Many-body theory of degenerate systems

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The many-body theory of degenerate systems is described in detail. More generally, this theory applies to systems with an initial state that cannot be described by a single Slater determinant. The double-source (or closed-time-path) formalism of nonequilibrium quantum field theory is used to derive an expression for the average value of a product of interacting fields when the initial state is not the vacuum or a Slater determinant. Quantum group techniques are applied to derive the hierarchy of unconnected Green functions and the hierarchy of connected ones.

I. INTRODUCTION

Degenerate systems are plenty (all systems containing an odd number of electrons, by Kramers theorem[1,2]) and degeneracy plays an important role in numerous interesting physical effects (e.g. magnetism or superconductivity). Thus, it seems relevant to develop calculation methods for degenerate systems. The density functional theory of degenerate systems is a subject of continued interest[3–7]. Green functions can be useful because they provide an exact expression for the exchange and correlation potential[8,9] and for their ability to calculate excitations, e.g. through the GW approximation[10] or Bethe-Salpeter equation[11,12]. Here, we study the Green functions of degenerate systems.

The quantum field theory of degenerate systems has been investigated since the sixties by two methods: either by calculating the S-matrix elements between different "in" and "out" states[13–17] or by assuming that the interacting ground state is a pure state evolving from a non-interacting pure state[18–22]. However, these works treat the electron-electron interaction as a perturbation, and we know that this is a rather crude approximation. So we need a non-perturbative approach to the Green functions of degenerate systems.

The first problem that we meet with such a program is the fact that we cannot always describe the system with a single wavefunction. For example, the electronic configuration of a boron atom in the ground state is $1s^2 2s^2 2p^1$. The Hamiltonian is invariant by rotation and, if the spin-orbit coupling is neglected, the six pure states $|p_i, s\rangle$ (with $i = x, y, z$ and $s = \pm 1/2$) are degenerate and are eigenstates of L^2 and S^2. However, none of these pure states gives a spherically symmetric electron density. More generally, if the ground state of a quantum system is a pure state with angular momentum $L \geq 1$, the charge density derived from this state is not spherically symmetric[23]. Therefore, the self-consistent pure state (with $L \geq 1$) of a spherical Hamiltonian breaks the spherical symmetry of the problem. A related results was proved by Bach et al.[24]: the solution of the unrestricted Hartree-Fock equations does not contain unfilled shells. Therefore, for the boron atom, the $2p$ shell is deformed to lift its degeneracy. To cure this defect of the Hartree-Fock approach, we have to assume that the boron atom is in the mixed state described by the density matrix $\hat\rho = (1/6)\sum_{i,s} |p_i, s\rangle\langle p_i, s|$, which preserves the rotational symmetry of the system. Similarly, it was shown rigorously that the density functional of a symmetric system is minimized by a symmetric charge density[25–27]. This symmetric charge density cannot be obtained from a single Slater determinant of the noninteracting Kohn-Sham system. The use of states that are not described by single Slater determinants was advocated in density functional theory by Ullrich and Kohn[5,6] and by van Leeuwen[28], even when the system is not degenerate.

Standard many-body theory is only valid when the unperturbed state is nondegenerate and can be described by a single Slater determinant. Therefore, for degenerate systems, we need to calculate an evolution starting not from a single pure state (usually called the vacuum $|0\rangle$), but from a density matrix $\hat\rho$. The best tool to do so is nonequilibrium quantum field theory, as created by Schwinger, Kadanoff, Baym and Keldysh[29–31] (see ref.[32] for a history of the subject). In particular, the closed time-path method will enable us to express the various Green functions we need as functional derivatives with respect to external sources.

