Reduced quantity functional theories: DFT and beyond

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Do we actually need the $N$-electron wavefunction?

- The exact ground-state energy of an electronic system can be obtained variationally, $E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$, or by solving the Schrödinger equation, $\hat{H} | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$.

- In both formulations (variational or non-variational), the basic variable is the electronic wavefunction $\Psi$.

- The expression of the electronic Hamiltonian (which only contains one- and two-body terms) and the fact that electrons are indistinguishable (fermionic) particles greatly simplifies the energy expression.

- In the "$r$ representation" (real space):

$$\hat{H} = -\frac{1}{2} \int \int drdr' \delta(r - r') \nabla_r^2 \hat{n}_1(r, r') + \frac{1}{2} \int \int drdr' \frac{\hat{n}_2(r, r')}{|r - r'|} + \int dr \, v_{ne}(r) \, \hat{n}(r)$$

where

$$\hat{n}_1(r, r') = \sum_{\sigma} \hat{\Psi}^\dagger(r\sigma) \hat{\Psi}(r'\sigma)$$

$$\hat{n}(r) = \hat{n}_1(r, r)$$

$$\hat{n}_2(r, r') = \sum_{\sigma, \sigma'} \hat{\Psi}^\dagger(r\sigma) \hat{\Psi}^\dagger(r'\sigma') \hat{\Psi}(r'\sigma') \hat{\Psi}(r\sigma)$$
Do we actually need the $N$-electron wavefunction?

- As readily seen, the expectation value for the energy $\langle \Psi | \hat{H} | \Psi \rangle$ is an explicit functional of the one-electron density matrix
  
  $$n^\Psi_1(r, r') = \langle \Psi | \hat{n}_1(r, r') | \Psi \rangle$$

  and the pair density

  $$n^\Psi_2(r, r') = \langle \Psi | \hat{n}_2(r, r') | \Psi \rangle.$$ 

- Note that both quantities are needed. In other words, the one-electron density matrix cannot be obtained from the pair density.

- If we want to use a single quantity, then we need to consider the more general 3-position function $n^\Psi_2(r, r', r'') = \langle \Psi | \hat{n}_2(r, r', r'') | \Psi \rangle$ where

  $$\hat{n}_2(r, r', r'') = \sum_{\sigma \sigma'} \hat{\Psi}^\dagger(r\sigma) \hat{\Psi}^\dagger(r' \sigma') \hat{\Psi}(r' \sigma') \hat{\Psi}(r'' \sigma)$$

  $$= \hat{n}_1(r, r'') \hat{n}(r') - \delta(r' - r'') \hat{n}_1(r, r'),$$

  thus leading to

  $$\int dr' \ n^\Psi_2(r, r', r'') = (N - 1) \times n^\Psi_1(r, r'')$$

  since

  $$\int dr' \ \hat{n}(r') |\Psi\rangle = N |\Psi\rangle.$$ 

  Moreover

  $$n^\Psi_2(r, r') = n^\Psi_2(r', r, r).$$
Do we actually need the $N$-electron wavefunction?

- Let us return to our main result: the exact ground-state (or excited-state) energy can be determined from two 2-position functions, namely the one-electron density matrix and the pair density.

- Regarding the two-electron interaction contribution, note that we could even use a function of the electron-electron distance (intracule density) rather than the pair density.

- Most importantly, in principle, we do not need the $N$-electron ground-state (anti-symmetrized and normalized) wavefunction

$$\Psi_0(r_1\sigma_1, r_2\sigma_2, \ldots, r_N\sigma_N)$$

for calculating the ground-state energy. What we need are $n_1^{\Psi_0}(r, r')$ and $n_2^{\Psi_0}(r, r')$.

- As readily seen, these two quantities depend on two electron positions whatever the number of electrons. Obviously, some information is "lost" when switching from $\Psi_0$ to $n_1^{\Psi_0}(r, r')$ and $n_2^{\Psi_0}(r, r')$, hence the name **reduced quantities**.
Do we actually need the $N$-electron wavefunction?

