University of Strasbourg, second year Master's level

Exam in advanced quantum chemistry

January 2018

duration of the exam session: 2h

Neither documents nor calculators are allowed.

The grading scale might be changed.

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1. Questions about the lectures (10 points)

a) **[2 pts]** What is the Born–Oppenheimer approximation ? Are the nuclei treated in classical mechanics within such an approximation ? How are vibrational energies and electronic energies related ?

b) **[1 pt]** Give the main difference between variational and non-variational quantum chemical methods.

c) **[2 pts]** Explain why the Hartree–Fock (HF) method can be formulated as an orbital rotation problem. How can the HF orbitals be optimized ? How can we verify in a CI calculation that the determinants are contructed from HF orbitals ? If we perform a FCI calculation with molecular orbitals that are *not* the HF orbitals (let us consider Kohn–Sham orbitals for example), do we obtain a different FCI energy ?

d) **[2 pts]** Define the concept of static correlation. What is the appropriate method for its description ? How is the wavefunction parameterized within this method ? Is it possible to describe excited states with this method ? Does it provide accurate results ?

e) **[1 pt]** Does the energy depend explicitly on the electron density ?

f) **[2 pts]** What are the differences and similarities between HF and Kohn–Sham (KS) density-functional approaches ?

2. Beyond the Hartree–Fock approximation: the fluctuation-dissipation theorem (14 points)

Let $\hat{H} = \sum_{PQ} h_{PQ}\, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle PQ|RS\rangle\, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$ be the electronic Hamiltonian (we work within the Born–Oppenheimer approximation) written in second quantization.

a) **[1 pt]** What do the indices P, Q, R and S refer to ? Which name is usually given to h_{PQ} and $\langle PQ|RS\rangle$, respectively ? Give their physical meaning.

b) **[1 pt]** Let Ψ_0 denote the exact normalized N-electron ground-state wavefunction of $\hat{H}$ with energy E_0. Explain why $E_0 = \left\langle \Psi_0 \middle| \hat{H} \middle| \Psi_0 \right\rangle$ and deduce that $\boxed{E_0 = \sum_{PQ} h_{PQ} D^{\Psi_0}_{PQ} + \frac{1}{2} \sum_{PQRS} \langle PQ|RS\rangle\, D^{\Psi_0}_{PQRS}}$ where the one- and two-electron density matrices are defined as follows for *any normalized N-electron wavefunction* Ψ: $D^{\Psi}_{PQ} = \left\langle \Psi \middle| \hat{a}^{\dagger}_P \hat{a}_Q \middle| \Psi \right\rangle$ and $D^{\Psi}_{PQRS} = \left\langle \Psi \middle| \hat{a}^{\dagger}_P \hat{a}^{\dagger}_Q \hat{a}_S \hat{a}_R \middle| \Psi \right\rangle$.

c) **[1.5 pts]** Show that $\boxed{D^{\Psi}_{PQRS} = \Gamma^{\Psi}_{PRQS} - \delta_{QR} D^{\Psi}_{PS}}$, where $\boxed{\Gamma^{\Psi}_{PRQS} = \left\langle \Psi \middle| \hat{a}^{\dagger}_P \hat{a}_R \hat{a}^{\dagger}_Q \hat{a}_S \middle| \Psi \right\rangle}$ will be referred to as the *reordered two-electron density matrix* in the following. **Hint:** use the anti-commutation rules of second quantization.

d) **[1 pt]** Show that the one-electron density matrix is completely known from the reordered two-electron one. **Hint:** Explain physically why $\left(\sum_R \hat{a}^{\dagger}_R \hat{a}_R \right) |\Psi\rangle = N |\Psi\rangle$ and deduce that $\sum_R \Gamma^{\Psi}_{PQRR} = N D^{\Psi}_{PQ}$. Conclude.

e) **[1 pt]** Conclude from questions 2. b), c), and d) that the ground-state energy is an explicit functional of the ground-state reordered two-electron density matrix.

