

Introduction to many-body Green-function theory

Julien Toulouse
Laboratoire de Chimie Théorique
Sorbonne Université et CNRS, 75005 Paris, France
toulouse@lct.jussieu.fr

March 17, 2019

http://www.lct.jussieu.fr/pagesperso/toulouse/enseignement/introduction_green.pdf

Lecture notes for courses given at:

- 2nd edition of the International summer School in electronic structure Theory: electron correlation in Physics and Chemistry (ISTPC), 18 June - 1 July 2017, Aussois, France.
- International summer School in electronic structure Theory: electron correlation in Physics and Chemistry (ISTPC), 14-27 June 2015, Aussois, France.

Contents

1	A tour of many-body Green function theory	2
1.1	One-particle Green function	2
1.2	Two-particle Green function and linear-response function	3
1.3	Dyson equation	4
1.4	Quasiparticle equations	5
1.5	Bethe-Salpeter equation	6
2	Hartree-Fock approximation	7
2.1	One-particle Green function	7
2.2	Linear-response function	9
2.3	Linear-response equation in a spin-orbital basis	10
2.4	Spin-adapted linear-response equation for closed-shell systems	12
2.5	Example: H ₂ in a minimal basis	13
	Appendices	15
	A Fourier-transform formulas	15
	B Equation of motion for the one-particle Green function	16
	C Schwinger functional derivative technique	17
	References	19

These notes provide an introduction to many-body Green function theory, with some links to the quantum chemistry perspective. For more details, see Refs. [1–7].

1 A tour of many-body Green function theory

We consider a many-body Hamiltonian operator expressed in real-space second quantization

$$\hat{H} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) h(\mathbf{r}) \hat{\psi}(\mathbf{x}) + \frac{1}{2} \iint d\mathbf{x}_1 d\mathbf{x}_2 \hat{\psi}^\dagger(\mathbf{x}_1) \hat{\psi}^\dagger(\mathbf{x}_2) v(\mathbf{r}_1, \mathbf{r}_2) \hat{\psi}(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1), \quad (1)$$

where $h(\mathbf{r}) = (-1/2)\nabla^2 + v_{\text{ne}}(\mathbf{r})$ is the one-electron Hamiltonian, and $v(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ is the electron-electron interaction. The creation $\hat{\psi}^\dagger(\mathbf{x})$ and annihilation $\hat{\psi}(\mathbf{x})$ field operators written with space-spin coordinates $\mathbf{x} = (\mathbf{r}, \sigma)$, obey usual anticommutation rules: $\{\hat{\psi}^\dagger(\mathbf{x}_1), \hat{\psi}^\dagger(\mathbf{x}_2)\} = \{\hat{\psi}(\mathbf{x}_1), \hat{\psi}(\mathbf{x}_2)\} = 0$ and $\{\hat{\psi}^\dagger(\mathbf{x}_1), \hat{\psi}(\mathbf{x}_2)\} = \delta(\mathbf{x}_1 - \mathbf{x}_2)$.

We consider a system of N electrons described by the Hamiltonian \hat{H} with a normalized ground state denoted by $|N\rangle$. The one-particle and two-particle Green functions of such a system are useful quantities that encapsulate information about the excited states of the system.

1.1 One-particle Green function

The *time-ordered one-particle Green function* is defined as

$$\begin{aligned} iG(1, 2) &= \langle N | T[\hat{\psi}(1) \hat{\psi}^\dagger(2)] | N \rangle \\ &= \theta(t_1 - t_2) \langle N | \hat{\psi}(1) \hat{\psi}^\dagger(2) | N \rangle - \theta(t_2 - t_1) \langle N | \hat{\psi}^\dagger(2) \hat{\psi}(1) | N \rangle, \end{aligned} \quad (2)$$

where the indices 1 and 2 stand for space-spin-time coordinates $1 = (\mathbf{x}_1, t_1)$ and $2 = (\mathbf{x}_2, t_2)$, T is the Wick time-ordering operator which orders the operators with larger times on the left, and θ is the Heaviside step function. The whole time-dependence is contained in the annihilation and creation field operators in the Heisenberg picture: $\hat{\psi}(1) = e^{i\hat{H}t_1} \hat{\psi}(\mathbf{x}_1) e^{-i\hat{H}t_1}$ and $\hat{\psi}^\dagger(2) = e^{i\hat{H}t_2} \hat{\psi}^\dagger(\mathbf{x}_2) e^{-i\hat{H}t_2}$. In the particle-hole language, the first term of the right-hand-side of Eq. (2) describes the propagation of a *particle* (i.e., an added electron in the system), while the second term describes the propagation of a *hole* (i.e., a removed electron from the system).

The one-particle Green function can be considered as a time-dependent generalization of the one-particle density matrix. Indeed, the one-particle density matrix $n_1(\mathbf{x}_1, \mathbf{x}_2)$ is just

$$n_1(\mathbf{x}_1, \mathbf{x}_2) = \langle N | \hat{\psi}^\dagger(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1) | N \rangle = -iG(\mathbf{x}_1 t_1, \mathbf{x}_2 t_1^+), \quad (3)$$

where t_1^+ means that an infinitesimal positive shift has been added to the time variable, $t_1^+ = t_1 + 0^+$, in order to select the second term in the right-hand side of Eq. (2). The one-particle density can also be obtained by setting $\mathbf{x}_1 = \mathbf{x}_2$ and summing over the spin coordinate

$$n(\mathbf{r}_1) = -i \int d\sigma_1 G(\mathbf{r}_1 \sigma_1 t_1, \mathbf{r}_1 \sigma_1 t_1^+). \quad (4)$$

In the absence of a time-dependent external potential, the system is invariant under time translation, therefore the Green function depends only on $\tau = t_1 - t_2$. By introducing the completeness relations for $(N - 1)$ - and $(N + 1)$ -electron states, one can get

$$\begin{aligned} iG(\mathbf{x}_1, \mathbf{x}_2; \tau) &= \theta(\tau) \sum_a \langle N | \hat{\psi}(\mathbf{x}_1) | N + 1, a \rangle \langle N + 1, a | \hat{\psi}^\dagger(\mathbf{x}_2) | N \rangle e^{-i(E_{N+1,a} - E_N)\tau} \\ &\quad - \theta(-\tau) \sum_i \langle N | \hat{\psi}^\dagger(\mathbf{x}_2) | N - 1, i \rangle \langle N - 1, i | \hat{\psi}(\mathbf{x}_1) | N \rangle e^{-i(E_N - E_{N-1,i})\tau}, \end{aligned} \quad (5)$$

where E_N is the energy of the N -electron ground state $|N\rangle$, and $E_{N+1,a}$ and $E_{N-1,i}$ are the energies of the a -th $(N+1)$ -electron state $|N+1,a\rangle$ and of the i -th $(N-1)$ -electron state $|N-1,i\rangle$, respectively.

Exercise 1 : Derive Eq. (5) from Eq. (2).

The Lehmann representation of the one-particle Green function is then obtained by Fourier transform (cf. Appendix A)

$$G(\mathbf{x}_1, \mathbf{x}_2; \omega) = \sum_a \frac{f_a(\mathbf{x}_1) f_a^*(\mathbf{x}_2)}{\omega - \mathcal{E}_a + i0^+} + \sum_i \frac{f_i(\mathbf{x}_1) f_i^*(\mathbf{x}_2)}{\omega - \mathcal{E}_i - i0^+}, \quad (6)$$

where $f_a(\mathbf{x}) = \langle N | \hat{\psi}(\mathbf{x}) | N+1, a \rangle$ and $f_i(\mathbf{x}) = \langle N-1, i | \hat{\psi}(\mathbf{x}) | N \rangle$ are the Dyson orbitals (also called Lehmann amplitudes or quasiparticle wave functions), and $\mathcal{E}_a = E_{N+1,a} - E_N = -A_a$ and $\mathcal{E}_i = E_N - E_{N-1,i} = -I_i$ are the quasiparticle energies, i.e. minus the electron affinities A_a and ionization energies I_i , respectively. Therefore, the one-particle Green function contains information relative to photoelectron and inverse photoelectron spectroscopies.

