac{\mathrm{d}(\nabla n)^2}{\mathrm{d}\nabla n} = 2 \frac{\partial f}{\partial (\nabla n)^2} \nabla n. \quad \text{(S.42)}
$$

Exercise 15

For a one-electron system, there is only one occupied orbital, which can be explicitly written in terms of the density, $\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})}$, up to a unimportant phase factor. It is then immediate to check that the kinetic energy density of such a system is the von Weizsäcker kinetic energy density:

$$
\tau^{\text{1-elec}}(\mathbf{r}) = \frac{1}{2} |\nabla \phi(\mathbf{r})|^2 = \frac{1}{2} \left(\nabla \sqrt{n(\mathbf{r})} \right)^2 = \frac{1}{2} \left(\frac{\nabla n(\mathbf{r})}{2\sqrt{n(\mathbf{r})}} \right)^2 = \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})} = \tau^{\text{W}}(\mathbf{r}). \quad \text{(S.43)}
$$

Note that, for a two-electron closed-shell system, there is also only one occupied KS spatial orbital, $\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}$, and it is easy to show that the *non-interacting* kinetic energy density is again the von Weizsäcker kinetic energy density.

Exercise 16

The variation of the HF exchange energy [Eq. (3.18)] due to a variation of $\phi_{i\sigma}^*(\mathbf{r})$ is

$$
\begin{aligned}
\delta E_{\text{x}}^{\text{HF}} &= -\frac{1}{2} \sum_{j=1}^{N_\sigma} \iint \frac{\delta\phi_{i\sigma}^*(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \\
&\quad -\frac{1}{2} \sum_{j=1}^{N_\sigma} \iint \frac{\phi_{j\sigma}^*(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_1)\delta\phi_{i\sigma}^*(\mathbf{r}_2)\phi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \\
&= -\sum_{j=1}^{N_\sigma} \iint \frac{\delta\phi_{i\sigma}^*(\mathbf{r}_1)\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \quad \text{(S.44)}
\end{aligned}
$$

and the functional derivative is thus

$$
\frac{\delta E_{\text{x}}^{\text{HF}}}{\delta\phi_{i\sigma}^*(\mathbf{r}_1)} = -\sum_{j=1}^{N_\sigma} \int \frac{\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \mathrm{d}\mathbf{r}_2 = \int v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2) \mathrm{d}\mathbf{r}_2, \quad \text{(S.45)}
$$

where $v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)$ is the nonlocal HF exchange potential

$$
v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = -\sum_{j=1}^{N_\sigma} \frac{\phi_{j\sigma}(\mathbf{r}_1)\phi_{j\sigma}^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad \text{(S.46)}
$$

Alternatively, the functional derivative of Eq. (S.45) can be reformulated as $\delta E_{\text{x}}^{\text{HF}}/\delta\phi_{i\sigma}^*(\mathbf{r}_1) = v_{\text{x},i\sigma}^{\text{HF}}(\mathbf{r}_1)\phi_{i\sigma}(\mathbf{r}_1)$ where $v_{\text{x},i\sigma}^{\text{HF}}(\mathbf{r})$ is a local HF exchange potential depending on each orbital it acts on

$$
v_{\text{x},i\sigma}^{\text{HF}}(\mathbf{r}_1) = \frac{1}{\phi_{i\sigma}(\mathbf{r}_1)} \int v_{\text{x},\sigma}^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2) \mathrm{d}\mathbf{r}_2. \quad \text{(S.47)}
$$

Exercise 17

The error function is written as $\text{erf}(x) = (2/\sqrt{\pi})F(x)$ with $F(x) = \int_0^x e^{-t^2}\mathrm{d}t$. Its Taylor expansion for $x \to 0$ is

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}}\left(F(0) + F'(0)x + \cdots\right). \tag{S.48}$$

We have $F(0) = 0$, and since $F'(x) = e^{-x^2}$, we have $F'(0) = 1$, leading to $\text{erf}(x) \underset{x \to 0}{\sim} (2/\sqrt{\pi})x$. The limit $x \to +\infty$ is easily obtained by using the Gaussian integral $\int_0^{+\infty} e^{-t^2}\mathrm{d}t = \sqrt{\pi}/2$, leading to $\text{erf}(x) \xrightarrow[x \to +\infty]{} 1$.