In the rest of the problem we focus on the calculation of $\Gamma^{\Psi_0}_{PRQS}$.

f) **[1 pt]** Explain why $\left| \hat{a}^{\dagger}_R \hat{a}_P \Psi_0 \right\rangle$ and $\left| \hat{a}^{\dagger}_Q \hat{a}_S \Psi_0 \right\rangle$ are N-electron quantum states.

g) **[2 pts]** Let $\{\Psi_i\}_{i=0,1,2,\ldots}$ be the complete orthonormal basis of N-electron ground *and* excited states of $\hat{H}$ with energies $\{E_i\}_{i=0,1,2,\ldots}$. Show that $\boxed{\left\langle \hat{a}^{\dagger}_R \hat{a}_P \Psi_0 \middle| \hat{\mathbb{1}}_N \middle| \hat{a}^{\dagger}_Q \hat{a}_S \Psi_0 \right\rangle = \Gamma^{\Psi_0}_{PRQS} = D^{\Psi_0}_{PR} D^{\Psi_0}_{QS} + \sum_{i \geq 1} D^{0\rightarrow i}_{PR} D^{0\rightarrow i}_{SQ}}$, where, for any N-electron wavefunction Ψ, $\hat{\mathbb{1}}_N |\Psi\rangle = |\Psi\rangle$, and the so-called *transition* one-electron density matrix elements are defined for any spin-orbitals U and V as $D^{0\rightarrow i}_{UV} = \left\langle \Psi_0 \middle| \hat{a}^{\dagger}_U \hat{a}_V \middle| \Psi_i \right\rangle$. **Hint:** use real algebra and the resolution of the identity formula $\hat{\mathbb{1}}_N = |\Psi_0\rangle\langle\Psi_0| + \sum_{i \geq 1} |\Psi_i\rangle\langle\Psi_i|$.

h) **[1.5 pts]** Show that, when the summation over excited states is neglected in the expression of $\Gamma^{\Psi_0}_{PRQS}$, the (approximate) ground-state energy can be expressed explicitly in terms of the ground-state one-electron density matrix as $E_0 \approx \sum_{PQ} h_{PQ} D^{\Psi_0}_{PQ} + \frac{1}{2} \sum_{PQRS} \langle PQ|RS\rangle \left(D^{\Psi_0}_{PR} D^{\Psi_0}_{QS} - \delta_{QR} D^{\Psi_0}_{PS} \right)$. Show that if, in addition, we approximate the exact ground-state wavefunction Ψ_0 by the Hartree-Fock (HF) Slater determinant Φ_0, whose occupied spin-orbitals are denoted $\{I\}_{I=1,\ldots,N}$, and we sum over spin-orbitals occupied in Φ_0 only, then we recover the HF energy expression $E_{\mathrm{HF}} = \sum_{I}^{\text{occupied}} h_{II} + \frac{1}{2} \sum_{IJ}^{\text{occupied}} \Big(\langle IJ|IJ\rangle - \langle IJ|JI\rangle \Big)$. **Hints:** First, use questions 2. b), c) and g). Then, explain why $D^{\Phi_0}_{IJ} = \delta_{IJ}$ where I and J denote occupied spin-orbitals in Φ_0. Conclude.

BONUS

Let us return to the exact theory. Even though the problem we are interested in, namely the calculation of the ground-state energy, has in appearance nothing to do with a time-dependent problem, it is possible to establish mathematically a connection between the response of the molecule to a time-dependent perturbation (which plays a crucial role in the interpretation of spectroscopy experiments) and the exact calculation of E_0*. For convenience, we will rewrite the energy contribution that was neglected in question* 2. h) *as follows,*

$$\frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\sum_{i\geq 1}D_{PR}^{0\rightarrow i}D_{SQ}^{0\rightarrow i}=\frac{1}{8}\sum_{PQRS}\langle PQ|RS\rangle\sum_{i\geq 1}\left(D_{PR}^{0\rightarrow i}+D_{RP}^{0\rightarrow i}\right)\left(D_{SQ}^{0\rightarrow i}+D_{QS}^{0\rightarrow i}\right). \tag{1}$$

i) **[2 pts]** Let us imagine that the molecule is in the presence of an external *time-dependent perturbation* with frequency ω and strength ϵ which is described by the operator $\hat{V}_\epsilon(t)=\epsilon\cos\omega t\times\left(\hat{a}_S^\dagger\hat{a}_Q+\hat{a}_Q^\dagger\hat{a}_S\right)$. Since the total Hamiltonian $\hat{H}(t)=\hat{H}+\hat{V}_\epsilon(t)$ is now time-dependent, the wavefunction $\Psi(t)$ becomes time-dependent (and complex). It is possible to show that the real part of the one-electron density matrix, which is also time-dependent, can be expanded as follows through first order in ϵ,