Exercise 2 : Using the Fourier-transform formulas given in Appendix A, derive Eq. (6).

1.2 Two-particle Green function and linear-response function

The *time-ordered two-particle Green function* is defined as

$$i^2 G_2(1, 2; 1', 2') = \langle N | T[\hat{\psi}(1) \hat{\psi}(2) \hat{\psi}^\dagger(2') \hat{\psi}^\dagger(1')] | N \rangle. \quad (7)$$

Depending on the time ordering, it describes the propagation of a pair of particles, of holes, or of a particle and a hole. A related quantity is the *four-point linear-response function* defined as

$$i\chi(1, 2; 1', 2') = i^2 G_2(1, 2; 1', 2') - iG(1, 1') iG(2, 2'). \quad (8)$$

It describes the coupled motion of a pair of two particles, or two holes, or a particle and a hole, minus the motion of the independent ones. When the time variables are appropriately ordered, the four-point linear-response function reduces to the *particle-hole linear-response function* (or polarization propagator or, simply, linear-response function)

$$i\chi(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2; \mathbf{x}'_1 t_1^+, \mathbf{x}'_2 t_2^+) = \langle N | T[\hat{\psi}^\dagger(\mathbf{x}'_1 t_1) \hat{\psi}(\mathbf{x}_1 t_1) \hat{\psi}^\dagger(\mathbf{x}'_2 t_2) \hat{\psi}(\mathbf{x}_2 t_2)] | N \rangle - \langle N | \hat{\psi}^\dagger(\mathbf{x}'_1 t_1) \hat{\psi}(\mathbf{x}_1 t_1) | N \rangle \langle N | \hat{\psi}^\dagger(\mathbf{x}'_2 t_2) \hat{\psi}(\mathbf{x}_2 t_2) | N \rangle, \quad (9)$$

where $t_1^+ = t_1 + 0^+$ and $t_2^+ = t_2 + 0^+$. It describes the propagation of a particle-hole pair, and it is the relevant quantity to consider for optical absorption or emission spectroscopy. Due to time translation invariance, the linear-response function depends only on $\tau = t_1 - t_2$. By introducing the completeness relation for N -electron states, one can get

$$i\chi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \tau) = \theta(\tau) \sum_{n \neq 0} \langle N | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | N, n \rangle \langle N, n | \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}(\mathbf{x}_2) | N \rangle e^{-i(E_{N,n} - E_N)\tau} + \theta(-\tau) \sum_{n \neq 0} \langle N | \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}(\mathbf{x}_2) | N, n \rangle \langle N, n | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | N \rangle e^{i(E_{N,n} - E_N)\tau}, \quad (10)$$

where $E_{N,n}$ is the energy of n -th N -electron excited state $|N, n\rangle$. The ground state $|N, 0\rangle = |N\rangle$ is excluded from the sum. The Lehmann representation of the linear-response function is thus

$$\chi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) = \sum_{n \neq 0} \left[\frac{\langle N | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | N, n \rangle \langle N, n | \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}(\mathbf{x}_2) | N \rangle}{\omega - \omega_n + i0^+} - \frac{\langle N | \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}(\mathbf{x}_2) | N, n \rangle \langle N, n | \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) | N \rangle}{\omega + \omega_n - i0^+} \right], \quad (11)$$

where $\omega_n = E_{N,n} - E_N$ are the excitation energies. Therefore, the linear-response function has poles in ω at the excitation energies ω_n and at the de-excitation energies $-\omega_n$.

Exercise 3 : Derive Eq. (10) and Eq. (11).

It is also useful to define the independent-particle (IP) four-point linear-response function

$$\chi_{\text{IP}}(1, 2; 1', 2') = -iG(1, 2')G(2, 1'), \quad (12)$$

and the corresponding IP linear-response function

$$\chi_{\text{IP}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \tau) = \chi_{\text{IP}}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2; \mathbf{x}'_1 t_1^+, \mathbf{x}'_2 t_2^+) = -iG(\mathbf{x}_1, \mathbf{x}'_2; \tau)G(\mathbf{x}_2, \mathbf{x}'_1; -\tau). \quad (13)$$

Its Lehmann representation is easily obtained by using Eq. (5) and taking the Fourier transform,

$$\chi_{\text{IP}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) = \sum_i \sum_a \left[\frac{f_i^*(\mathbf{x}'_1) f_a(\mathbf{x}_1) f_a^*(\mathbf{x}'_2) f_i(\mathbf{x}_2)}{\omega - (\mathcal{E}_a - \mathcal{E}_i) + i0^+} - \frac{f_i^*(\mathbf{x}'_2) f_a(\mathbf{x}_2) f_a^*(\mathbf{x}'_1) f_i(\mathbf{x}_1)}{\omega + (\mathcal{E}_a - \mathcal{E}_i) - i0^+} \right], \quad (14)$$

where we see that it contains quasiparticle energy differences as poles in ω . The fundamental gap, $E_{\text{gap}} = I_0 - A_0$, corresponds to the smallest of such quasiparticle energy differences.

Exercise 4 : Derive Eq. (14).

Having seen their useful physical contents, we would like to calculate the one-particle Green function and the linear-response function without solving the full many-body problem. We will derive now the Dyson equation for calculating the one-particle Green function, and the Bethe-Salpeter equation for calculating the four-point linear-response function.

1.3 Dyson equation

In Appendix B, it is shown that the one-particle Green function satisfies the following equation of motion

$$\left[i \frac{\partial}{\partial t_1} - h(1) \right] G(1, 2) + i \int d3 v(1, 3) G_2(1, 3^+; 2, 3^{++}) = \delta(1, 2), \quad (15)$$

with the notations $h(1) = h(\mathbf{r}_1)$ and $v(1, 3) = v(\mathbf{r}_1, \mathbf{r}_3) \delta(t_1 - t_3)$, and 3^+ means that the time variable has an infinitesimal positive shift $t_3^+ = t_3 + 0^+$, and 3^{++} means another shift $t_3^{++} =$

$t_3^+ + 0^+$. Thus, the equation of motion of the one-particle Green function involves the two-particle Green function. One can formally close this equation as

$$\left[i \frac{\partial}{\partial t_1} - h(1) \right] G(1, 2) - \int d3 \Sigma_{\text{Hxc}}(1, 3) G(3, 2) = \delta(1, 2), \quad (16)$$

where $\Sigma_{\text{Hxc}}(1, 3)$ is the Hartree-exchange-correlation *self-energy* which encompasses all the two-electron effects. The self-energy is defined by

$$\int d3 \Sigma_{\text{Hxc}}(1, 3) G(3, 2) = -i \int d3 v(1, 3) G_2(1, 3^+; 2, 3^{++}), \quad (17)$$

or, more explicitly, after multiplying from the right by the inverse of the Green function $G^{-1}(2, 4)$ and integrating over the coordinate 2,

$$\Sigma_{\text{Hxc}}(1, 4) = -i \iint d2 d3 v(1, 3) G_2(1, 3^+; 2, 3^{++}) G^{-1}(2, 4), \quad (18)$$

where we have used the definition of the inverse, $\int d2 G(3, 2) G^{-1}(2, 4) = \delta(3, 4)$.