We describe now the main result of this paper. The differential form of the hierarchy of Green functions[30,33] is

$$(i\frac{\partial}{\partial t_1} + \frac{\Delta_1}{2m})G(1,1') \;=\; \delta(1-1') - i\int v(\mathbf{r}_1 - \mathbf{r}_2) G_2(1,2;1',2^+)\mathrm{d}\mathbf{r}_2.$$

For non-degenerate systems that can be described by a single Slater determinant, the integral form of this equation is

$$G(1,1') \;=\; G_0(1,1') - i\int G_0(1,3) v(\mathbf{r}_3 - \mathbf{r}_2) G_2(3,2;1',2^+)\mathrm{d}\mathbf{r}_2\mathrm{d}\mathbf{r}_3,$$

where $G_0(1,1')$ is the Green function for the free Schrödinger equation

$$(i\frac{\partial}{\partial t_1} + \frac{\Delta_1}{2m})G_0(1,1') \;=\; \delta(1-1').$$

The unperturbed Green function $G^0(x,y)$ is given by the following expression (see[34] p.124)

$$\begin{aligned} G_0(x,x') \;=\; & -i\theta(t-t') \sum_{\epsilon_n>\epsilon_F} \mathrm{e}^{-i\epsilon_n(t-t')} u_n(\mathbf{r})\bar{u}_n(\mathbf{r}') \\ & +i\theta(t'-t) \sum_{\epsilon_n\le\epsilon_F} \mathrm{e}^{-i\epsilon_n(t-t')} u_n(\mathbf{r})\bar{u}_n(\mathbf{r}'), \end{aligned} \tag{1}$$

with $x=(t,\mathbf{r})$, $x'=(t',\mathbf{r}')$ and the orbital $u_n(\mathbf{r})$ is the solution of the unperturbed Schrödinger equation for energy ϵ_n. The Fermi energy ϵ_F is chosen so that the total charge $-i\int \mathrm{tr}(G_0(t,\mathbf{r},t,\mathbf{r}))\mathrm{d}\mathbf{r}$ is equal to the number N of electrons in the system. In this independent-particle picture, the ground state is degenerate if the Fermi level is degenerate and not completely filled. Therefore, the definition (1) must be modified because it assumes that the Fermi level is full. We shall see that the definition of G_0 for a degenerate system is non trivial.

Moreover, for degenerate systems, the relation between the differential and the integral Kadanoff-Baym equations is modified, because the solutions of the free Schrödinger equation intervene. In fact, the full hierarchy of Green functions is changed.

The correct hierarchy of Green function is important because it is the basis of the non perturbative approximations.

In this paper, we give the proper expression for G_0 and the integral form of the Kadanoff-Baym equation for a general density matrix. Compared to previous results, the present equations have two advantages: they are adapted to a self-consistent treatment and they do not break the symmetry of the problem.

Although the quantum field theory of degenerate systems seems to be a rather natural problem, it was not solved before because it poses technical difficulties that can hardly be overcome with the standard many-body techniques. Our main tool here will be the quantum group (or Hopf algebra) approach to quantum field theory, developed in[35,36].

In this paper, we give a self-contained presentation of the calculation of the expectation values of products of quantum field operators in the interaction picture. Then we compute interacting Green functions using functional derivatives with respect to external sources. The Hopf algebra of derivations is then introduced and used to derive the hierarchy of Green functions for systems with degenerate initial states, or more generally for systems with initial correlation. Explicit hierarchies are obtained for unconnected and connected Green functions. In the second paper of this series, the special case of a single electron in a system with closed shells and a two-fold degenerate orbital will be calculated in detail. In the third paper, non perturbative methods inspired by the GW approximation and the Bethe-Salpeter equations will be developed. The generalization of these standard methods to degenerate systems is difficult because many familiar equations are no longer available. For instance, the Dyson equation $G = G_0 + G_0\Sigma G$ does not hold for degenerate systems (the correct structure of G was discovered by Hall[37]). For all these developments, the hierarchy of Green functions developed in the present paper will be essential.