$$\mathrm{Re}\left[\left\langle\Psi(t)\middle|\hat{a}_P^\dagger\hat{a}_R\middle|\Psi(t)\right\rangle\right]=\mathrm{Re}\left[D_{PR}^{\Psi(t)}\right]=D_{PR}^{\Psi_0}+2\epsilon\cos\omega t\times\mathcal{R}_{PR,SQ}(\omega)+\ldots, \tag{2}$$

where the so-called frequency-dependent *linear response function* equals

$$\mathcal{R}_{PR,SQ}(\omega)=-\frac{1}{4}\sum_{i\geq 1}\left(D_{PR}^{0\rightarrow i}+D_{RP}^{0\rightarrow i}\right)\left(D_{SQ}^{0\rightarrow i}+D_{QS}^{0\rightarrow i}\right)\times\left[\frac{1}{\omega_i-\omega}+\frac{1}{\omega_i+\omega}\right], \tag{3}$$

and $\omega_i=E_i-E_0$ is the exact *excitation energy* for the transition $\Psi_0\rightarrow\Psi_i$.

We now employ a mathematical trick which consists in using a pure imaginary frequency $\mathrm{i}\omega$ [where $\mathrm{i}^2=-1$] instead of a real one. Give a simplified expression for $\mathcal{R}_{PR,SQ}(\mathrm{i}\omega)$ and conclude that

$$-\frac{1}{\pi}\int_0^{+\infty}\mathcal{R}_{PR,SQ}(\mathrm{i}\omega)\,\mathrm{d}\omega=\frac{1}{4}\sum_{i\geq 1}\left(D_{PR}^{0\rightarrow i}+D_{RP}^{0\rightarrow i}\right)\left(D_{SQ}^{0\rightarrow i}+D_{QS}^{0\rightarrow i}\right). \tag{4}$$

This important result is known as the *fluctuation-dissipation theorem.*
Hint: use the formula $\displaystyle\int_0^{+\infty}\frac{\omega_i}{\omega_i^2+\omega^2}\,\mathrm{d}\omega=\frac{\pi}{2}$ and note that the result does not depend on ω_i.

j) **[2 pts]** Conclude from Eqs. (1) and (4), and questions 2. b), c), g) that, even though the one-electron density matrix is not sufficient for calculating the ground-state energy E_0, its time-dependent version, which describes the reponse of the electrons to a time-dependent perturbation, gives access, in principle exactly, to E_0.

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a) P, Q, R and S refer to spin-orbitals.

$$\underbrace{h_{PQ}}_{} \leftarrow \text{one-electron integral} \;;\; \langle PQ|RS\rangle \rightarrow \text{two-electron integral}$$

h_{PQ}: describes the kinetic energy of the electron and the attraction between the electron and the nu

$\langle PQ|RS\rangle$ → describes the repulsion between two electrons

b) $\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$ so that

$$\langle\Psi_0|\hat{H}|\Psi_0\rangle = E_0\underbrace{\langle\Psi_0|\Psi_0\rangle}_{1} = E_0,$$

thus leading to

$$E_0 = \sum_{PQ} h_{PQ}\underbrace{\langle\Psi_0|\hat{a}^\dagger_P\hat{a}_Q|\Psi_0\rangle}_{D^{\Psi_0}_{PQ}} + \frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\underbrace{\langle\Psi_0|\hat{a}^\dagger_P\hat{a}^\dagger_Q\hat{a}_S\hat{a}_R|\Psi_0\rangle}_{D^{\Psi_0}_{PQRS}}$$

c)
$$D^{\Psi}_{PQRS} = \langle\Psi|\hat{a}^\dagger_P\hat{a}^\dagger_Q\hat{a}_S\hat{a}_R|\Psi\rangle = -\langle\Psi|\hat{a}^\dagger_P\underbrace{\hat{a}^\dagger_Q\hat{a}_R}_{\delta_{QR}-\hat{a}_R\hat{a}^\dagger_Q}\hat{a}_S|\Psi\rangle$$

