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 Ψ.

- 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 "$\mathbf{r}$ representation" (real space):

$$\hat{H} = -\frac{1}{2} \int \int \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' \, \delta(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}'}^2 \hat{n}_1(\mathbf{r}, \mathbf{r}') + \frac{1}{2} \int \int \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' \frac{\hat{n}_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int \mathrm{d}\mathbf{r} \, v_{\mathrm{ne}}(\mathbf{r}) \, \hat{n}(\mathbf{r})$$

where

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

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

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

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

$$n_1^{\Psi}(\mathbf{r}, \mathbf{r}') = \langle \Psi | \hat{n}_1(\mathbf{r}, \mathbf{r}') | \Psi \rangle$$

  and the pair density

$$n_2^{\Psi}(\mathbf{r}, \mathbf{r}') = \langle \Psi | \hat{n}_2(\mathbf{r}, \mathbf{r}') | \Psi \rangle.$$

- 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 $n_2^{\Psi}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = \langle \Psi | \hat{n}_2(\mathbf{r}, \mathbf{r}', \mathbf{r}'') | \Psi \rangle$ where

$$
\begin{aligned}
\hat{n}_2(\mathbf{r}, \mathbf{r}', \mathbf{r}'') &= \sum_{\sigma \sigma'} \hat{\Psi}^{\dagger}(\mathbf{r}\sigma) \hat{\Psi}^{\dagger}(\mathbf{r}'\sigma') \hat{\Psi}(\mathbf{r}'\sigma') \hat{\Psi}(\mathbf{r}''\sigma) \\
&= \hat{n}_1(\mathbf{r}, \mathbf{r}'') \hat{n}(\mathbf{r}') - \delta(\mathbf{r}' - \mathbf{r}'') \hat{n}_1(\mathbf{r}, \mathbf{r}'),
\end{aligned}
$$

thus leading to $\boxed{\displaystyle\int d\mathbf{r}' \, n_2^{\Psi}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = (N-1) \times n_1^{\Psi}(\mathbf{r}, \mathbf{r}'')}$ since

$$\int d\mathbf{r}' \, \hat{n}(\mathbf{r}') | \Psi \rangle = N | \Psi \rangle.$$ Moreover $\boxed{n_2^{\Psi}(\mathbf{r}, \mathbf{r}') = n_2^{\Psi}(\mathbf{r}, \mathbf{r}', \mathbf{r})}$.

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

$$\Psi_0(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \ldots, \mathbf{r}_N\sigma_N)$$

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

- As readily seen, these two quantities depend on two electron positions whatever the number of electrons. Obviously, some information is "lost" when switching from Ψ_0 to $n_1^{\Psi_0}(\mathbf{r}, \mathbf{r}')$ and $n_2^{\Psi_0}(\mathbf{r}, \mathbf{r}')$, 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

$$|\Psi_0\rangle = \frac{1}{\sqrt{N!}} \sum_{\sigma_1 \ldots \sigma_N} \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_N \, \Psi_0(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N) \hat{\Psi}^\dagger(\mathbf{r}_1\sigma_1) \ldots \hat{\Psi}^\dagger(\mathbf{r}_N\sigma_N)|\text{vac}\rangle,$$

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

$$n_1^{\Psi_0}(\mathbf{r}, \mathbf{r}') = \sum_\sigma \left\langle \Psi_0 \left| \hat{\Psi}^\dagger(\mathbf{r}\sigma)\hat{\Psi}(\mathbf{r}'\sigma) \right| \Psi_0 \right\rangle$$

$$= N \sum_\sigma \sum_{\sigma_2 \ldots \sigma_N} \int d\mathbf{r}_2 \ldots \int d\mathbf{r}_N \, \Psi_0^*(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2 \ldots, \mathbf{r}_N\sigma_N) \Psi_0(\mathbf{r}'\sigma, \mathbf{r}_2\sigma_2, \ldots, \mathbf{r}_N\sigma_N),$$

and, for the pair density,

$$n_2^{\Psi_0}(\mathbf{r}, \mathbf{r}') = \sum_{\sigma\sigma'} \left\langle \Psi_0 \left| \hat{\Psi}^\dagger(\mathbf{r}\sigma)\hat{\Psi}^\dagger(\mathbf{r}'\sigma')\hat{\Psi}(\mathbf{r}'\sigma')\hat{\Psi}(\mathbf{r}\sigma) \right| \Psi_0 \right\rangle$$

$$= N(N-1) \sum_{\sigma\sigma'} \sum_{\sigma_3 \ldots \sigma_N} \int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N \left| \Psi_0(\mathbf{r}\sigma, \mathbf{r}'\sigma', \mathbf{r}_3\sigma_3 \ldots, \mathbf{r}_N\sigma_N) \right|^2.$$