II. EVOLUTION OF EXPECTATIONS VALUES

We saw in the introduction that a self-consistent calculation of degenerate systems requires the use of density matrices. In this section we investigate how the unperturbed density matrix evolves with time under perturbation. As a first step, we calculate the evolution of an unperturbed wavefunction, then we extend this to the evolution of a density matrix, and we use this result to calculate the evolution of an expectation value. The calculation of transition amplitudes in quantum field theory is not completely standard, so we give here a detailed derivation. As an application, we obtain a formula for the Green function of a degenerate system.

A. Evolution of wavefunctions

We start from a time-independent free Hamiltonian $H_0 = \int \bar{\psi}_S(\mathbf{r})h_0(\mathbf{r})\psi_S(\mathbf{r})\mathrm{d}\mathbf{r}$, where $h_0(\mathbf{r})$ is a one-particle Hamiltonian and $\psi_S(\mathbf{r})$ is the field operator in the Schrödinger picture. A convient form of $\psi_S(\mathbf{r})$ is $\psi_S(\mathbf{r}) = \sum_n u_n(\mathbf{r})b_n$, where $u_n(\mathbf{r})$ is an eigenstate of h_0: $h_0u_n = \epsilon_n u_n$, and b_n is the annihilation operator for the one-particle state $u_n(\mathbf{r})$. We first look for the solutions of the Schrödinger equation

$$i\frac{\partial}{\partial t}|\Phi^0_n(t)\rangle \;=\; H_0|\Phi^0_n(t)\rangle.$$

As usually, we isolate the time dependence by putting $|\Phi_n^0(t)\rangle = \mathrm{e}^{-iE_n^0 t}|\Phi_n^0\rangle$ so that $H_0|\Phi_n^0\rangle = E_n^0|\Phi_n^0\rangle$. We assume that the $|\Phi_n^0\rangle$ provide a complete set of states. The matrix elements of the operator $A_S(t)$ in the Schrödinger picture is $\langle\Phi_m^0(t)|A_S(t)|\Phi_n^0(t)\rangle$. We go now to the Heisenberg picture by

$$\begin{aligned}\langle\Phi_m^0(t)|A_S(t)|\Phi_n^0(t)\rangle &= \langle\Phi_m^0|\mathrm{e}^{iE_m^0 t}A_S(t)\mathrm{e}^{-iE_n^0 t}|\Phi_n^0\rangle \\ &= \langle\Phi_m^0|\mathrm{e}^{iH_0 t}A_S(t)\mathrm{e}^{-iH_0 t}|\Phi_n^0\rangle = \langle\Phi_m^0|A(t)|\Phi_n^0\rangle,\end{aligned}$$

where $A(t) = \mathrm{e}^{iH_0 t}A_S(t)\mathrm{e}^{-iH_0 t}$ is the operator $A_S(t)$ in the Heisenberg picture. In particular $\mathrm{e}^{iH_0 t}H_0\mathrm{e}^{-iH_0 t} = H_0$, so that H_0 is the same in both picture. The field operator in the Heisenberg picture is (see[38] p.146) $\psi(x) = \mathrm{e}^{iH_0 t}\psi_S(\mathbf{r})\mathrm{e}^{-iH_0 t} = \sum_n u_n(\mathbf{r})\mathrm{e}^{-i\epsilon_n t}b_n$, with $x = (t,\mathbf{r})$.

We are interested in the interacting theory, so we add a possibly time-dependent interaction term to the Hamiltonian. This gives us $H_S(t) = H_0 + H_S^{\mathrm{int}}(t)$ in the Schrödinger picture and $H(t) = H_0 + H^{\mathrm{int}}(t)$ in the Heisenberg picture, with $H^{\mathrm{int}}(t) = \mathrm{e}^{iH_0 t}H_S^{\mathrm{int}}(t)\mathrm{e}^{-iH_0 t}$. In practice, $H_S^{\mathrm{int}}(t)$ is a polynomial in $\psi_S(\mathbf{r})$ and $\bar\psi_S(\mathbf{r})$, and $H^{\mathrm{int}}(t)$ is the same polynomial where $\psi_S(\mathbf{r})$ is replaced by $\psi(t,\mathbf{r})$ and $\bar\psi_S(\mathbf{r})$ is replaced by $\bar\psi(t,\mathbf{r})$.