The non-interacting Green function G_h corresponding to the one-electron Hamiltonian h has no two-electron contributions and therefore follows the equation of motion¹

$$\left[i \frac{\partial}{\partial t_1} - h(1) \right] G_h(1, 2) = \delta(1, 2). \quad (19)$$

Writing $G(1, 2) = \iint d3 d4 G_h(1, 4) G_h^{-1}(4, 3) G(3, 2)$ in the first term of Eq. (16) and using Eq. (19), one gets

$$\int d3 [G_h^{-1}(1, 3) - \Sigma_{\text{Hxc}}(1, 3)] G(3, 2) = \delta(1, 2), \quad (20)$$

which can be rewritten as, after multiplying from the left by $\int d1 G_h(4, 1)$ and renaming the indices,

$$\boxed{G(1, 2) = G_h(1, 2) + \iint d3 d4 G_h(1, 3) \Sigma_{\text{Hxc}}(3, 4) G(4, 2)}, \quad (21)$$

or, equivalently, after multiplying from the right Eq. (20) by $G^{-1}(2, 4)$, integrating over the coordinate 2, and renaming the indices,

$$\boxed{G^{-1}(1, 2) = G_h^{-1}(1, 2) - \Sigma_{\text{Hxc}}(1, 2)}. \quad (22)$$

Eq. (21) or (22) constitutes the *Dyson equation* for the one-particle Green function. Knowing the non-interacting Green function G_h and an approximation for the self-energy Σ_{Hxc} , it allows one to calculate the corresponding interacting Green function G .

1.4 Quasiparticle equations

We will show now that the Dyson equation can be conveniently reformulated as eigenvalue equations for the Dyson orbitals and the quasiparticle energies.

¹Non-interacting one-particle Green functions are frequently denoted by G_0 in the literature. However, there are several possible non-interacting Green functions (Hartree, Hartree-Fock, Kohn-Sham, etc...), so we prefer the notation G_h which explicitly specifies the corresponding one-electron Hamiltonian h .

Just like the one-particle Green function, the self-energy depends only the time difference $\tau = t_1 - t_2$, i.e. $\Sigma_{\text{Hxc}}(1, 2) = \Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_2; \tau)$. Fourier transforming the equation of motion (16) then gives

$$[\omega - h(\mathbf{r}_1)] G(\mathbf{x}_1, \mathbf{x}_2; \omega) - \int d\mathbf{x}_3 \Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_3; \omega) G(\mathbf{x}_3, \mathbf{x}_2; \omega) = \delta(\mathbf{x}_1, \mathbf{x}_2), \quad (23)$$

where $\Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_3; \omega)$ is the Fourier transform of $\Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_3; \tau)$.

Exercise 5 : Derive Eq. (23) from Eq. (16).

Inserting the Lehmann representation (6) of $G(\mathbf{x}_1, \mathbf{x}_2; \omega)$ in Eq. (23), one can select the term corresponding to a given pole \mathcal{E}_k (assumed to be discrete and nondegenerate) of $G(\mathbf{x}_1, \mathbf{x}_2; \omega)$ by multiplying the equation by $\omega - \mathcal{E}_k$ and taking the limit $\omega \rightarrow \mathcal{E}_k$, giving

$$[\mathcal{E}_k - h(\mathbf{r}_1)] f_k(\mathbf{x}_1) f_k^*(\mathbf{x}_2) - \int d\mathbf{x}_3 \Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_3; \mathcal{E}_k) f_k(\mathbf{x}_3) f_k^*(\mathbf{x}_2) = 0, \quad (24)$$

or, after simplifying by $f_k^*(\mathbf{x}_2)$,

$$h(\mathbf{r}_1) f_k(\mathbf{x}_1) + \int d\mathbf{x}_3 \Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_3; \mathcal{E}_k) f_k(\mathbf{x}_3) = \mathcal{E}_k f_k(\mathbf{x}_1). \quad (25)$$

Eq. (25) constitutes the *quasiparticle equations* giving the Dyson orbitals $f_k(\mathbf{x})$ and the corresponding quasiparticle energies \mathcal{E}_k (ionization energies or electron affinities). The self-energy $\Sigma_{\text{Hxc}}(\mathbf{x}_1, \mathbf{x}_3; \mathcal{E}_k)$ plays the role of a nonlocal energy-dependent potential. The quasiparticle equations may be thought of as an extension of the Hartree-Fock or Kohn-Sham orbital equations. Because of the dependence on the energy \mathcal{E}_k , each Dyson orbital $f_k(\mathbf{x})$ is an eigenfunction of a different operator. Consequently, the Dyson orbitals do not form a basis of the one-electron space, but constitutes an overcomplete set.

1.5 Bethe-Salpeter equation

The Bethe-Salpeter equation for the four-point linear-response function can be derived from the Dyson equation using the “functional derivative technique” of Schwinger. The idea is to add a time-dependent nonlocal external potential $u(1, 1') = u(\mathbf{x}_1, \mathbf{x}'_1; t_1) \delta(t_1 - t'_1)$ in the Hamiltonian, leading to generalized Green functions, and consider functional derivatives of Green functions with respect to $u(1, 1')$ to generate higher-particle Green functions. The potential u is then eventually set to zero at the end of the derivation.

For example, the four-point linear-response function can be expressed as the functional derivative

$$\chi(1, 2; 1', 2') = -i \frac{\delta G(1, 1')}{\delta u(2', 2)}, \quad (26)$$

where we consider variations of the one-particle Green function $\delta G(1, 1')$ induced by a variation of the external potential $\delta u(2', 2)$. Assuming that the inverse of $\chi(1, 2; 1', 2')$ exists, it can be written as²

$$\chi^{-1}(1, 2; 1', 2') = i \frac{\delta u(1, 1')}{\delta G(2', 2)}, \quad (27)$$

²The inverse of a 4-point function $\chi(1, 2; 1', 2')$ is defined according to $\int d1' d2' \chi(1, 2; 1', 2') \chi^{-1}(2', 1'; 4, 3) = \delta(1, 3) \delta(2, 4)$.

where we consider now variations of the external potential $\delta u(1, 1')$ induced by a variation of the one-particle Green function $\delta G(2', 2)$.

The Bethe-Salpeter can be derived by starting from the Dyson equation of Eq. (22), written in the presence of the external potential u ,

$$G^{-1}(1, 1') = G_h^{-1}(1, 1') - u(1, 1') - \Sigma_{\text{Hxc}}(1, 1'), \quad (28)$$

and taking the functional derivative with respect to $iG(2', 2)$. Since $G_h^{-1}(1, 1')$ is independent from u , its functional derivative vanishes, and it remains

$$-i \frac{\delta G^{-1}(1, 1')}{\delta G(2', 2)} = i \frac{\delta u(1, 1')}{\delta G(2', 2)} + i \frac{\delta \Sigma_{\text{Hxc}}(1, 1')}{\delta G(2', 2)}. \quad (29)$$

The term on the left-hand side of Eq. (29) can be directly calculated (see Exercise 6)

$$-i \frac{\delta G^{-1}(1, 1')}{\delta G(2', 2)} = i G^{-1}(1, 2') G^{-1}(2, 1') = \chi_{\text{IP}}^{-1}(1, 2; 1', 2'), \quad (30)$$

where $\chi_{\text{IP}}^{-1}(1, 2; 1', 2')$ is the inverse of the IP four-point linear-response function $\chi_{\text{IP}}(1, 2; 1', 2')$ defined in Eq. (12). The first term on the right-hand side of Eq. (29) is just the inverse of the four-point linear-response function $\chi^{-1}(1, 2; 1', 2')$ according to Eq. (27). Finally, the last term on the right-hand side of Eq. (29) defines the Hartree-exchange-correlation *Bethe-Salpeter kernel*

$$i \frac{\delta \Sigma_{\text{Hxc}}(1, 1')}{\delta G(2', 2)} = \Xi_{\text{Hxc}}(1, 2; 1', 2'). \quad (31)$$

We thus arrive at the *Bethe-Salpeter equation*

$$\boxed{\chi^{-1}(1, 2; 1', 2') = \chi_{\text{IP}}^{-1}(1, 2; 1', 2') - \Xi_{\text{Hxc}}(1, 2; 1', 2'),} \quad (32)$$

or, equivalently, after matrix multiplying by χ_{IP} from the left and by χ from the right,

$$\boxed{\chi(1, 2; 1', 2') = \chi_{\text{IP}}(1, 2; 1', 2') + \iiint d3d4d5d6 \chi_{\text{IP}}(1, 4; 1', 3) \Xi_{\text{Hxc}}(3, 6; 4, 5) \chi(5, 2; 6, 2').} \quad (33)$$

Knowing approximations for the IP four-point linear-response function χ_{IP} and the Bethe-Salpeter kernel Ξ_{Hxc} , it allows one to calculate the corresponding interacting four-point linear-response function χ .