- The "reduction" becomes more apparent when writing the normalized ground-state quantum state as

$$|\psi_0\rangle = \frac{1}{\sqrt{N!}} \sum_{\sigma_1...\sigma_N} \int \! dr_1 \ldots \int \! dr_N \, \psi_0(r_1\sigma_1, \ldots, r_N\sigma_N) \hat{\psi}^\dagger(r_1\sigma_1) \ldots \hat{\psi}^\dagger(r_N\sigma_N) |\text{vac}\rangle,$$

thus leading to, for the one-electron density matrix,

$$n^{\psi_0}_1 (r, r') = \sum_{\sigma} \langle \psi_0 | \hat{\psi}^\dagger (r\sigma) \hat{\psi} (r'\sigma) | \psi_0 \rangle$$

$$= N \sum_{\sigma} \sum_{\sigma_2 \ldots \sigma_N} \int \! dr_2 \ldots \int \! dr_N \, \psi_0^* (r\sigma, r_2\sigma_2, \ldots, r_N\sigma_N) \psi_0 (r'\sigma, r_2\sigma_2, \ldots, r_N\sigma_N),$$

and, for the pair density,

$$n^{\psi_0}_2 (r, r') = \sum_{\sigma \sigma'} \langle \psi_0 | \hat{\psi}^\dagger (r\sigma) \hat{\psi}^\dagger (r'\sigma') \hat{\psi} (r'\sigma') \hat{\psi} (r\sigma) | \psi_0 \rangle$$

$$= N(N - 1) \sum_{\sigma \sigma'} \sum_{\sigma_3 \ldots \sigma_N} \int \! dr_3 \ldots \int \! dr_N \, |\psi_0 (r\sigma, r'\sigma', r_3\sigma_3, \ldots, r_N\sigma_N)|^2.$$
Do we actually need the $N$-electron wavefunction?

- Let us stress that, once again, if the one-electron density matrix and the pair density are used as **basic variables**, the energy functional is known and its **explicit expression** is

$$ E[n_1, n_2] = -\frac{1}{2} \int \int \, dr \, dr' \, \delta(r - r') \nabla_r^2 n_1(r, r') + \frac{1}{2} \int \int \, dr \, dr' \, \frac{n_2(r, r')}{|r - r'|} $$

$$ + \int \, dr \, \nu_{ne}(r) \, n_1(r, r). $$

- Note that, by **differentiating** the energy with respect to some perturbation strength (nuclear displacement, electric or magnetic field, ...), one can in principle have access to (static) molecular response properties.

- An important question should be raised at this point: is it possible to calculate the energy **variationally** (*i.e.* by straight minimization) from the energy functional?

- Obviously, if there are no constraint on $n_1$ and $n_2$, the answer is NO!

- Indeed, by considering the particular case $n_1(r, r') = 0$ and $n_2(r, r') \to -\infty$, we obtain

$$ \min_{n_1, n_2} E[n_1, n_2] = -\infty. $$

- This case is **unphysical**. The minimization should be performed under constraint.
\textbf{\textit{N}-representability conditions}

- If we want to recover the true ground-state energy \( E_0 \) from the energy functional \( E[n_1, n_2] \) we must restrict the minimization to physical (so-called \( \text{N-} \)representable) one-electron density matrices and pair densities.

- A one-electron density matrix \( n_1 \) and a pair density \( n_2 \) are \( \text{N-} \)-representable if there exists an \( \text{N-} \)-electron (anti-symmetrized and normalized) wavefunction \( \Psi \) (with finite kinetic energy) such that

\[
\begin{align*}
n_1(r, r') &= n_\Psi^1(r, r') = \langle \Psi | \hat{n}_1(r, r') | \Psi \rangle, \\
n_2(r, r') &= n_\Psi^2(r, r') = \langle \Psi | \hat{n}_2(r, r') | \Psi \rangle.
\end{align*}
\]

- \textbf{Variational principle} under \( \text{N-} \)-representability constraints:

\[
\begin{align*}
E_0 &= \min_\Psi \langle \Psi | \hat{H} | \Psi \rangle \\
&= \min_\Psi E[n_\Psi^1, n_\Psi^2].
\end{align*}
\]

- \textbf{Basic \( \text{N-} \)-representability conditions:} \( n_\Psi^1(r, r) \) (electron density) and the pair density are positive functions and they integrate to \( N \) and \( N(N - 1) \), respectively:

\[
\int dr \ n_\Psi^1(r, r) = N, \quad \int \int drdr' \ n_\Psi^2(r, r') = N(N - 1).
\]
Explicit and implicit dependence on the electron density

- Density-functional theory (DFT) is using the electron density \( n^\Psi(r) = n^\Psi_1(r, r) \) as basic variable without actually knowing the \( N \)-electron wavefunction \( \Psi \).