Exercise 18

According to standard first-order perturbation theory, if a perturbation $v_{\rm s}(\mathbf{r}) \to v_{\rm s}(\mathbf{r}) + \delta v_{\rm s}(\mathbf{r})$ is applied on the KS system, the first-order variation of the orbital $\phi_{i\sigma}(\mathbf{r}')$ (assumed to be nondegenerate) is

$$\delta\phi_{i\sigma}(\mathbf{r}') = -\sum_{\substack{p=1 \\ p \neq i}}^{M} \frac{\int \phi_{p\sigma}^*(\mathbf{r})\delta v_{\rm s}(\mathbf{r})\phi_{i\sigma}(\mathbf{r})\mathrm{d}\mathbf{r}}{\varepsilon_{p\sigma} - \varepsilon_{i\sigma}}\phi_{p\sigma}(\mathbf{r}'), \tag{S.49}$$

where the sum is over all spatial orbitals p different from orbital i but of the same spin. The functional derivative of $\phi_{i\sigma}(\mathbf{r}')$ with respect to $v_{\rm s}(\mathbf{r})$ is thus

$$\frac{\delta\phi_{i\sigma}(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})} = -\sum_{\substack{p=1 \\ p \neq i}}^{M} \frac{\phi_{p\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}{\varepsilon_{p\sigma} - \varepsilon_{i\sigma}}\phi_{p\sigma}(\mathbf{r}'). \tag{S.50}$$

This result can be used to calculate the expression of $\chi_0(\mathbf{r}', \mathbf{r})$

$$
\begin{aligned}
\chi_0(\mathbf{r}', \mathbf{r}) = \frac{\delta n(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})} &= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\left[\phi_{i\sigma}^*(\mathbf{r}')\frac{\delta\phi_{i\sigma}(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})} + \text{ c.c.}\right] \\
&= -\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\sum_{\substack{p=1 \\ p \neq i}}^{M}\left[\phi_{i\sigma}^*(\mathbf{r}')\frac{\phi_{p\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r})}{\varepsilon_{p\sigma} - \varepsilon_{i\sigma}}\phi_{p\sigma}(\mathbf{r}') + \text{ c.c.}\right].
\end{aligned} \tag{S.51}
$$

The last sum can be simplified by decomposing it as $\sum_{i=1}^{N_\sigma}\sum_{p=1,p\neq i}^{M} = \sum_{i=1}^{N_\sigma}\sum_{p=1,p\neq i}^{N_\sigma} + \sum_{i=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}$ and realizing that the double sum $\sum_{i=1}^{N_\sigma}\sum_{p=1,p\neq i}^{N_\sigma}$ is zero because the summand inside the square bracket is antisymmetric with respect to the exchange of i and p. We thus arrive at the expected expression

$$\chi_0(\mathbf{r}', \mathbf{r}) = -\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}\frac{\phi_{i\sigma}^*(\mathbf{r}')\phi_{a\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r})\phi_{a\sigma}(\mathbf{r}')}{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}} + \text{ c.c. .} \tag{S.52}$$

As regards the functional derivative of $E_{\rm x}$ with respect to $v_{\rm s}(\mathbf{r})$, it is obtained by using chain rule with the orbitals and using Eqs. (S.45), (S.46), and (S.50)