Exercise 6 : Derive Eq. (30). For this, start from $\int d3 G^{-1}(1, 3)G(3, 4) = \delta(1, 4)$ and take the functional derivative with respect to $G(2', 2)$.

2 Hartree-Fock approximation

2.1 One-particle Green function

The starting point is the Hartree-Fock (HF) approximate form for the two-particle Green function

$$G_2^{\text{HF}}(1, 2; 1', 2') = G(1, 1') G(2, 2') - G(1, 2') G(2, 1'), \quad (34)$$

with a direct (or Hartree) and an exchange (or Fock) term. Injecting Eq. (34) into Eq. (18) gives the HF self-energy

$$\Sigma_{\text{HX}}^{\text{HF}}(1, 2) = \Sigma_{\text{H}}(1, 2) + \Sigma_{\text{x}}(1, 2), \quad (35)$$

where $\Sigma_{\text{H}}(1, 2)$ is the Hartree contribution

$$\Sigma_{\text{H}}(1, 2) = -i\delta(1, 2) \int d3G(3, 3^+)v(1, 3), \quad (36)$$

and $\Sigma_{\text{x}}(1, 2)$ is the exchange contribution,

$$\Sigma_{\text{x}}(1, 2) = iG(1, 2^+)v(1, 2). \quad (37)$$

Exercise 7 : Derive Eqs. (36) and (37) from Eq. (18) and (34).

The Hartree self-energy can be written more explicitly as

$$\begin{aligned} \Sigma_{\text{H}}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) &= \delta(t_1 - t_2)\delta(\mathbf{x}_1 - \mathbf{x}_2) \int d\mathbf{r}_3 n(\mathbf{r}_3)v(\mathbf{r}_1, \mathbf{r}_3) \\ &= \delta(t_1 - t_2)\delta(\mathbf{x}_1 - \mathbf{x}_2)v_{\text{H}}(\mathbf{r}_1), \end{aligned} \quad (38)$$

where we have used Eq. (4) to introduce the density $n(\mathbf{r}_3)$, and $v_{\text{H}}(\mathbf{r}_1)$ is the local Hartree potential. Similarly, the exchange self-energy can be written as

$$\begin{aligned} \Sigma_{\text{x}}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) &= -\delta(t_1 - t_2)n_1(\mathbf{x}_1, \mathbf{x}_2)v(\mathbf{r}_1, \mathbf{r}_2) \\ &= \delta(t_1 - t_2)v_{\text{x}}^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2), \end{aligned} \quad (39)$$

where we have used Eq. (3) to introduce the one-particle density matrix $n_1(\mathbf{x}_1, \mathbf{x}_2)$, and $v_{\text{x}}^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2)$ is the nonlocal HF exchange potential.

The delta function $\delta(t_1 - t_2)$ in Eqs. (38) and (39) implies that the Fourier transforms of Σ_{H} and Σ_{x} are independent from the frequency ω . The quasiparticle equations (25) just reduce to the usual HF equations

$$h(\mathbf{r}_1)\psi_k(\mathbf{x}_1) + v_{\text{H}}(\mathbf{r}_1)\psi_k(\mathbf{x}_1) + \int d\mathbf{x}_3 v_{\text{x}}^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_3)\psi_k(\mathbf{x}_3) = \varepsilon_k\psi_k(\mathbf{x}_1), \quad (40)$$

where $\psi_k(\mathbf{x}_1)$ and ε_k are the HF spin orbitals and orbital energies, which thus constitute first approximations to the Dyson orbitals and quasiparticle energies. The corresponding non-interacting HF one-particle Green function has the following Lehmann representation [see Eq. (6)]

$$G_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \omega) = \sum_a^{\text{vir}} \frac{\psi_a(\mathbf{x}_1)\psi_a^*(\mathbf{x}_2)}{\omega - \varepsilon_a + i0^+} + \sum_i^{\text{occ}} \frac{\psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)}{\omega - \varepsilon_i - i0^+}, \quad (41)$$

where i and a run over occupied and virtual HF spin orbitals, respectively.

Approximations beyond HF are obtained by adding in Eq. (40) a nonlocal energy-dependent correlation self-energy $\Sigma_c(\mathbf{x}_1, \mathbf{x}_2; \mathcal{E}_k)$.

2.2 Linear-response function

In the framework of the HF approximation, the IP four-point linear-response function of Eq. (12) becomes the non-interacting HF four-point linear-response function obtained from the non-interacting HF Green function

$$\chi_{\text{HF}}(1, 2; 1', 2') = -iG_{\text{HF}}(1, 2')G_{\text{HF}}(2, 1'), \quad (42)$$

and the IP linear-response function of Eq. (14) becomes the non-interacting HF linear-response function

$$\chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) = \sum_i^{\text{occ}} \sum_a^{\text{virt}} \left[\frac{\psi_i^*(\mathbf{x}'_1)\psi_a(\mathbf{x}_1)\psi_a^*(\mathbf{x}'_2)\psi_i(\mathbf{x}_2)}{\omega - (\varepsilon_a - \varepsilon_i) + i0^+} - \frac{\psi_i^*(\mathbf{x}'_2)\psi_a(\mathbf{x}_2)\psi_a^*(\mathbf{x}'_1)\psi_i(\mathbf{x}_1)}{\omega + (\varepsilon_a - \varepsilon_i) - i0^+} \right]. \quad (43)$$

Just as the HF self-energy, the HF Bethe-Salpeter kernel has Hartree and exchange contributions

$$\Xi_{\text{Hx}}^{\text{HF}}(1, 2; 1', 2') = \Xi_{\text{H}}(1, 2; 1', 2') + \Xi_{\text{x}}(1, 2; 1', 2'), \quad (44)$$

where the Hartree kernel is found by taking the functional derivatives of Eq. (36)

$$\begin{aligned} \Xi_{\text{H}}(1, 2; 1', 2') &= i \frac{\delta \Sigma_{\text{H}}(1, 1')}{\delta G(2', 2)} \\ &= v(1, 2)\delta(1, 1')\delta(2, 2') \\ &= v(\mathbf{r}_1, \mathbf{r}_2)\delta(t_1 - t_2)\delta(1, 1')\delta(2, 2'), \end{aligned} \quad (45)$$

and the exchange kernel is found by taking the functional derivatives of Eq. (37)

$$\begin{aligned} \Xi_{\text{x}}(1, 2; 1', 2') &= i \frac{\delta \Sigma_{\text{x}}(1, 1')}{\delta G(2', 2)} \\ &= -v(1, 2)\delta(1, 2')\delta(1', 2) \\ &= -v(\mathbf{r}_1, \mathbf{r}_2)\delta(t_1 - t_2)\delta(1, 2')\delta(1', 2). \end{aligned} \quad (46)$$