- It can be shown that the set of \( N \)-representable densities is the set of positive functions \( n(r) \) that integrate to the number of electrons \( N \) and that give a finite von Weizsäcker kinetic energy*:

\[
\frac{1}{2} \int \, \text{d}r \, \left| \nabla n^{1/2}(r) \right|^2 < +\infty.
\]

- Even though the domain of ”physical densities” is well identified (which is good), both kinetic and electronic repulsion energies are implicit functionals of the density (which is bad).

- The Hohenberg–Kohn variational principle for the Hamiltonian \( \hat{H}[\nu] = \hat{T} + \hat{W}_{\text{ee}} + \int \, \text{d}r \, \nu(r) \hat{n}(r) \) with ground-state energy \( E[\nu] \) reads

\[
E[\nu] = \min_n \left\{ F[n] + \int \, \text{d}r \, \nu(r)n(r) \right\} \quad \Leftrightarrow \quad F[n] = \max_\nu \left\{ E[\nu] - \int \, \text{d}r \, \nu(r)n(r) \right\}.
\]

What about using the one-electron density matrix as basic variable?

By expanding the field operators in an orthonormal orbital basis (and using real algebra) we obtain within a spin-restricted formalism

\[ n^\psi_1 (r, r') = \sum_{pq} \phi_p(r) \phi_q(r') \langle \psi | \hat{E}_{pq} | \psi \rangle \]

orbital basis representation \( \rightarrow \)

\[ D^\psi_{pq} = \sum_\sigma \langle \psi | \hat{a}_{p\sigma}^\dagger \hat{a}_{q\sigma} | \psi \rangle = \sum_\sigma D^{p\sigma}_{q\sigma}. \]

\( D^\psi \) is hermitian. It can therefore be diagonalized, in the so-called natural orbital basis \( \{ \tilde{\phi}_p(r) \}_{p} \), thus leading to

\[ n^\psi_1 (r, r') = \sum_p \tilde{\phi}_p(r) \tilde{\phi}_p(r') \tilde{n}_p \quad \text{where} \quad 0 \leq \tilde{n}_p \leq 2. \]

\( N \)-representable one-electron density matrices can therefore be parametrized in terms of natural orbitals and occupation numbers (both have to be determined).
Explicit functionals versus clear representability conditions

- In one-electron reduced density-matrix functional theory (or natural orbital functional theory if the previous parameterization is used), both exact kinetic and nuclear potential energy functionals are known (explicitly).

- The electronic repulsion energy remains an implicit functional of the one-electron reduced density matrix (1-RDM) for which approximations must be developed.

- Finally, we could use the two-electron reduced density matrix (2-RDM) as basic variable. Its representation in an orthonormal orbital basis is

\[
D_{pqrs}^\Psi = \langle \psi | \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} | \psi \rangle = \sum_{\sigma \sigma'} \langle \psi | \hat{a}_p^{\dagger} \hat{a}_r^{\dagger} \hat{a}_s \hat{a}_q | \psi \rangle = \sum_{\sigma \sigma'} D_{q \sigma \sigma'}^{p \sigma r \sigma'}.
\]

- Since \( \langle \psi | \hat{H} | \psi \rangle = \sum_{pq} h_{pq} D_{pq}^\Psi + \frac{1}{2} \sum_{pqrs} \langle pr | qs \rangle D_{pqrs}^\Psi \) where

\[
\sum_{r} D_{pqrr}^\Psi = (N - 1)D_{pq}^\Psi
\]

it comes that the total energy is an explicit functional of the 2-RDM. The challenge is then to identify \( N \)-representability conditions for the latter, which is far from trivial.