$$
\begin{aligned}
\frac{\delta E_{\rm x}}{\delta v_{\rm s}(\mathbf{r})} &= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\int \frac{\delta E_{\rm x}}{\delta\phi_{i\sigma}^*(\mathbf{r}_1)}\frac{\delta\phi_{i\sigma}^*(\mathbf{r}_1)}{\delta v_{\rm s}(\mathbf{r})}\mathrm{d}\mathbf{r}_1 + \text{ c.c.} \\
&= -\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\sum_{\substack{p=1 \\ p \neq i}}^{M}\iint v_{{\rm x},\sigma}^{\rm HF}(\mathbf{r}_1,\mathbf{r}_2)\phi_{i\sigma}(\mathbf{r}_2)\frac{\phi_{p\sigma}(\mathbf{r})\phi_{i\sigma}^*(\mathbf{r})}{\varepsilon_{p\sigma} - \varepsilon_{i\sigma}}\phi_{p\sigma}^*(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 + \text{ c.c.} \\
&= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_\sigma}\sum_{\substack{p=1 \\ p \neq i}}^{M}\left[(\phi_{p\sigma}\phi_{j\sigma}|\phi_{j\sigma}\phi_{i\sigma})\frac{\phi_{p\sigma}(\mathbf{r})\phi_{i\sigma}^*(\mathbf{r})}{\varepsilon_{p\sigma} - \varepsilon_{i\sigma}} + \text{ c.c.}\right] \\
&= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{N_\sigma}\sum_{j=1}^{N_\sigma}\sum_{a=N_\sigma+1}^{M}(\phi_{a\sigma}\phi_{j\sigma}|\phi_{j\sigma}\phi_{i\sigma})\frac{\phi_{a\sigma}(\mathbf{r})\phi_{i\sigma}^*(\mathbf{r})}{\varepsilon_{a\sigma} - \varepsilon_{i\sigma}} + \text{ c.c. ,}
\end{aligned} \tag{S.53}
$$

where again it was used that $\sum_{i=1}^{N_\sigma} \sum_{p=1, p\neq i}^{M} = \sum_{i=1}^{N_\sigma} \sum_{p=1, p\neq i}^{N_\sigma} + \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{M} = \sum_{i=1}^{N_\sigma} \sum_{a=N_\sigma+1}^{M}$ since the summand inside the square bracket is antisymmetric with respect to the exchange of i and p.

Exercise 19

In the GL2 correlation energy expression of Eq. (4.11), only double and single excitations contribute

$$E_c^{\text{GL2}} = -\sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{a=N+1}^{2M} \sum_{b=a+1}^{2M} \frac{|\langle \Phi | \hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}} | \Phi_{ij}^{ab} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} - \sum_{i=1}^{N} \sum_{a=N+1}^{2M} \frac{|\langle \Phi | \hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}} | \Phi_i^a \rangle|^2}{\varepsilon_a - \varepsilon_i}. \quad (S.54)$$

Applying the standard Slater's rules, $\langle \Phi | \hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}} | \Phi_{ij}^{ab} \rangle = \langle \Phi | \hat{W}_{\text{ee}} | \Phi_{ij}^{ab} \rangle = \langle ij || ab \rangle$, the first term gives the MP2-like contribution

$$E_c^{\text{MP2}} = -\sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{a=N+1}^{2M} \sum_{b=a+1}^{2M} \frac{|\langle \psi_i \psi_j || \psi_a \psi_b \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} = -\frac{1}{4} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{a=N+1}^{2M} \sum_{b=N+1}^{2M} \frac{|\langle \psi_i \psi_j || \psi_a \psi_b \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \quad (S.55)$$

As regards the second term, using $\langle \Phi | \hat{W}_{\text{ee}} - \hat{V}_{\text{Hx}} | \Phi_i^a \rangle = \sum_{j=1}^{N} \langle \psi_i \psi_j || \psi_a \psi_j \rangle - \langle \psi_i | \hat{V}_{\text{Hx}} | \psi_a \rangle = \langle \psi_i | \hat{V}_{\text{Hx}}^{\text{HF}} - \hat{V}_{\text{Hx}} | \psi_a \rangle = \langle \psi_i | \hat{V}_{\text{x}}^{\text{HF}} - \hat{V}_{\text{x}} | \psi_a \rangle$, we find the expected expression

$$E_c^{\text{S}} = -\sum_{i=1}^{N} \sum_{a=N+1}^{2M} \frac{|\langle \psi_i | \hat{V}_{\text{x}}^{\text{HF}} - \hat{V}_{\text{x}} | \psi_a \rangle|^2}{\varepsilon_a - \varepsilon_i}. \quad (S.56)$$