The presence of the delta functions in Eqs. (45) and (46) implies that the integration over the time variables can easily be performed in the Bethe-Salpeter equation (33), which can then be written for the linear-response function in Fourier space

$$\begin{aligned} \chi_{\text{TDHF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) &= \chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) \\ &+ \iiint \iiint d\mathbf{x}_3 d\mathbf{x}_4 d\mathbf{x}_5 d\mathbf{x}_6 \chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_4; \mathbf{x}'_1, \mathbf{x}_3; \omega) \Xi_{\text{Hx}}^{\text{HF}}(\mathbf{x}_3, \mathbf{x}_6; \mathbf{x}_4, \mathbf{x}_5) \chi_{\text{TDHF}}(\mathbf{x}_5, \mathbf{x}_2; \mathbf{x}_6, \mathbf{x}'_2; \omega), \end{aligned} \quad (47)$$

with the frequency-independent HF Bethe-Salpeter kernel

$$\Xi_{\text{Hx}}^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = v(\mathbf{r}_1, \mathbf{r}_2) [\delta(\mathbf{x}_1 - \mathbf{x}'_1)\delta(\mathbf{x}_2 - \mathbf{x}'_2) - \delta(\mathbf{x}_1 - \mathbf{x}'_2)\delta(\mathbf{x}'_1 - \mathbf{x}_2)]. \quad (48)$$

Equivalently, Eq. (47) can be written more compactly with inverses (with respect to space-spin coordinates)

$$\chi_{\text{TDHF}}^{-1}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) = \chi_{\text{HF}}^{-1}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega) - \Xi_{\text{Hx}}^{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2). \quad (49)$$

By solving Eq. (47) or (49), we obtain the *time-dependent Hartree-Fock (TDHF)* linear-response function $\chi_{\text{TDHF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega)$.

Exercise 8 : Derive Eq. (47) from Eq. (33).

2.3 Linear-response equation in a spin-orbital basis

Now, we work out the TDHF linear-response equation in the orthonormal HF spin-orbital basis $\{\psi_k(\mathbf{x})\}$ for practical calculations.

One can notice that $\chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega)$ in Eq. (43) is expanded into products of two spin orbitals $\psi_p^*(\mathbf{x}'_1)\psi_q(\mathbf{x}_1)$ and $\psi_r(\mathbf{x}_2)\psi_s^*(\mathbf{x}'_2)$. The matrix elements of $\chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega)$ will thus be labelled by two double indices pq and rs , and are defined by

$$[\chi_{\text{HF}}(\omega)]_{pq,rs} = \iiint d\mathbf{x}_1 d\mathbf{x}'_1 d\mathbf{x}_2 d\mathbf{x}'_2 \psi_p(\mathbf{x}'_1)\psi_q^*(\mathbf{x}_1)\chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega)\psi_r^*(\mathbf{x}_2)\psi_s(\mathbf{x}'_2). \quad (50)$$

In fact, as seen in Eq. (43), $\chi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2; \omega)$ has non vanishing contributions only on occupied-virtual (ov) and virtual-occupied (vo) products of HF spin orbitals, and is diagonal in this subspace. The matrix representation of its inverse, in the (ov,vo) subspace, is thus immediately found from Eq. (43) to be

$$\chi_{\text{HF}}^{-1}(\omega) = - \left[\begin{pmatrix} \Delta\epsilon & \mathbf{0} \\ \mathbf{0} & \Delta\epsilon \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right], \quad (51)$$

where $\mathbf{1}$ is the identity matrix and $\Delta\epsilon$ is a diagonal matrix of elements $\Delta\epsilon_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}$, where i, j refer to occupied HF spin-orbitals and a, b to virtual HF spin orbitals. The dimension of the matrix is thus $2M_{\text{occ}}M_{\text{vir}} \times 2M_{\text{occ}}M_{\text{vir}}$ where M_{occ} and M_{vir} are the numbers of occupied and virtual spin orbitals, respectively.

The matrix elements of the HF Bethe-Salpeter kernel of Eq. (48) are defined in the same way as in Eq. (50). We find

$$[\Xi_{\text{HX}}^{\text{HF}}]_{pq,rs} = \langle qr||ps \rangle, \quad (52)$$

where $\langle qr||ps \rangle = \langle qr|ps \rangle - \langle qr|sp \rangle$ are the antisymmetrized two-electron integrals, with the definition

$$\langle qr|ps \rangle = \iint d\mathbf{x}_1 d\mathbf{x}_2 \psi_q^*(\mathbf{x}_1)\psi_r^*(\mathbf{x}_2)v(\mathbf{r}_1, \mathbf{r}_2)\psi_p(\mathbf{x}_1)\psi_s(\mathbf{x}_2). \quad (53)$$

From the Bethe-Salpeter equation (49), we finally find the matrix representation of the inverse of the TDHF linear-response function, in the (ov,vo) subspace,

$$\chi_{\text{TDHF}}^{-1}(\omega) = - \left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \right], \quad (54)$$

with the matrices \mathbf{A} and \mathbf{B} of elements

$$A_{ia,jb} = \Delta\epsilon_{ia,jb} + \langle aj||ib \rangle, \quad (55a)$$

$$B_{ia,jb} = \langle ab||ij \rangle. \quad (55b)$$

The block structure of Eq. (54) is a consequence of the symmetry of the two-electron integrals, $\langle qr||ps \rangle = \langle ps||qr \rangle^*$. Moreover, the matrix \mathbf{A} is Hermitian (i.e., $A_{jb,ia} = A_{ia,jb}^*$) and the matrix \mathbf{B} is symmetric (i.e., $B_{jb,ia} = B_{ia,jb}$).

Exercise 9 : Check Eq. (54) and the symmetry properties of the matrices \mathbf{A} and \mathbf{B} .

Similarly to Eq. (11), the TDHF excitation energies ω_n are given by the poles of $\chi_{\text{TDHF}}(\omega)$. They correspond to the values of ω giving zero eigenvalues of the matrix $\chi_{\text{TDHF}}^{-1}(\omega)$ in Eq. (54), leading to the following generalized eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix} = \omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{pmatrix}, \quad (56)$$

which is known as the *TDHF linear-response equation*. The solutions of Eq. (56) come in pairs: if $(\mathbf{X}_n, \mathbf{Y}_n)$ is an eigenvector with eigenvalue ω_n , then it is easy to check that $(\mathbf{Y}_n^*, \mathbf{X}_n^*)$ is also an eigenvector with opposite eigenvalue $-\omega_n$. The positive eigenvalues, $\omega_n > 0$, correspond to excitation energies, while the negative eigenvalues, $\omega_n < 0$, correspond to de-excitation energies.

The 2×2 -block matrix on the left-hand-side of Eq. (56) is Hermitian, but the 2×2 -block matrix on the right-hand-side of Eq. (56) is not positive definite. Consequently, Eq. (56) is not a Hermitian eigenvalue equation but a *pseudo-Hermitian eigenvalue equation*. One can show that if the 2×2 -block matrix on the left-hand-side of Eq. (56) is positive definite then all the eigenvalues ω_n are guaranteed to be real numbers (see Exercise 10). Since this matrix corresponds to the Hessian of the HF total energy with respect to the orbital rotation parameters, it is positive definite if the HF solution is a stable minimum with respect to the variation of all orbital parameters. This is known as the *Hartree-Fock stability conditions*.

Exercise 10 : Defining the matrices

$$\mathbb{L} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \quad \text{and} \quad \mathbb{\Delta} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}, \quad (57)$$

Eq. (56) is equivalent to finding the eigenvalues of $\mathbb{H} = \mathbb{\Delta}^{-1} \mathbb{L}$.

1. Check that \mathbb{L} and $\mathbb{\Delta}$ are Hermitian.
2. Show that \mathbb{H} is pseudo-Hermitian with respect to \mathbb{L} , i.e. $\mathbb{H}^\dagger = \mathbb{L} \mathbb{H} \mathbb{L}^{-1}$.
3. If \mathbb{L} is positive definite, show that $\tilde{\mathbb{H}} = \mathbb{L}^{1/2} \mathbb{H} \mathbb{L}^{-1/2}$ is Hermitian. Show then that \mathbb{H} has the same eigenvalues than $\tilde{\mathbb{H}}$, and are thus real.