- **Conclusion:** A given reduced quantity will lead either to an explicit energy functional (2-RDM theory) or well-defined \( N \)-representability conditions (DFT) but never both at the same time :-(
Representability and higher-order reduced density matrices

- Ground-state $p$-electron reduced density matrix ($p$-RDM) elements in a given orthonormal spin-orbital basis ($1 \leq p \leq N$):

$$D_{I_1 I_2 \ldots I_p}^{J_1 J_2 \ldots J_p} = \left\langle \Psi_0 \left| \hat{a}_{I_1}^\dagger \hat{a}_{J_1}^\dagger \ldots \hat{a}_{I_p}^\dagger \hat{a}_{J_p} \ldots \hat{a}_{I_2} \hat{a}_{I_1} \right| \Psi_0 \right\rangle.$$ 

- The ground-state energy is a functional of the 2-RDM.

- The latter is in principle deduced from the ground-state wavefunction $\Psi_0$ which is completely determined by the $N$-RDM.

- Indeed, from the full configuration interaction (FCI) expansion,

$$|\Psi_0\rangle = \sum_{I_1 < I_2 < \ldots < I_N} C_{I_1 I_2 \ldots I_N} \hat{a}_{I_1}^\dagger \hat{a}_{I_2}^\dagger \ldots \hat{a}_{I_N}^\dagger |\text{vac}\rangle,$$

it comes

$$D_{I_1 I_2 \ldots I_N}^{J_1 J_2 \ldots J_N} = C_{J_1 J_2 \ldots J_N} C_{I_1 I_2 \ldots I_N}.$$ 

- Therefore, $|C_{I_1 I_2 \ldots I_N}| = \sqrt{D_{I_1 I_2 \ldots I_N}^{J_1 J_2 \ldots J_N}}$. The sign is determined from the $N$-RDM by fixing the sign of one single coefficient.
Representability and higher-order reduced density matrices

- Rewriting the FCI expansion as $|\Psi_0\rangle = \sum_{\mathcal{I}} C_{\mathcal{I}} |\det_{\mathcal{I}}\rangle$ leads to the following expression for the $p$-RDM elements,

$$D_{I_1 I_2 \ldots I_p}^{J_1 J_2 \ldots J_p} = \sum_{\mathcal{I}, \mathcal{J}} C_{\mathcal{I}} C_{\mathcal{J}} \left\langle \det \mathcal{J} \left| \hat{a}_{J_1}^{\dagger} \hat{a}_{J_2}^{\dagger} \ldots \hat{a}_{J_p}^{\dagger} \hat{a}_{I_p} \ldots \hat{a}_{I_2} \hat{a}_{I_1} \right| \det \mathcal{I} \right\rangle$$

known (anti-commutation rules)

- A $p$-RDM is $N$-representable if it can be written as above with the normalization condition $\sum_{\mathcal{I}} C_{\mathcal{I}}^2 = 1$.

- Let us focus on the 2-RDM elements:

$$D_{I_1 I_2}^{J_1 J_2} = \sum_{\mathcal{I}, \mathcal{J}} C_{\mathcal{I}} C_{\mathcal{J}} \left\langle \det \mathcal{J} \left| \hat{a}_{J_1}^{\dagger} \hat{a}_{J_2}^{\dagger} \hat{a}_{I_2} \hat{a}_{I_1} \right| \det \mathcal{I} \right\rangle.$$  

In contrast to the $N$-RDM, many $C_{\mathcal{I}}$ coefficients will contribute!

- Obviously, we do not want to parametrize the 2-RDM with these coefficients (this would simply correspond to making a FCI calculation).
Instead, we want to use the 2-RDM elements $D_{J_1J_2}^{I_1I_2}$ as basic variables.

The $N$-representability is connected to the fact that the $N$-RDM elements can be written as $D_{I_1I_2...I_N}^{J_1J_2...J_N} = C_{J_1J_2...J_N} C_{I_1I_2...I_N}$.

The higher the order $p$ of the RDM is, the more we know about the wavefunction $\Psi_0$ and the higher the control on the $N$-representability of the 2-RDM is.

Connections between the 2-RDM and the higher-order RDMs can be established from the so-called anti-Hermitian contracted Schrödinger equation* (ACSE).

The ACSE is obtained by projection (nonvariational approach).