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

$$
\begin{aligned}
E[n_1, n_2] &= -\frac{1}{2} \int \int \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' \, \delta(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}'}^2 \, n_1(\mathbf{r}, \mathbf{r}') + \frac{1}{2} \int \int \mathrm{d}\mathbf{r} \mathrm{d}\mathbf{r}' \frac{n_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&+ \int \mathrm{d}\mathbf{r} \, v_{\mathrm{ne}}(\mathbf{r}) \, n_1(\mathbf{r}, \mathbf{r}).
\end{aligned}
$$

- 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 $n_1(\mathbf{r}, \mathbf{r}') = 0$ and $n_2(\mathbf{r}, \mathbf{r}') \to -\infty$, we obtain $\boxed{\min_{n_1, n_2} E[n_1, n_2] = -\infty}$.

- This case is unphysical. The minimization should be performed under constraint.

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 *N*-representable) one-electron density matrices and pair densities.

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

$$
\begin{aligned}
n_1(\mathbf{r}, \mathbf{r}') &= n_1^{\Psi}(\mathbf{r}, \mathbf{r}') = \langle \Psi | \hat{n}_1(\mathbf{r}, \mathbf{r}') | \Psi \rangle, \\
n_2(\mathbf{r}, \mathbf{r}') &= n_2^{\Psi}(\mathbf{r}, \mathbf{r}') = \langle \Psi | \hat{n}_2(\mathbf{r}, \mathbf{r}') | \Psi \rangle.
\end{aligned}
$$

- **Variational principle** under *N*-representability constraints:

$$
\begin{aligned}
E_0 &= \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \\
&= \min_{\Psi} E[n_1^{\Psi}, n_2^{\Psi}].
\end{aligned}
$$

- **Basic *N*-representability conditions**: $n_1^{\Psi}(\mathbf{r}, \mathbf{r})$ (electron density) and the pair density are positive functions and they integrate to N and $N(N-1)$, respectively:

$$
\int d\mathbf{r}\, n_1^{\Psi}(\mathbf{r}, \mathbf{r}) = N, \qquad \int\int d\mathbf{r} d\mathbf{r}'\, n_2^{\Psi}(\mathbf{r}, \mathbf{r}') = N(N-1).
$$

Explicit and implicit dependence on the electron density

- Density-functional theory (DFT) is using the electron density $n^{\Psi}(\mathbf{r}) = n_1^{\Psi}(\mathbf{r}, \mathbf{r})$ as basic variable without actually knowing the N-electron wavefunction Ψ.

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

$$\frac{1}{2} \int d\mathbf{r} \left| \nabla n^{1/2}(\mathbf{r}) \right|^2 < +\infty.$$

- 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 $\hat{H}[v] = \hat{T} + \hat{W}_{ee} + \int d\mathbf{r}\, v(\mathbf{r}) \hat{n}(\mathbf{r})$ with ground-state energy $E[v]$ reads

$$E[v] = \min_n \left\{ F[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\} \quad \Leftrightarrow \quad F[n] = \max_v \left\{ E[v] - \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}.$$

[*] *Principles of DFT*, lecture given by **Trygve Helgaker** at the GDR Correl mini-school on mathematics in electronic structure theory, Paris, January 2017.

One-electron density-matrix functional theory

- 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

$$n_1^{\Psi}(\mathbf{r}, \mathbf{r}') = \sum_{pq} \phi_p(\mathbf{r}) \phi_q(\mathbf{r}') \underbrace{\left\langle \Psi \middle| \hat{E}_{pq} \middle| \Psi \right\rangle}$$

orbital basis representation $\rightarrow$ $\quad D_{pq}^{\Psi} = \sum_{\sigma} \left\langle \Psi \middle| \hat{a}_{p\sigma}^{\dagger} \hat{a}_{q\sigma} \middle| \Psi \right\rangle = \sum_{\sigma} D_{q\sigma}^{p\sigma}.$