For real-valued spin orbitals, and if $\mathbf{A} - \mathbf{B}$ is positive definite, the pseudo-Hermitian eigenvalue equation (56) can be transformed into a convenient half-size symmetric eigenvalue equation

$$\mathbf{M} \mathbf{Z}_n = \omega_n^2 \mathbf{Z}_n, \quad (58)$$

with $\mathbf{M} = (\mathbf{A} - \mathbf{B})^{1/2} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{1/2}$ and new eigenvectors \mathbf{Z}_n .

Exercise 11 : Derive Eq. (58) from Eq. (56).

Finally, it is common to consider the so-called *Tamm-Dancoff approximation (TDA)* to linear-response theory which corresponds to neglecting the matrix \mathbf{B} in Eq. (56). After setting $\mathbf{B} = \mathbf{0}$, Eq. (56) simplifies to a standard Hermitian eigenvalue equation

$$\mathbf{A} \mathbf{X}_n = \omega_n \mathbf{X}_n. \quad (59)$$

With the matrix \mathbf{A} in Eq. (55a), Eq. (59) corresponds in fact to the configuration-interaction method with only single excitations (CIS).

2.4 Spin-adapted linear-response equation for closed-shell systems

We give now the expressions for spin-restricted closed-shell calculations. We thus consider spatial HF orbitals $\phi_{i\sigma}(\mathbf{r})$ with spin $\sigma = \uparrow$ or \downarrow , so that $\phi_{i\uparrow}(\mathbf{r}) = \phi_{i\downarrow}(\mathbf{r})$. The matrices \mathbf{A} and \mathbf{B} have then each the following spin block structure

$$\mathbf{C} = \begin{pmatrix} \mathbf{C}_{\uparrow\uparrow,\uparrow\uparrow} & \mathbf{C}_{\uparrow\uparrow,\downarrow\downarrow} & \mathbf{0} & \mathbf{0} \\ \mathbf{C}_{\downarrow\downarrow,\uparrow\uparrow} & \mathbf{C}_{\downarrow\downarrow,\downarrow\downarrow} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{C}_{\uparrow\downarrow,\uparrow\downarrow} & \mathbf{C}_{\uparrow\downarrow,\downarrow\uparrow} \\ \mathbf{0} & \mathbf{0} & \mathbf{C}_{\downarrow\uparrow,\uparrow\downarrow} & \mathbf{C}_{\downarrow\uparrow,\downarrow\uparrow} \end{pmatrix}, \quad (60)$$

and can be transformed to block-diagonal spin-adapted matrices $\tilde{\mathbf{C}} = \mathbf{U}^T \mathbf{C} \mathbf{U}$ by the orthogonal transformation

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} \mathbf{1} & \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{1} & -\mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{1} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & -\mathbf{1} \end{pmatrix}. \quad (61)$$

Applying this transformation to the matrix \mathbf{A} gives the following decomposition into singlet and triplet excitation contributions

$$\tilde{\mathbf{A}} = \begin{pmatrix} {}^1\mathbf{A} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & {}^3\mathbf{A} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & {}^3\mathbf{A} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & {}^3\mathbf{A} \end{pmatrix}, \quad (62)$$

with

$${}^1A_{ia,jb} = \Delta\varepsilon_{ia,jb} + 2\langle aj|ib\rangle - \langle aj|bi\rangle, \quad (63a)$$

$${}^3A_{ia,jb} = \Delta\varepsilon_{ia,jb} - \langle aj|bi\rangle. \quad (63b)$$

Similarly, applying the transformation (61) to the matrix \mathbf{B} gives

$$\tilde{\mathbf{B}} = \begin{pmatrix} {}^1\mathbf{B} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & {}^3\mathbf{B} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & {}^3\mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & -{}^3\mathbf{B} \end{pmatrix}, \quad (64)$$

with

$${}^1B_{ia,jb} = 2\langle ab|ij\rangle - \langle ab|ji\rangle, \quad (65a)$$

$${}^3B_{ia,jb} = -\langle ab|ji\rangle. \quad (65b)$$

Exercise 12 : Check that the matrices \mathbf{A} and \mathbf{B} have indeed the form given in Eq. (60), and work out Eqs. (62) and (64).

The linear-response eigenvalue equation (56) then decouples into a singlet eigenvalue equation

$$\begin{pmatrix} {}^1\mathbf{A} & {}^1\mathbf{B} \\ {}^1\mathbf{B}^* & {}^1\mathbf{A}^* \end{pmatrix} \begin{pmatrix} {}^1\mathbf{X}_n \\ {}^1\mathbf{Y}_n \end{pmatrix} = {}^1\omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} {}^1\mathbf{X}_n \\ {}^1\mathbf{Y}_n \end{pmatrix}, \quad (66)$$

and a three-fold degenerate triplet eigenvalue equation

$$\begin{pmatrix} {}^3\mathbf{A} & {}^3\mathbf{B} \\ {}^3\mathbf{B}^* & {}^3\mathbf{A}^* \end{pmatrix} \begin{pmatrix} {}^3\mathbf{X}_n \\ {}^3\mathbf{Y}_n \end{pmatrix} = {}^3\omega_n \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} {}^3\mathbf{X}_n \\ {}^3\mathbf{Y}_n \end{pmatrix}. \quad (67)$$

Note that the minus sign in the last triplet block in Eq. (64) can be absorbed in ${}^3\mathbf{Y}_n$ so that the three triplet eigenvalue equations can be written in a common form. Again, for real orbitals, each eigenvalue equation (66) or (67) can be transformed into a half-size symmetric eigenvalue equation as in Eq. (58).

2.5 Example: H_2 in a minimal basis

As a pedagogical example, we consider the calculation of the TDHF excitation energies of the H_2 minimal in a minimal basis consisting of two basis functions, $\varphi_a(\mathbf{r})$ and $\varphi_b(\mathbf{r})$, centered on each hydrogen atom. This is a closed-shell molecule, therefore all the calculations are done with spin adaptation in a spatial orbital basis. The molecular orbitals are fixed by spatial symmetry

$$\phi_1(\mathbf{r}) = \frac{\varphi_a(\mathbf{r}) + \varphi_b(\mathbf{r})}{\sqrt{2(1 + S_{ab})}} \quad (\text{symmetry } \sigma_g), \quad (68)$$

and

$$\phi_2(\mathbf{r}) = \frac{\varphi_a(\mathbf{r}) - \varphi_b(\mathbf{r})}{\sqrt{2(1 - S_{ab})}} \quad (\text{symmetry } \sigma_u), \quad (69)$$

where S_{ab} is the overlap between $\varphi_a(\mathbf{r})$ and $\varphi_b(\mathbf{r})$. In HF, the orbital 1 is occupied and the orbital 2 is virtual. The corresponding HF orbital energies are

$$\varepsilon_1 = h_{11} + J_{11}, \quad (70)$$

and

$$\varepsilon_2 = h_{22} + 2J_{12} - K_{12}, \quad (71)$$

where h_{11} and h_{22} are one-electron integrals, and $J_{11} = \langle 11|11 \rangle$ and $K_{12} = \langle 11|22 \rangle$ are two-electron integrals.