As discussed further in the following, the ACSE can also be used in 1-RDM theory, thus providing interesting formal connections between RDM and Green’s functions formalisms.

Connecting 1-RDM and Green’s function formalisms

- We would like to derive an equation for the ground-state 1-RDM that would be the analog of the equation of motion for the one-electron Green’s function (1-GF).

- Let us start with the Schrödinger equation $\hat{H}|\psi_0\rangle = E_0|\psi_0\rangle$, apply a one-electron excitation $\hat{a}_I^\dagger \hat{a}_J$ on both sides and project onto $\psi_0$, thus leading to

$$\left\langle \psi_0 \right| \hat{a}_I^\dagger \hat{a}_J \hat{H} \left| \psi_0 \right\rangle = E_0 \left\langle \psi_0 \right| \hat{a}_I^\dagger \hat{a}_J \left| \psi_0 \right\rangle$$

$$D^I_J \leftarrow \text{exact 1-RDM}!$$

- The latter projection onto the one-electron space is usually referred to as contraction, hence the name Contracted Schrödinger Equation (CSE).

- Using $\hat{H} = \sum_{KL} h_{KL} \hat{a}_K^\dagger \hat{a}_L + \frac{1}{2} \sum_{KLMN} \langle KL | MN \rangle \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M$ leads to

$$\sum_L h_{JL} D^I_L - \sum_{KL} h_{KL} D^{IK}_{LJ} + \frac{1}{2} \sum_{KMN} \langle JK || MN \rangle D^{IK}_{MN} + \frac{1}{2} \sum_{KLMN} \langle KL | MN \rangle D^{IKL}_{MNJ} = E_0 D^I_J$$

where $\langle JK || MN \rangle = \langle JK | MN \rangle - \langle KJ | MN \rangle$. 
Connecting 1-RDM and Green’s function formalisms

- As readily seen, it is far from straightforward to obtain the 1-RDM from the CSE.
- Indeed, we need the (unknown) exact ground-state energy $E_0$.
- Moreover, we need the 2- and 3-RDMs.
- It is actually more convenient to split the CSE as follows,
  \[ \mathcal{H}_J^I = \langle \psi_0 \left| \hat{a}_I^\dagger \hat{a}_J \hat{H} \right| \psi_0 \rangle = \frac{1}{2} \langle \psi_0 \left| [\hat{a}_I^\dagger \hat{a}_J, \hat{H}] \right| \psi_0 \rangle + \frac{1}{2} \langle \psi_0 \left| [\hat{a}_I^\dagger \hat{a}_J, \hat{H}] + \hat{H} \right| \psi_0 \rangle = E_0 D_J^I, \]
  \[ \mathcal{H}_J^I - \mathcal{H}_I^J \quad \text{and} \quad \mathcal{H}_J^I + \mathcal{H}_I^J \]
- The anti-Hermitian part of the CSE (ACSE) reads
  \[ \langle \psi_0 \left| [\hat{a}_I^\dagger \hat{a}_J, \hat{H}] \right| \psi_0 \rangle = 0. \]
- The advantage of using the ACSE is that the commutator of $\hat{a}_I^\dagger \hat{a}_J$ with $\hat{H}$ will generate one- and two-electron excitations only, thus making the connection between the 1-RDM and the 2-RDM explicit.
EXERCISE: By using the relations

\[
[\hat{A}, \hat{B} \hat{C}] = [\hat{A}, \hat{B}] \hat{C} + \hat{B} [\hat{A}, \hat{C}] = [\hat{A}, \hat{B}] \hat{C} - \hat{B} [\hat{A}, \hat{C}],
\]

show that

\[
[\hat{a}_I^{\dagger} \hat{a}_J, \hat{a}_K^{\dagger} \hat{a}_L] = \delta_{JK} \hat{a}_I^{\dagger} \hat{a}_L - \delta_{IL} \hat{a}_K^{\dagger} \hat{a}_J \quad \text{and}
\]

\[
[\hat{a}_I^{\dagger} \hat{a}_J, \hat{a}_K^{\dagger} \hat{a}_L \hat{a}_N \hat{a}_M] = \delta_{JK} \hat{a}_I^{\dagger} \hat{a}_L \hat{a}_N \hat{a}_M + \delta_{JL} \hat{a}_K^{\dagger} \hat{a}_I^{\dagger} \hat{a}_N \hat{a}_M - \delta_{IN} \hat{a}_K^{\dagger} \hat{a}_L^{\dagger} \hat{a}_J \hat{a}_M - \delta_{IM} \hat{a}_K^{\dagger} \hat{a}_L^{\dagger} \hat{a}_N \hat{a}_J.
\]