- $\mathbf{D}^{\Psi}$ is hermitian. It can therefore be diagonalized, in the so-called natural orbital basis $\left\{ \tilde{\phi}_p(\mathbf{r}) \right\}_p$, thus leading to

$$n_1^{\Psi}(\mathbf{r}, \mathbf{r}') = \sum_p \tilde{\phi}_p(\mathbf{r}) \tilde{\phi}_p(\mathbf{r}') \tilde{n}_p \qquad \text{where} \quad 0 \leq \tilde{n}_p \leq 2.$$

- 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

$$D_{pqrs}^{\Psi} = \left\langle \Psi \middle| \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps} \middle| \Psi \right\rangle = \sum_{\sigma\sigma'} \left\langle \Psi \middle| \hat{a}_{p\sigma}^{\dagger}\hat{a}_{r\sigma'}^{\dagger}\hat{a}_{s\sigma'}\hat{a}_{q\sigma} \middle| \Psi \right\rangle = \sum_{\sigma\sigma'} D_{q\sigma s\sigma'}^{p\sigma r\sigma'}.$$

- Since $\left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \sum_{pq} h_{pq}D_{pq}^{\Psi} + \frac{1}{2}\sum_{pqrs}\langle pr|qs\rangle D_{pqrs}^{\Psi}$ where

$$\boxed{\sum_{r} D_{pqrr}^{\Psi} = (N-1)D_{pq}^{\Psi}}$$
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 ($1 \leq p \leq N$):

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

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

- The latter is in principle deduced from the ground-state wavefunction Ψ_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 $\boxed{D_{I_1 I_2 \ldots I_N}^{J_1 J_2 \ldots J_N} = C_{J_1 J_2 \ldots J_N} \, C_{I_1 I_2 \ldots I_N}}$.

- Therefore, $|C_{I_1 I_2 \ldots I_N}| = \sqrt{D_{I_1 I_2 \ldots I_N}^{I_1 I_2 \ldots I_N}}$. 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,

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

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ known (anti-commutation rules)

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

- Let us focus on the 2-RDM elements:

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

  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).

Representability and higher-order reduced density matrices

- Instead, we want to use the 2-RDM elements $D_{I_1 I_2}^{J_1 J_2}$ as basic variables.

- The N-representability is connected to the fact that the N-RDM elements can be written as $D_{I_1 I_2 \ldots I_N}^{J_1 J_2 \ldots J_N} = C_{J_1 J_2 \ldots J_N} C_{I_1 I_2 \ldots I_N}$.

- The higher the order p of the RDM is, the more we know about the wavefunction Ψ_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.

[*] D. A. Mazziotti, Phys. Rev. Lett. **97**, 143002 (2006).

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 Ψ_0, thus leading to

$$\left\langle \Psi_0 \left| \hat{a}_I^\dagger \hat{a}_J \hat{H} \right| \Psi_0 \right\rangle = E_0 \underbrace{\left\langle \Psi_0 \left| \hat{a}_I^\dagger \hat{a}_J \right| \Psi_0 \right\rangle}$$

$$D_J^I \quad \leftarrow \quad \text{exact 1-RDM !}$$

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

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

$$\sum_L h_{JL} D_L^I - \sum_{KL} h_{KL} D_{LJ}^{IK} + \frac{1}{2}\sum_{KMN}\langle JK||MN\rangle D_{MN}^{IK} + \frac{1}{2}\sum_{KLMN}\langle KL|MN\rangle D_{MNJ}^{IKL} = E_0 D_J^I$$

where $\quad \langle JK||MN\rangle = \langle JK|MN\rangle - \langle KJ|MN\rangle.$

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,

$$\mathcal{H}_J^I = \left\langle \Psi_0 \left| \hat{a}_I^\dagger \hat{a}_J \hat{H} \right| \Psi_0 \right\rangle = \frac{1}{2} \underbrace{\left\langle \Psi_0 \left| \left[\hat{a}_I^\dagger \hat{a}_J, \hat{H} \right] \right| \Psi_0 \right\rangle}_{\mathcal{H}_J^I - \mathcal{H}_I^J} + \frac{1}{2} \underbrace{\left\langle \Psi_0 \left| \left[\hat{a}_I^\dagger \hat{a}_J, \hat{H} \right]_+ \right| \Psi_0 \right\rangle}_{\mathcal{H}_J^I + \mathcal{H}_I^J} = E_0 D_J^I,$$

- The anti-Hermitian part of the CSE (ACSE) reads

$$\boxed{\left\langle \Psi_0 \left| \left[\hat{a}_I^\dagger \hat{a}_J, \hat{H} \right] \right| \Psi_0 \right\rangle = 0}.$$