$$= -\delta_{QR}\underbrace{\langle\Psi|\hat{a}^\dagger_P\hat{a}_S|\Psi\rangle}_{D^{\Psi}_{PS}} + \underbrace{\langle\Psi|\hat{a}^\dagger_P\hat{a}_R\hat{a}^\dagger_Q\hat{a}_S|\Psi\rangle}_{\Gamma^{\Psi}_{PRQS}}$$

d)
$$\sum_R \hat{a}^\dagger_R\hat{a}_R = \hat{N}$$

$\hat{N}$ ↳ counting operator

$\hat{a}^\dagger_R$: "restores" the electron

$\hat{a}_R$: removes an electron in spin-orbital R

$\hat{a}^\dagger_R\hat{a}_R$: counts the number of electrons that occupy the spin-orbital R.

$\hat{N}|\Psi\rangle = N|\Psi\rangle$. Consequently

N: number of electrons

$$\sum_R \Gamma^{\Psi}_{PQRR} = \sum_R\langle\Psi|\hat{a}^\dagger_P\hat{a}_Q\hat{a}^\dagger_R\hat{a}_R|\Psi\rangle$$
$$= \langle\Psi|\hat{a}^\dagger_P\hat{a}_Q\left(\sum_R\hat{a}^\dagger_R\hat{a}_R\right)|\Psi\rangle$$
$$= \langle\Psi|\hat{a}^\dagger_P\hat{a}_Q\underbrace{\hat{N}|\Psi\rangle}_{N|\Psi\rangle}$$
$$= N\underbrace{\langle\Psi|\hat{a}^\dagger_P\hat{a}_Q|\Psi\rangle}_{D^{\Psi}_{PQ}},$$

thus leading to
$$\boxed{D^{\Psi}_{PQ} = \frac{1}{N}\sum_R \Gamma^{\Psi}_{PQRR}}$$

e)
$$E_0 = \sum_{PQ} h_{PQ}D^{\Psi_0}_{PQ} + \frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\times\left(\Gamma^{\Psi_0}_{PRQS} - \delta_{QR}D^{\Psi_0}_{PS}\right) = \sum_{PQ}h_{PQ}D^{\Psi_0}_{PQ} - \frac{1}{2}\underbrace{\sum_{PQS}\langle PQ|QS\rangle D^{\Psi_0}_{PS}}_{\substack{Q\to R\\ S\to Q}} + \frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\Gamma^{\Psi_0}_{PRQS}$$

$$\sum_{PQS}\langle PQ|QS\rangle D^{\Psi_0}_{PS} = \sum_{PQR}\langle PR|RQ\rangle D^{\Psi_0}_{PQ}$$

$$E_0 = \sum_{PQ}\left(h_{PQ} - \frac{1}{2}\sum_R\langle PR|RQ\rangle\right)D^{\Psi_0}_{PQ} + \frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\Gamma^{\Psi_0}_{PRQS}$$

or, equivalently,
$$E_0 = \underbrace{\frac{1}{N}\sum_{PQS}\left(h_{PQ} - \frac{1}{2}\sum_R\langle PR|RQ\rangle\right)\Gamma^{\Psi_0}_{PQSS}}_{\sum_{PQST}\frac{\delta_{ST}}{N}\left(h_{PQ}-\frac{1}{2}\sum_R\langle PR|RQ\rangle\right)\Gamma^{\Psi_0}_{PQTS}} + \underbrace{\frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\Gamma^{\Psi_0}_{PRQS}}_{\substack{R\to Q\\ Q\to T}},$$

$$\frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\Gamma^{\Psi_0}_{PRQS} = \frac{1}{2}\sum_{PQST}\langle PT|QS\rangle\Gamma^{\Psi_0}_{PQTS}$$

Thus leading to the final expression

$$\boxed{E_0 = \frac{1}{2}\sum_{PQST}\left(\langle PT|QS\rangle - \left[\sum_R\langle PR|RQ\rangle - 2h_{PQ}\right]\times\frac{\delta_{ST}}{N}\right)\Gamma^{\Psi_0}_{PQTS}}$$