From the second-quantized expression of the Hamiltonian and the ACSE we finally obtain (by using real algebra)

\[
\sum_K \left( D_K^I h_{KJ} - h_{IK} D_J^K \right) + \sum_{KLM} \left( \langle JM | LK \rangle D_{MI}^{KL} - \langle IM | LK \rangle D_{MJ}^{KL} \right) = 0
\]

\[
[D, h]_{IJ}
\]

As readily seen, the ACSE involves the 1- and 2-RDMS only :-)

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\[
[D, h]_{IJ} + \sum_{KLM} \left( \langle JM|LK\rangle D_{MI}^{KL} - \langle IM|LK\rangle D_{MJ}^{KL} \right) = 0
\]

- We can formally rewrite the latter equation in terms of the 1-RDM only simply by introducing a (frequency-independent) analog \(\Sigma\) of the self-energy matrix defined as follows,

\[
\left( \Sigma D \right)_{IJ} = \sum_{KLM} \langle IM|LK\rangle D_{MJ}^{KL},
\]

or, equivalently,

\[
\Sigma_{IP} = \sum_{KLMN} \langle IM|LK\rangle D_{MN}^{KL} \left[ D^{-1} \right]_{NP},
\]

thus leading to

\[
[D, h]_{IJ} + \left( \Sigma D \right)_{JI} - \left( \Sigma D \right)_{IJ} = 0 \quad \text{or, in a compact form,}
\]

\[
[D, h] + D \Sigma^\dagger - \Sigma D = 0.
\]

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Note that, in the \( \mathbf{x} \equiv (\mathbf{r}, \sigma) \) representation, the (local in space) two-electron repulsion operator is diagonal, thus leading to

\[
\Sigma_{IP} \quad \rightarrow \quad \Sigma(\mathbf{x}_1, \mathbf{x}_4) = \int d\mathbf{x}_2 \int d\mathbf{x}_3 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} \Gamma(\mathbf{x}_1, \mathbf{x}_3; \mathbf{x}_2, \mathbf{x}_3) \gamma^{-1}(\mathbf{x}_2, \mathbf{x}_4)
\]

where

\[
\gamma(\mathbf{x}_1, \mathbf{x}_2) = \langle \psi_0 | \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_2) | \psi_0 \rangle \quad \text{and}
\]

\[
\Gamma(\mathbf{x}_1, \mathbf{x}_3; \mathbf{x}_2, \mathbf{x}_3) = \langle \psi_0 | \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}^\dagger(\mathbf{x}_3) \hat{\psi}(\mathbf{x}_3) \hat{\psi}(\mathbf{x}_2) | \psi_0 \rangle
\]

are connected to the (time-dependent) one- and two-particle Green’s functions as follows,

\[
\gamma(\mathbf{x}_1, \mathbf{x}_2) = - \langle \psi_0 | T \left[ \hat{\psi}(\mathbf{x}_2, t_2) \hat{\psi}^\dagger(\mathbf{x}_1, t_2^+) \right] | \psi_0 \rangle = -iG(\mathbf{x}_2 t_2, \mathbf{x}_1 t_2^+)
\]

and

\[
\Gamma(\mathbf{x}_1, \mathbf{x}_3; \mathbf{x}_2, \mathbf{x}_3) = \langle \psi_0 | T \left[ \hat{\psi}(\mathbf{x}_3, t_3) \hat{\psi}(\mathbf{x}_2, t_3^-) \hat{\psi}^\dagger(\mathbf{x}_1, t_3^{++}) \hat{\psi}^\dagger(\mathbf{x}_3, t_3^+) \right] | \psi_0 \rangle
\]

\[
= -G_2(\mathbf{x}_3 t_3, \mathbf{x}_2 t_3^-; \mathbf{x}_3 t_3^+, \mathbf{x}_1 t_3^{++}).
\]
Connecting 1-RDM and Green’s function formalisms