- 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

$$\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right] = \left[\hat{A}, \hat{B}\right]_{+}\hat{C} - \hat{B}\left[\hat{A}, \hat{C}\right]_{+},$$

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

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

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

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

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

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

Connecting 1-RDM and Green's function formalisms

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

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

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

or, equivalently,

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

thus leading to $[\mathbf{D}, \mathbf{h}]_{IJ} + \left(\mathbf{\Sigma D} \right)_{JI} - \left(\mathbf{\Sigma D} \right)_{IJ} = 0$ or, in a compact form,

$$\boxed{ [\mathbf{D}, \mathbf{h}] + \mathbf{D}\mathbf{\Sigma}^{\dagger} - \mathbf{\Sigma D} = 0 }.$$

Connecting 1-RDM and Green's function formalisms

- 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 $\quad \gamma(\mathbf{x}_1, \mathbf{x}_2) = \left\langle \Psi_0 \middle| \hat{\Psi}^\dagger(\mathbf{x}_1) \hat{\Psi}(\mathbf{x}_2) \middle| \Psi_0 \right\rangle \quad$ and

$$\Gamma(\mathbf{x}_1, \mathbf{x}_3; \mathbf{x}_2, \mathbf{x}_3) = \left\langle \Psi_0 \middle| \hat{\Psi}^\dagger(\mathbf{x}_1) \hat{\Psi}^\dagger(\mathbf{x}_3) \hat{\Psi}(\mathbf{x}_3) \hat{\Psi}(\mathbf{x}_2) \middle| \Psi_0 \right\rangle$$

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

$$\gamma(\mathbf{x}_1, \mathbf{x}_2) = - \left\langle \Psi_0 \middle| T \left[\hat{\Psi}(\mathbf{x}_2, t_2) \hat{\Psi}^\dagger(\mathbf{x}_1, t_2^+) \right] \middle| \Psi_0 \right\rangle = -iG(\mathbf{x}_2 t_2, \mathbf{x}_1 t_2^+)$$

and

$$\begin{aligned}
\Gamma(\mathbf{x}_1, \mathbf{x}_3; \mathbf{x}_2, \mathbf{x}_3) &= \left\langle \Psi_0 \middle| T \left[\hat{\Psi}(\mathbf{x}_3, t_3) \hat{\Psi}(\mathbf{x}_2, t_3^-) \hat{\Psi}^\dagger(\mathbf{x}_1, t_3^{++}) \hat{\Psi}^\dagger(\mathbf{x}_3, t_3^+) \right] \middle| \Psi_0 \right\rangle \\
&= -G_2(\mathbf{x}_3 t_3, \mathbf{x}_2 t_3^-; \mathbf{x}_3 t_3^+, \mathbf{x}_1 t_3^{++}).
\end{aligned}$$

- 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:

$$\Sigma(\mathbf{x}_1, \mathbf{x}_4) = \int d\mathbf{x}_2 \int d\mathbf{x}_3 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} \Gamma(\mathbf{x}_1, \mathbf{x}_3; \mathbf{x}_2, \mathbf{x}_3) \gamma^{-1}(\mathbf{x}_2, \mathbf{x}_4)$$

$$\Sigma(1, 4) = -i \int \int d2 d3 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} \delta(t_1 - t_3) G_2(1, 3^+; 2, 3^{++}) G^{-1}(2, 4)$$

where $1 \equiv (\mathbf{x}_1, t_1)$, $2 \equiv (\mathbf{x}_2, t_2)$, $3 \equiv (\mathbf{x}_3, t_3)$, $4 \equiv (\mathbf{x}_4, t_4)$.

- 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 $\hat{\Psi}(1) = e^{i\hat{H}t_1}\hat{\Psi}(\mathbf{x}_1)e^{-i\hat{H}t_1}$ and $\boxed{\frac{\partial\hat{\Psi}(1)}{\partial t_1} = -ie^{i\hat{H}t_1}[\hat{\Psi}(\mathbf{x}_1), \hat{H}]e^{-i\hat{H}t_1}}$.

Exact energy from the 1-RDM and the self-energy

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

$$\boxed{[\mathbf{D}, \mathbf{h}] + \mathbf{D}\boldsymbol{\Sigma}^\dagger - \boldsymbol{\Sigma}\mathbf{D} = 0}.$$

- Note that, if the exact self-energy matrix $\boldsymbol{\Sigma}$ is known, we obtain the exact 1-RDM $\mathbf{D}$ by solving the ACSE.