Exercise 20

The linear-response function of Eq. (4.19) can be written as

$$
\begin{aligned}
i\chi_\lambda(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \quad & \theta(t_1 - t_2) \langle \Psi^\lambda | e^{i\hat{H}^\lambda t_1} \hat{n}(\mathbf{r}_1) e^{-i\hat{H}^\lambda t_1} e^{i\hat{H}^\lambda t_2} \hat{n}(\mathbf{r}_2) e^{-i\hat{H}^\lambda t_2} | \Psi^\lambda \rangle \\
& + \theta(t_2 - t_1) \langle \Psi^\lambda | e^{i\hat{H}^\lambda t_2} \hat{n}(\mathbf{r}_2) e^{-i\hat{H}^\lambda t_2} e^{i\hat{H}^\lambda t_1} \hat{n}(\mathbf{r}_1) e^{-i\hat{H}^\lambda t_1} | \Psi^\lambda \rangle \\
& - \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle,
\end{aligned}
\quad (S.57)
$$

or, after introducing a complete set of orthornormal eigenstates of the Hamiltonian, $\hat{H}^\lambda | \Psi_n^\lambda \rangle = E_n^\lambda | \Psi_n^\lambda \rangle$ (with $\Psi_0^\lambda = \Psi^\lambda$),

$$
\begin{aligned}
i\chi_\lambda(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \quad & \theta(t_1 - t_2) \sum_n \langle \Psi^\lambda | e^{i\hat{H}^\lambda t_1} \hat{n}(\mathbf{r}_1) e^{-i\hat{H}^\lambda t_1} | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | e^{i\hat{H}^\lambda t_2} \hat{n}(\mathbf{r}_2) e^{-i\hat{H}^\lambda t_2} | \Psi^\lambda \rangle \\
& + \theta(t_2 - t_1) \sum_n \langle \Psi^\lambda | e^{i\hat{H}^\lambda t_2} \hat{n}(\mathbf{r}_2) e^{-i\hat{H}^\lambda t_2} | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | e^{i\hat{H}^\lambda t_1} \hat{n}(\mathbf{r}_1) e^{-i\hat{H}^\lambda t_1} | \Psi^\lambda \rangle \\
& - \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle.
\end{aligned}
\quad (S.58)
$$

After applying the Hamiltonian $\hat{H}^\lambda$ on its eigenstates, it is apparent that $\chi_\lambda(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)$ only depends on $\tau = t_1 - t_2$

$$
\begin{aligned}
i\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau) = \quad & \theta(\tau) \sum_n \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle e^{-i\omega_n^\lambda \tau} \\
& + \theta(-\tau) \sum_n \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle e^{i\omega_n^\lambda \tau} \\
& - \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle,
\end{aligned}
\quad (S.59)
$$

where $\omega_n^\lambda = E_n^\lambda - E_0^\lambda$ are the excitation energies. Since the last term in Eq. (S.59) just corresponds to the $n = 0$ contribution from the sums, we finally find

$$
\begin{aligned}
i\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau) = \quad & \theta(\tau) \sum_{n \neq 0} \langle \Psi^\lambda | \hat{n}(\mathbf{r}_1) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_2) | \Psi^\lambda \rangle e^{-i\omega_n^\lambda \tau} \\
& + \theta(-\tau) \sum_{n \neq 0} \langle \Psi^\lambda | \hat{n}(\mathbf{r}_2) | \Psi_n^\lambda \rangle \langle \Psi_n^\lambda | \hat{n}(\mathbf{r}_1) | \Psi^\lambda \rangle e^{i\omega_n^\lambda \tau}.
\end{aligned}
\quad (S.60)
$$

Using the Fourier-transform formulas for the Heaviside step function, $\theta(\tau) = -1/(2\pi i) \int_{-\infty}^{\infty} d\omega \, e^{-i\omega\tau}/(\omega + i0^+)$ and $\theta(\tau) = 1/(2\pi i) \int_{-\infty}^{\infty} d\omega \, e^{-i\omega\tau}/(\omega - i0^+)$, we can express $i\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau)$ as

$$
\begin{aligned}
i\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau) &= -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \sum_{n\neq 0} \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_1)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_2)|\Psi^\lambda\rangle}{\omega + i0^+} e^{-i(\omega+\omega_n^\lambda)\tau} \\
&\quad + \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \sum_{n\neq 0} \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle}{\omega - i0^-} e^{-i(\omega-\omega_n^\lambda)\tau},
\end{aligned}
$$
(S.61)

which, after making the substitutions $\omega \to \omega - \omega_n^\lambda$ and $\omega \to \omega + \omega_n^\lambda$ in the first and second integrals, respectively, can be recast in the form

$$
\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} \sum_{n\neq 0} \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_1)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_2)|\Psi^\lambda\rangle}{\omega - \omega_n^\lambda + i0^+} - \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle}{\omega + \omega_n^\lambda - i0^-},
$$
(S.62)

meaning that the Fourier transform of $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \tau)$ is

$$
\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{n\neq 0} \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_1)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_2)|\Psi^\lambda\rangle}{\omega - \omega_n^\lambda + i0^+} - \frac{\langle \Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle}{\omega + \omega_n^\lambda - i0^-}.
$$
(S.63)