- As readily seen in the following equations there are strong similarities between the (static) self-energy function we introduced and the conventional (time-dependent) self-energy:

\[
\Sigma(x_1, x_4) = \int dx_2 \int dx_3 \frac{1}{|r_1 - r_3|} \Gamma(x_1, x_3; x_2, x_3) \gamma^{-1}(x_2, x_4)
\]

\[
\Sigma(1, 4) = -i \int \int d2d3 \frac{1}{|r_1 - r_3|} \delta(t_1 - t_3) G_2(1, 3^+; 2, 3^{++}) G^{-1}(2, 4)
\]

where \( 1 \equiv (x_1, t_1), \ 2 \equiv (x_2, t_2), \ 3 \equiv (x_3, t_3), \ 4 \equiv (x_4, t_4). \)

- The connection between the ACSE and the equation of motion for the 1-GF (and, consequently, between the two self-energies) lies in the fact that, for an operator written in the Heisenberg picture, a differentiation with respect to time is equivalent to the calculation of its commutator with the Hamiltonian:

\[
i \frac{\partial G(1, 2)}{\partial t_1} = \delta(1, 2) + \theta(t_1 - t_2) \langle \psi_0 | \frac{\partial \hat{\psi}(1)}{\partial t_1} \hat{\psi}^\dagger(2) | \psi_0 \rangle - \theta(t_2 - t_1) \langle \psi_0 | \hat{\psi}^\dagger(2) \frac{\partial \hat{\psi}(1)}{\partial t_1} | \psi_0 \rangle
\]

where \( \hat{\psi}(1) = e^{i\hat{H}t_1} \hat{\psi}(x_1) e^{-i\hat{H}t_1} \) and \[
\frac{\partial \hat{\psi}(1)}{\partial t_1} = -ie^{i\hat{H}t_1} [\hat{\psi}(x_1), \hat{H}] e^{-i\hat{H}t_1}.
\]
Exact energy from the 1-RDM and the self-energy

Let us return to the ACSE for the 1-RDM:

\[
[D, h] + D \Sigma^\dagger - \Sigma D = 0.
\]

Note that, if the exact self-energy matrix \( \Sigma \) is known, we obtain the exact 1-RDM \( D \) by solving the ACSE.

The exact ground-state energy can be rewritten in terms of \( D \) and \( \Sigma \) as follows,

\[
E_0 = \sum_{KL} h_{KL} D^K_L + \frac{1}{2} \sum_{KLMN} \langle KL|MN \rangle D^{KL}_{MN} \\
= \sum_L [hD]_{LL} + \frac{1}{2} \sum_{KLMNPQ} \langle NM|LK \rangle D^{KL}_{MP} \left[ D^{-1} \right]_{PQ} D^Q_N \\
= \sum_L [hD]_{LL} + \frac{1}{2} \sum_{NQ} \Sigma_{NQ} D^Q_N,
\]

thus leading to the compact expression

\[
E_0 = \text{Tr} \left[ \left( h + \frac{1}{2} \Sigma \right) D \right],
\]

where \( \text{Tr} \) denotes the trace.
Non-interacting ACSE

Let us consider the non-interacting case first ($\Sigma = 0$).

According to the ACSE, the solution $D_h$ commutes with the one-electron Hamiltonian matrix:

$$[D_h, h] = 0.$$

Therefore, the eigenfunctions of $h$ (molecular spin-orbitals) diagonalize the non-interacting 1-RDM. If the former are ordered with increasing energies $\varepsilon_1 \leq \varepsilon_2 \leq \ldots \leq \varepsilon_N \leq \ldots$ then

$$h \equiv \begin{bmatrix}
\varepsilon_1 & 0 & 0 & 0 & 0 & 0 \\
0 & \varepsilon_2 & 0 & 0 & 0 & 0 \\
0 & 0 & \ddots & 0 & 0 & 0 \\
0 & 0 & 0 & \varepsilon_N & 0 & 0 \\
0 & 0 & 0 & 0 & \varepsilon_{N+1} & 0 \\
0 & 0 & 0 & 0 & 0 & \ddots
\end{bmatrix}, \quad D_h \equiv \begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & \ddots & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \ddots
\end{bmatrix}.$$

Note that $D_h$ is idempotent i.e. $D_h^2 = D_h$. 
First-order approximation in $\Sigma$

- From the non-interacting solution $D_h$, we can construct an approximate solution $D_h + D^{(1)}$ through first order in $\Sigma$ by solving
  \[ [D^{(1)} , h] + D_h \Sigma^\dagger - \Sigma D_h = 0 \].