⇒ The ground-state energy E_0 is an explicit functional of $\{\Gamma^{\Psi_0}_{PQTS}\}$

f)
$$|\hat{a}^\dagger_R\hat{a}_P\Psi_0\rangle = \hat{a}^\dagger_R|\underbrace{\hat{a}_P\Psi_0}_{}\rangle \longrightarrow \text{N-electron state!}$$

$\hat{a}_P$ ↳ removes an electron

Ψ_0 ↳ N-electron state

$\hat{a}_P\Psi_0$: (N-1)-electron state

$\hat{a}^\dagger_R$ ↳ creates an electron

g)
$$\Gamma^{\Psi_0}_{PRQS} = \langle\Psi_0|\hat{a}^\dagger_P\hat{a}_R\hat{a}^\dagger_Q\hat{a}_S|\Psi_0\rangle$$
$$= \langle\underbrace{\hat{a}^\dagger_R\hat{a}_P\Psi_0}_{\text{N-electron state}}|\underbrace{\hat{a}^\dagger_Q\hat{a}_S\Psi_0}_{\text{N-electron state}}\rangle,$$

thus leading to
$$\Gamma^{\Psi_0}_{PRQS} = \langle\hat{a}^\dagger_R\hat{a}_P\Psi_0|\left(|\Psi_0\rangle\langle\Psi_0| + \sum_{i\geq 1}|\Psi_i\rangle\langle\Psi_i|\right)|\hat{a}^\dagger_Q\hat{a}_S\Psi_0\rangle$$

$$= \underbrace{\langle\Psi_0|\hat{a}^\dagger_P\hat{a}_R|\Psi_0\rangle}_{D^{\Psi_0}_{PR}}\underbrace{\langle\Psi_0|\hat{a}^\dagger_Q\hat{a}_S|\Psi_0\rangle}_{D^{\Psi_0}_{QS}} + \sum_{i\geq 1}\underbrace{\langle\Psi_0|\hat{a}^\dagger_P\hat{a}_R|\Psi_i\rangle}_{D^{0\to i}_{PR}}\langle\Psi_i|\hat{a}^\dagger_Q\hat{a}_S|\Psi_0\rangle$$

real algebra!

$$\langle\Psi_i|\hat{a}^\dagger_Q\hat{a}_S|\Psi_0\rangle = \langle\Psi_i|\hat{a}^\dagger_Q\hat{a}_S|\Psi_0\rangle^* = \underbrace{\langle\Psi_0|\hat{a}^\dagger_S\hat{a}_Q|\Psi_i\rangle}_{D^{0\to i}_{SQ}}$$

$$\boxed{\Gamma^{\Psi_0}_{PRQS} = D^{\Psi_0}_{PR}D^{\Psi_0}_{QS} + \sum_{i\geq 1}D^{0\to i}_{PR}D^{0\to i}_{SQ}}$$

h) Approximations: $\Gamma^{\Psi_0}_{PRQS} \simeq D^{\Psi_0}_{PR} D^{\Psi_0}_{QS}$

$$E_0 \simeq \sum_{PQ} h_{PQ} D^{\Psi_0}_{PQ} + \frac{1}{2}\sum_{PQRS} \langle PQ|RS\rangle \times \left(D^{\Psi_0}_{PR} D^{\Psi_0}_{QS} - \delta_{QR} D^{\Psi_0}_{PS}\right)$$

$$\Psi_0 \simeq \Phi_0 \rightarrow D^{\Psi_0}_{PQ} \simeq D^{\Phi_0}_{PQ} = \langle \Phi_0|\hat{a}^{+}_{P}\hat{a}_{Q}|\Phi_0\rangle$$
$$= \langle \hat{a}_{P}\Phi_0|\hat{a}_{Q}\Phi_0\rangle$$

We will only keep indices referring to occupied spin-orbitals in Φ_0.

must be occupied in Φ_0 otherwise it gives 0.

and $D_{IJ} = \langle \Phi_0|\hat{a}^{+}_{I}\hat{a}_{J}|\Phi_0\rangle = \delta_{IJ}\underbrace{\langle\Phi_0|\Phi_0\rangle}_{1}$

or, equivalently,

$$-\underbrace{\langle \Phi_0|\hat{a}_{J}\hat{a}^{+}_{I}|\Phi_0\rangle}_{0}$$

Since I is already occupied in Φ_0.