After extending the function $\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$ on the ω-complex plane by analytic continuation, and noting that the integral of $e^{i\omega 0^+}\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$ is zero on the infinite upper semi-circle C according to Jordan's lemma (since $|\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)|$ goes to zero when $|\omega| \to +\infty$), the integral of $e^{i\omega 0^+}\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega)$ over the real axis $]-\infty, +\infty[$ is identical to the integral over the closed path $\gamma =]-\infty, +\infty[\cup C$

$$
\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega 0^+} \chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) = \oint_\gamma \frac{d\omega}{2\pi i} e^{i\omega 0^+} \chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega).
$$
(S.64)

Only the second term in Eq. (S.63) gives poles in the upper-half of the complex plane, $\omega = -\omega_n^\lambda + i0^-$, enclosed by γ, therefore according to the residue theorem only their associated residues contribute to the integral

$$
\begin{aligned}
\oint_\gamma \frac{d\omega}{2\pi i} e^{i\omega 0^+} \chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) &= -\sum_{n\neq 0} \langle\Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle \\
&= -\left[\sum_n \langle\Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi_n^\lambda\rangle\langle\Psi_n^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle - \langle\Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi^\lambda\rangle\langle\Psi^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle\right] \\
&= -\left[\langle\Psi^\lambda|\hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle - \langle\Psi^\lambda|\hat{n}(\mathbf{r}_2)|\Psi^\lambda\rangle\langle\Psi^\lambda|\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle\right].
\end{aligned}
$$
(S.65)

We thus correctly recover the fluctuation-dissipation theorem of Eq. (4.23)

$$
\begin{aligned}
-\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega 0^+} [\chi_\lambda(\mathbf{r}_1, \mathbf{r}_2; \omega) - \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega)] &= \langle\Psi^\lambda|\hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1)|\Psi^\lambda\rangle - \langle\Phi|\hat{n}(\mathbf{r}_2)\hat{n}(\mathbf{r}_1)|\Phi\rangle \\
&= n_{2,c}^\lambda(\mathbf{r}_1, \mathbf{r}_2).
\end{aligned}
$$
(S.66)

Exercise 21
The variation of $F[f]$ induced by a variation of $f(x)$ is

$$
\begin{aligned}
\delta F[f] &= \int \left[\frac{\partial h}{\partial f(x)}\delta f(x) + \frac{\partial h}{\partial f'(x)}\delta f'(x) + \frac{\partial h}{\partial f''(x)}\delta f''(x) + \cdots + \frac{\partial h}{\partial f^{(n)}(x)}\delta f^{(n)}(x)\right] dx \\
&= \int \left[\frac{\partial h}{\partial f(x)} - \frac{d}{dx}\left(\frac{\partial h}{\partial f'(x)}\right) + \frac{d^2}{dx^2}\left(\frac{\partial h}{\partial f''(x)}\right) + \cdots + (-1)^n \frac{d^n}{dx^n}\left(\frac{\partial h}{\partial f^{(n)}(x)}\right)\right] \delta f(x) dx,
\end{aligned}
$$
(S.67)

where, in the nth-order term, it was used that $\delta f^{(n)}(x) = [\delta f(x)]^{(n)}$ (since differentiation is a linear operation) and n consecutive integrations by parts were performed (and assuming that all boundary terms vanish). The functional derivative is thus

$$\frac{\delta F[f]}{\delta f(x)} \;=\; \frac{\partial h}{\partial f(x)} - \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial h}{\partial f'(x)}\right) + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(\frac{\partial h}{\partial f''(x)}\right) + \cdots + (-1)^n \frac{\mathrm{d}^n}{\mathrm{d}x^n}\left(\frac{\partial h}{\partial f^{(n)}(x)}\right). \qquad \text{(S.68)}$$

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