- The exact ground-state energy can be rewritten in terms of $\mathbf{D}$ and $\boldsymbol{\Sigma}$ as follows,

$$
\begin{aligned}
E_0 &= \sum_{KL} h_{KL} D_L^K + \frac{1}{2} \sum_{KLMN} \langle KL|MN \rangle D_{MN}^{KL} \\
&= \sum_L [\mathbf{h}\mathbf{D}]_{LL} + \frac{1}{2} \sum_{KLMNPQ} \langle NM|LK \rangle D_{MP}^{KL} \left[\mathbf{D}^{-1} \right]_{PQ} D_N^Q \\
&= \sum_L [\mathbf{h}\mathbf{D}]_{LL} + \frac{1}{2} \sum_{NQ} \Sigma_{NQ} D_N^Q,
\end{aligned}
$$

thus leading to the compact expression $\boxed{E_0 = \mathrm{Tr}\left[\left(\mathbf{h} + \frac{1}{2}\boldsymbol{\Sigma} \right) \mathbf{D} \right]}$,

where Tr denotes the trace.

Non-interacting ACSE

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

- According to the ACSE, the solution $\mathbf{D}_h$ commutes with the one-electron Hamiltonian matrix:

$$[\mathbf{D}_h, \mathbf{h}] = 0.$$

- Therefore, the eigenfunctions of $\mathbf{h}$ (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

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

- Note that $\mathbf{D}_h$ is idempotent *i.e.* $\boxed{\mathbf{D}_h^2 = \mathbf{D}_h}$.

First-order approximation in $\boldsymbol{\Sigma}$

- From the non-interacting solution $\mathbf{D}_h$ we can construct an approximate solution $\mathbf{D}_h + \mathbf{D}^{(1)}$ through first order in $\boldsymbol{\Sigma}$ by solving

$$[\mathbf{D}^{(1)}, \mathbf{h}] + \mathbf{D}_h \boldsymbol{\Sigma}^\dagger - \boldsymbol{\Sigma} \mathbf{D}_h = 0.$$

- If we denote $I, J, \ldots$ and $A, B, \ldots$ the occupied and unoccupied (virtual) spin-orbitals in $\mathbf{D}_h$, respectively, it comes for the occupied-occupied block

$$(\varepsilon_J - \varepsilon_I) D_{IJ}^{(1)} = \Sigma_{IJ} - \Sigma_{JI},$$

and for the virtual-virtual block

$$(\varepsilon_B - \varepsilon_A) D_{AB}^{(1)} = 0.$$

- Similarly, we obtain for the occupied-virtual block,

$$(\varepsilon_A - \varepsilon_I) D_{IA}^{(1)} = -\Sigma_{AI}.$$

- 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 $\mathbf{D}^{(1)} = 0$. This was expected as unitary transformations inside the occupied spin-orbital space leave $\mathbf{D}_h$ unchanged.

Hartree-Fock approximation

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

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

$$D_{KL}^{IJ} \quad \rightarrow \quad \left\langle \Phi \left| \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K \right| \Phi \right\rangle = \delta_{JL} D_K^I - \delta_{JK} D_L^I$$

$$= D_K^I D_L^J - D_K^J D_L^I$$

- 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 Φ).

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

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

become an explicit functional of the 1-RDM:

$$\boxed{\Sigma_{PQ}^{\mathrm{mf}}\left[\mathbf{D}\right] = \sum_{RT} \left(\langle PT|QR\rangle - \langle PT|RQ\rangle\right) D_T^R.}$$

Hartree-Fock approximation

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

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

$$\Sigma_{PQ}^{\mathrm{mf}} = \sum_{I}^{\mathrm{occ}} \underbrace{\langle PI|QI\rangle}_{\text{Hartree}} - \underbrace{\langle PI|IQ\rangle}_{\text{exchange}} = [\boldsymbol{\Sigma}_{\mathrm{Hx}}]_{PQ},$$

where we recognize the Hartree–Fock potential $\boldsymbol{\Sigma}_{\mathrm{Hx}}$ expression in the canonical orbital basis.

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

$$\boxed{[\mathbf{D}, \mathbf{f}(\mathbf{D})] = 0}$$
where $\quad \mathbf{f}(\mathbf{D}) = \mathbf{h} + \boldsymbol{\Sigma}_{\mathrm{Hx}}(\mathbf{D}) \quad \leftarrow$ 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 $\mathbf{D}_h$.

- 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.