Combining the two approximations leads to

$$E_0 \simeq \sum_{IJ}^{\text{occupied}} h_{IJ}\underset{\substack{\downarrow\\ D^{\Phi_0}_{IJ}}}{\delta_{IJ}} + \frac{1}{2}\sum_{IJKL}^{\text{occupied}} \langle IJ|KL\rangle \times \left(\underset{D^{\Phi_0}_{IK}}{\delta_{IK}}\overset{\substack{D^{\Phi_0}_{JL}\\ \uparrow}}{\delta_{JL}} - \delta_{JK}\underset{\substack{\downarrow\\ D^{\Phi_0}_{IJ}}}{\delta_{IL}}\right)$$

$$E_0 \simeq \sum_{I}^{\text{occ.}} h_{II} + \frac{1}{2}\sum_{IJ}^{\text{occ.}}\langle IJ|IJ\rangle - \frac{1}{2}\sum_{IJ}\langle IJ|JI\rangle \leftarrow \text{Hartree-Fock energy!}$$

i) $$\mathcal{R}_{PR,SQ}(i\omega) = -\frac{1}{4}\sum_{i\geq 1}\underbrace{\left(D^{0\to i}_{PR}+D^{0\to i}_{RP}\right)\left(D^{0\to i}_{SQ}+D^{0\to i}_{QS}\right)}\times\underbrace{\left[\frac{1}{\omega_i - i\omega}+\frac{1}{\omega_i + i\omega}\right]}_{\frac{2\omega_i}{\omega_i^2+\omega^2}}$$

thus leading to

$$\int_0^{+\infty}\mathcal{R}_{PR,SQ}(i\omega)d\omega = -\frac{1}{4}\sum_{i\geq 1} \downarrow \times \underbrace{\int_0^{+\infty}\frac{2\omega_i}{\omega_i^2+\omega^2}d\omega}_{\pi}$$

or, equivalently,

$$\boxed{\frac{1}{4}\sum_{i\geq 1}\left(D^{0\to i}_{PR}+D^{0\to i}_{RP}\right)\left(D^{0\to i}_{SQ}+D^{0\to i}_{QS}\right) = -\frac{1}{\pi}\int_0^{+\infty}\mathcal{R}_{PR,SQ}(i\omega)d\omega}$$

j) $$E_0 = \sum_{PQ} h_{PQ} D^{\Psi_0}_{PQ} + \frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\left(D^{\Psi_0}_{PR}D^{\Psi_0}_{QS} - \delta_{QR}D^{\Psi_0}_{PS}\right)$$
$$+\frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle\sum_{i\geq 1}D^{0\to i}_{PR}D^{0\to i}_{SQ}$$
$$= \sum_{PQ} h_{PQ}D^{\Psi_0}_{PQ} + \frac{1}{2}\sum_{PQRS}\langle PQ|RS\rangle \underbrace{D^{\Psi_0}_{PR}D^{\Psi_0}_{QS}}_{\substack{R\to Q\\ Q\to R}} - \frac{1}{2}\sum_{PQS}\underbrace{\langle PQ|QS\rangle D^{\Psi_0}_{PS}}_{\substack{S\to Q\\ Q\to R}}$$
$$-\frac{1}{2\pi}\sum_{PQRS}\langle PQ|RS\rangle\int_0^{+\infty}d\omega\,\mathcal{R}_{PR,SQ}(i\omega)$$

$$\frac{1}{2}\sum_{PQRS}\langle PR|QS\rangle D^{\Psi_0}_{PQ}D^{\Psi_0}_{RS} - \frac{1}{2}\sum_{PRQ}\langle PR|RQ\rangle D^{\Psi_0}_{PQ}$$

thus leading to

$$E_0 = \sum_{PQ}\left(h_{PQ} + \frac{1}{2}\sum_{RS}\langle PR|QS\rangle D^{\Psi_0}_{RS} - \frac{1}{2}\sum_{R}\langle PR|RQ\rangle\right)D^{\Psi_0}_{PQ}$$
$$-\frac{1}{2\pi}\int_0^{+\infty}d\omega\sum_{PQRS}\langle PQ|RS\rangle\,\mathcal{R}_{PR,SQ}(i\omega)$$

unperturbed one-electron density matrix.

linear response function

Both are given by the time-dependent one-electron density matrix (which is connected to the one-electron Green function)