The singlet matrices 1A and 1B are each one-dimensional

$${}^1A = \Delta\varepsilon + 2K_{12} - J_{12}, \quad (72a)$$

$${}^1B = K_{12}, \quad (72b)$$

where $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$, leading to the singlet excitation energy

$${}^1\omega = \sqrt{({}^1A + {}^1B)({}^1A - {}^1B)} = \sqrt{(\Delta\varepsilon + 3K_{12} - J_{12})(\Delta\varepsilon + K_{12} - J_{12})}. \quad (73)$$

Similarly, the triplet matrices 3A and 3B are each one-dimensional

$${}^3A = \Delta\varepsilon - J_{12}, \quad (74a)$$

$${}^3B = -K_{12}, \quad (74b)$$

leading to the triplet excitation energy

$${}^3\omega = \sqrt{({}^3A + {}^3B)({}^3A - {}^3B)} = \sqrt{(\Delta\varepsilon - K_{12} - J_{12})(\Delta\varepsilon + K_{12} - J_{12})}. \quad (75)$$

Appendices

A Fourier-transform formulas

We use the following convention for the Fourier transform a function $f(\tau)$

$$f(\omega) = \int_{-\infty}^{\infty} d\tau f(\tau) e^{i\omega\tau}, \quad (76)$$

and the inverse Fourier transform is thus

$$f(\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) e^{-i\omega\tau}. \quad (77)$$

Here are some useful Fourier-transform formulas involving the Dirac delta function

$$\delta(\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau}, \quad (78)$$

and the Heaviside step function

$$\theta(\tau) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega\tau}}{\omega + i0^+}, \quad (79)$$

$$\theta(-\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega\tau}}{\omega - i0^+}. \quad (80)$$

B Equation of motion for the one-particle Green function

The annihilation field operator in the Heisenberg picture $\hat{\psi}(1) = e^{i\hat{H}t_1}\hat{\psi}(\mathbf{x}_1)e^{-i\hat{H}t_1}$ obeys the following equation of motion

$$\frac{\partial\hat{\psi}(1)}{\partial t_1} = -i\left[\hat{\psi}(1), \hat{H}\right] = -ie^{i\hat{H}t_1}\left[\hat{\psi}(\mathbf{x}_1), \hat{H}\right]e^{-i\hat{H}t_1}. \quad (81)$$

The commutator $\left[\hat{\psi}(\mathbf{x}_1), \hat{H}\right]$ is easily calculated from the expression of the Hamiltonian in Eq. (1) using the anticommutation relations of the field operators

$$\left[\hat{\psi}(\mathbf{x}_1), \hat{H}\right] = h(\mathbf{r}_1)\hat{\psi}(\mathbf{x}_1) + \int d\mathbf{x}_2\hat{\psi}^\dagger(\mathbf{x}_2)v(\mathbf{r}_1, \mathbf{r}_2)\hat{\psi}(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_1), \quad (82)$$

where we have used the symmetry of the two-electron interaction, $v(\mathbf{r}_1, \mathbf{r}_2) = v(\mathbf{r}_2, \mathbf{r}_1)$. Introducing now the time exponentials that were in Eq. (81), we find

$$\frac{\partial\hat{\psi}(1)}{\partial t_1} = -ih(1)\hat{\psi}(1) - i\int d3\hat{\psi}^\dagger(3)v(1, 3)\hat{\psi}(3)\hat{\psi}(1), \quad (83)$$

where we have introduced the notations $h(1) = h(\mathbf{r}_1)$ and $v(1, 3) = v(\mathbf{r}_1, \mathbf{r}_3)\delta(t_1 - t_3)$ for convenience.

We can now calculate the derivative of the one-particle Green function $G(1, 2)$ with respect to t_1

$$\begin{aligned} i\frac{\partial}{\partial t_1}G(1, 2) &= \frac{\partial}{\partial t_1}\left(\theta(t_1 - t_2)\langle N|\hat{\psi}(1)\hat{\psi}^\dagger(2)|N\rangle - \theta(t_2 - t_1)\langle N|\hat{\psi}^\dagger(2)\hat{\psi}(1)|N\rangle\right) \\ &= \frac{\partial\theta(t_1 - t_2)}{\partial t_1}\langle N|\hat{\psi}(1)\hat{\psi}^\dagger(2)|N\rangle + \theta(t_1 - t_2)\langle N|\frac{\partial\hat{\psi}(1)}{\partial t_1}\hat{\psi}^\dagger(2)|N\rangle \\ &\quad - \frac{\partial\theta(t_2 - t_1)}{\partial t_1}\langle N|\hat{\psi}^\dagger(2)\hat{\psi}(1)|N\rangle - \theta(t_2 - t_1)\langle N|\hat{\psi}^\dagger(2)\frac{\partial\hat{\psi}(1)}{\partial t_1}|N\rangle. \end{aligned} \quad (84)$$

Using $\partial\theta(t_1 - t_2)/\partial t_1 = -\partial\theta(t_2 - t_1)/\partial t_1 = \delta(t_1 - t_2)$ and Eq. (83), we find after some simplifications

$$\begin{aligned} i\frac{\partial}{\partial t_1}G(1, 2) &= \delta(1, 2) + h(1)G(1, 2) - i\int d3v(1, 3) \\ &\quad \times \left[\theta(t_1 - t_2)\langle N|\hat{\psi}^\dagger(3)\hat{\psi}(3)\hat{\psi}(1)\hat{\psi}^\dagger(2)|N\rangle - \theta(t_2 - t_1)\langle N|\hat{\psi}^\dagger(2)\hat{\psi}^\dagger(3)\hat{\psi}(3)\hat{\psi}(1)|N\rangle\right]. \end{aligned} \quad (85)$$

The second term can be written with the two-particle Green function

$$i^2G_2(1, 3; 2, 3') = \langle N|T[\hat{\psi}(1)\hat{\psi}(3)\hat{\psi}^\dagger(3')\hat{\psi}^\dagger(2)]|N\rangle. \quad (86)$$

Paying attention to the time ordering and the anticommutations of field operators, we find

$$i\frac{\partial}{\partial t_1}G(1, 2) = \delta(1, 2) + h(1)G(1, 2) - i\int d3v(1, 3)G_2(1, 3^+; 2, 3^{++}), \quad (87)$$

where 3^+ means that the time variable has an infinitesimal positive shift $t_3^+ = t_3 + 0^+$, and 3^{++} means another shift $t_3^{++} = t_3^+ + 0^+$. After some rearrangements, we finally write the equation of the motion of $G(1, 2)$ as

$$\left[i\frac{\partial}{\partial t_1} - h(1)\right]G(1, 2) + i\int d3v(1, 3)G_2(1, 3^+; 2, 3^{++}) = \delta(1, 2). \quad (88)$$

C Schwinger functional derivative technique

WARNING: this appendix needs to be checked, improved, and extended. See Refs. [1, 2, 8].

We define a time-dependent Hamiltonian

$$\hat{H}(t) = \hat{H} + \hat{U}(t), \quad (89)$$

where \hat{H} is the time-independent many-body Hamiltonian of Eq. (1) and $\hat{U}(t)$ is a time-dependent external perturbation

$$\hat{U}(t_1) = \iint d\mathbf{x}_1 d1' \hat{\psi}^\dagger(\mathbf{x}_1) u(1, 1') \hat{\psi}(\mathbf{x}'_1) \quad (90)$$

where $u(1, 1') = u(\mathbf{x}_1, \mathbf{x}'_1; t_1) \delta(t_1 - t'_1)$ is an arbitrary nonlocal potential, assumed to be Hermitian at any t_1 , $u(\mathbf{x}_1, \mathbf{x}'_1; t_1)^* = u(\mathbf{x}'_1, \mathbf{x}_1; t_1)$, and to vanish sufficiently fast at $t_1 \rightarrow \pm\infty$. The time-dependent N -electron state is denoted by $|N(t)\rangle$ and satisfies the time-dependent Schrödinger equation

$$i \frac{\partial |N(t)\rangle}{\partial t} = \hat{H}(t) |N(t)\rangle. \quad (91)$$

C.1 Generalized Green functions and Dyson equation

By convention we use the N -electron state at $t = 0$, $|N(0)\rangle$, to define the *generalized one-particle Green function*

$$iG(1, 2) = \frac{\langle N(0) | T[\hat{\psi}(1) \hat{\psi}^\dagger(2)] | N(0) \rangle}{\langle N(0) | N(0) \rangle}, \quad (92)$$

where $\hat{\psi}(1) = \hat{U}(0, t_1) \hat{\psi}(\mathbf{x}_1) \hat{U}(t_1, 0)$ and $\hat{\psi}^\dagger(2) = \hat{U}(0, t_2) \hat{\psi}^\dagger(\mathbf{x}_2) \hat{U}(t_2, 0)$ are the annihilation and creation operators in the Heisenberg picture, where $\hat{U}(t, 0)$ is the time-evolution operator from 0 to t , defined by $|N(t)\rangle = \hat{U}(t, 0) |N(0)\rangle$.