- If we denote $I, J, \ldots$ and $A, B, \ldots$ the occupied and unoccupied (virtual) spin-orbitals in $D_h$, respectively, it comes for the occupied-occupied block
  \[ (\varepsilon_J - \varepsilon_I)D^{(1)}_{IJ} = \Sigma_{IJ} - \Sigma_{JI} \],
  and for the virtual-virtual block
  \[ (\varepsilon_B - \varepsilon_A)D^{(1)}_{AB} = 0 \].

- Similarly, we obtain for the occupied-virtual block,
  \[ (\varepsilon_A - \varepsilon_I)D^{(1)}_{IA} = -\Sigma_{AI} \].

- Note that, if the self-energy matrix is non-zero only in the occupied-occupied block and hermitian (of course it does not have to be), then $D^{(1)} = 0$. This was expected as unitary transformations inside the occupied spin-orbital space leave $D_h$ unchanged.
Hartree-Fock approximation

- At this point we should raise an important question: how do we approximate $\Sigma$?
- The simplest approximation is the mean-field (mf) one:

$$\Psi_0 \rightarrow \Phi \quad \text{(single Slater determinant)}$$

$$D_{KL}^{IJ} \rightarrow \left\langle \Phi \left| \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K \right| \Phi \rightangle = \delta_{JL} D_{IK}^I - \delta_{JK} D_{IL}^I$$

$$= D_{K}^I D_{L}^I - D_{K}^J D_{L}^J$$

- Note that the latter expression for the 2-RDM element actually holds on the entire spin-orbital space (it gives zero if one of the spin-orbital is not occupied in $\Phi$).

- Consequently, the corresponding mean-field self-energy matrix elements,

$$\Sigma_{PQ}^{mf} = \sum_{RSTU} \left\langle PT | SR \right| D_{TU}^{RS} \left[ D^{-1} \right]_{UQ},$$

become an explicit functional of the 1-RDM:

$$\Sigma_{PQ}^{mf} [D] = \sum_{RT} \left( \left\langle PT | QR \right| - \left\langle PT | RQ \right| \right) D_{T}^{R}.$$
Hartree-Fock approximation

- Note that $\Sigma^{\text{mf}}[D]$ is **hermitian** (unlike the exact self-energy).

- Note also that, in the occupied/unoccupied orbital basis associated to $\Phi$, the mean-field self-energy reads

$$
\Sigma^{\text{mf}}_{PQ} = \sum_{I}^{\text{occ}} \langle PI | QI \rangle - \langle PI | I Q \rangle = [\Sigma_{\text{Hx}}]_{PQ},
$$

where we recognize the **Hartree–Fock potential** $\Sigma_{\text{Hx}}$ expression in the canonical orbital basis.

- Within the mean-field approximation, we obtain from the ACSE the following **self-consistent** equation

$$
[D, f(D)] = 0
$$

where

$$
f(D) = h + \Sigma_{\text{Hx}}(D) \quad \leftarrow \text{Fock matrix!}
$$

which is equivalent to the **Hartree–Fock** equations.
Beyond Hartree-Fock

- One could think about developing a perturbation theory based on the converged mean-field 1-RDM rather than the bare non-interacting one $D_h$.

- **Diagrammatic techniques** could be used for expanding the (time-independent) self-energy in perturbation.

- One may wonder if Hedin-type equations can be derived in this context.

- Note that the exact self-energy matrix is in principle *not* hermitian.

- In this formalism there is no need to work in the (delocalized) canonical molecular orbital basis.

- The 1-RDM elements (in any orthonormal basis) are used as variables. **Localized orbitals** could therefore be used in this context which is convenient for large scale calculations.