From the time-dependent Schrödinger equation (91), it is easy to check that the operator $\hat{U}(0, t)$ obeys the evolution equation

$$\frac{\partial \hat{U}(t, 0)}{\partial t} = -i \hat{H}(t) \hat{U}(t, 0), \quad (93)$$

and, since $\hat{U}(t, 0)^\dagger = \hat{U}(0, t)$,

$$\frac{\partial \hat{U}(0, t)}{\partial t} = i \hat{U}(0, t) \hat{H}(t). \quad (94)$$

The annihilation operator $\hat{\psi}(1)$ thus satisfies an equation of motion similar to Eq. (81)

$$\frac{\partial \hat{\psi}(1)}{\partial t_1} = -i \hat{U}(0, t_1) \left[\hat{\psi}(\mathbf{x}_1), \hat{H}(t) \right] \hat{U}(t_1, 0), \quad (95)$$

which leads to an equation similar to Eq. (83) but with the external potential $u(1, 1')$

$$\frac{\partial \hat{\psi}(1)}{\partial t_1} = -ih(1) \hat{\psi}(1) - i \int d1' u(1, 1') \hat{\psi}(1') - i \int d3 \hat{\psi}^\dagger(3) v(1, 3) \hat{\psi}(3) \hat{\psi}(1). \quad (96)$$

The same steps used from Eq. (84) to Eq. (88) then give the equation of the motion in the presence of the external potential

$$\left[i \frac{\partial}{\partial t_1} - h(1) \right] G(1, 2) - \int d1' u(1, 1') G(1', 2) + i \int d3 v(1, 3) G_2(1, 3^+; 2, 3^{++}) = \delta(1, 2). \quad (97)$$

Repeating the calculations done in Section 1.3, we finally find the Dyson equation satisfied by the generalized one-particle Green function in the presence of the external potential

$$\boxed{G^{-1}(1, 1') = G_h^{-1}(1, 1') - u(1, 1') - \Sigma_{\text{Hxc}}(1, 1')}. \quad (98)$$

C.2 Interaction picture and functional derivative

We can rewrite the generalized one-particle Green function in the *interaction picture*

$$\boxed{iG(1, 2) = \frac{\langle N | T[\hat{S}\hat{\psi}_I(1)\hat{\psi}_I^\dagger(2)] | N \rangle}{\langle N | \hat{S} | N \rangle}}, \quad (99)$$

where $\psi_I(1) = e^{i\hat{H}t_1}\psi(\mathbf{x}_1)e^{-i\hat{H}t_1}$ and $\psi_I^\dagger(2) = e^{i\hat{H}t_2}\psi^\dagger(\mathbf{x}_2)e^{-i\hat{H}t_2}$ are the annihilation and creation operators in the interaction picture, and \hat{S} is the evolution operator from $-\infty$ to ∞ in the interaction picture

$$\hat{S} = U_I(\infty, -\infty) = T \exp \left(-i \int_{-\infty}^{\infty} dt_1 \hat{U}_I(t_1) \right), \quad (100)$$

with the interaction-picture perturbation operator $\hat{U}_I(t_1) = e^{i\hat{H}t_1}\hat{U}(t_1)e^{-i\hat{H}t_1}$. In Eq. (99), $|N\rangle$ is the ground state of the unperturbed Hamiltonian \hat{H} which is assumed to be the state at $t = \pm\infty$, so that $|N(0)\rangle = \hat{U}_I(0, -\infty)|N\rangle$ and $\langle N(0)| = \langle N|\hat{U}_I(\infty, 0)$. Using Eq. (90), the operator \hat{S} can be written as

$$\boxed{\hat{S} = T \exp \left(-i \iint d1d1' \hat{\psi}_I^\dagger(1)u(1, 1')\hat{\psi}_I(1') \right)}. \quad (101)$$

Similarly, the generalized two-particle Green function is

$$i^2 G_2(1, 2; 1', 2') = \frac{\langle N | T[\hat{S}\hat{\psi}_I(1)\hat{\psi}_I(2)\hat{\psi}_I^\dagger(2')\hat{\psi}_I^\dagger(1')] | N \rangle}{\langle N | \hat{S} | N \rangle}. \quad (102)$$

The generalized Green functions depend on the potential u only through the operator \hat{S} . The functional derivative of $G(1, 1')$ with respect to $u(2', 2)$ is

$$\frac{\delta G(1, 1')}{\delta u(2', 2)} = -i \left[\frac{\langle N | T[\frac{\delta \hat{S}}{\delta u(2', 2)}\hat{\psi}_I(1)\hat{\psi}_I^\dagger(1')] | N \rangle}{\langle N | \hat{S} | N \rangle} - \frac{\langle N | T[\hat{S}\hat{\psi}_I(1)\hat{\psi}_I^\dagger(1')] | N \rangle}{\langle N | \hat{S} | N \rangle} \frac{\langle N | \frac{\delta \hat{S}}{\delta u(2', 2)} | N \rangle}{\langle N | \hat{S} | N \rangle} \right]. \quad (103)$$

The functional derivative of \hat{S} is easily obtained from Eq. (101)

$$\frac{\delta \hat{S}}{\delta u(2', 2)} = -iT[\hat{S}\hat{\psi}_I^\dagger(2')\hat{\psi}_I(2)] = iT[\hat{S}\hat{\psi}_I(2)\hat{\psi}_I^\dagger(2')], \quad (104)$$

and, when inserted in Eq. (103), leads to

$$\frac{\delta G(1, 1')}{\delta u(2', 2)} = i^2 G_2(1, 2; 1', 2') - iG(1, 1')iG(2', 2) = i\chi(1, 2; 1', 2'). \quad (105)$$

We thus show that

$$\boxed{\chi(1, 2; 1', 2') = -i \frac{\delta G(1, 1')}{\delta u(2', 2)}}. \quad (106)$$

References

- [1] G. Csanak, H. Taylor and R. Yaris (Academic Press, 1971), vol. 7 of *Adv. At. Mol. Phys.*, p. 287.
- [2] G. Strinati, *Rivista del Nuovo Cimento* **11**, 1 (1988).
- [3] E. K. U. Gross, E. Runge and O. Heinonen, *Many-particle theory* (Verlag Adam Hilger, Bristol, 1991).
- [4] G. Onida, L. Reining and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
- [5] F. Bruneval, Ph.D. thesis, Ecole Polytechnique (2005).
- [6] J. Toulouse, W. Zhu, J. G. Ángyán and A. Savin, *Phys. Rev. A* **82**, 032502 (2010).
- [7] E. Rebolini, J. Toulouse and A. Savin, in *Electronic Structure and Reactivity*, edited by S. K. Ghosh and P. K. Chattaraj (CRC Press, 2013), *Concepts and Methods in Modern Theoretical Chemistry Vol. 1*, pp. 367–390, preprint at <http://arxiv.org/abs/1304.1314>.
- [8] F. Aryasetiawan, <http://www.teorfys.lu.se/staff/Claudio.Verdozzi/FunctionalD.pdf>.