We look for solutions of the Schrödinger equation

$$i\frac{\partial}{\partial t}|\Phi_n^S(t)\rangle = H_S(t)|\Phi_n^S(t)\rangle.$$

We go to the Heisenberg reprensentation with respect to H_0 (which is called the interaction picture) and we define $|\Phi_n(t)\rangle = \mathrm{e}^{iH_0 t}|\Phi_n^S(t)\rangle$. Therefore,

$$i\frac{\partial}{\partial t}|\Phi_n(t)\rangle = \mathrm{e}^{iH_0 t}(-H_0 + H_S(t))|\Phi_n^S(t)\rangle = H^{\mathrm{int}}(t)|\Phi_n(t)\rangle.$$

To solve this problem, we look for an operator $V(t)$ such that $|\Phi_n(t)\rangle = V(t)|\Phi_n^0\rangle$. The Schrödinger equation becomes

$$i\frac{\partial}{\partial t}V(t)|\Phi_n^0\rangle = H^{\mathrm{int}}(t)V(t)|\Phi_n^0\rangle.$$

This must be true for the complete set of $|\Phi_n^0\rangle$, thus

$$i\frac{\partial}{\partial t}V(t) = H^{\mathrm{int}}(t)V(t). \tag{2}$$

B. Calculation of $V(t)$

To solve equation (2), we put $U(t,t') = V(t)V^{-1}(t')$. Therefore, $U(t,t) = 1$ and

$$i\frac{\partial}{\partial t}U(t,t') = H^{\mathrm{int}}(t)U(t,t').$$

We are going to prove some properties of $U(t,t')$. We first prove the group property $U(t,t')U(t',t'') = U(t,t'')$. From the fact that $V(t)V^{-1}(t) = 1$ we deduce

$$i\frac{\partial}{\partial t}V^{-1}(t) = -V^{-1}(t)H^{\mathrm{int}}(t),$$

and

$$i\frac{\partial}{\partial t'}U(t,t') = -U(t,t')H^{\mathrm{int}}(t'),$$

Thus

$$i\frac{\partial}{\partial t'}U(t,t')U(t',t) = U(t,t')(-H^{\mathrm{int}}(t') + H^{\mathrm{int}}(t'))U(t',t) = 0.$$

Hence, the product $U(t,t')U(t',t)$ is independent of t'. To find its value, we put $t' = t$, so that $U(t,t')U(t',t'') = U(t,t)U(t,t'') = U(t,t'')$. Then we show that $U(t,t')$ is unitary. We take the adjoint of equation (2):

$$-i\frac{\partial}{\partial t}V^\dagger(t) = V^\dagger(t)H^{\mathrm{int}}(t),$$

because $H^{\rm int}(t)$ is Hermitian. This implies

$$i\frac{\partial}{\partial t}U^\dagger(t,t') \;=\; {V^{-1}}^\dagger(t')i\frac{\partial}{\partial t}V^\dagger(t) = -U^\dagger(t,t')H^{\rm int}(t).$$

Therefore, $U^\dagger(t,t') = U(t',t)$ because both operators satisfy the same equation and the same boundary condition $U(t,t) = U^\dagger(t,t) = 1$. But the group property leads to $U(t,t')U(t',t) = U(t,t) = 1$, so that $U^\dagger(t,t') = U(t',t) = U^{-1}(t,t')$, and $U(t,t')$ is unitary.

The construction of $U(t,t')$ is standard (see, e.g.[38,39]) and yields

$$U(t,t') \;=\; T\exp\big(-i\int_{t'}^{t} H^{\rm int}(\tau){\rm d}\tau\big). \tag{3}$$

Here, T is the time-ordering operator that orders its arguments by decreasing time from left to right. For example $T(A(t)B(t'))$ is $A(t)B(t')$ if $t>t'$ and is $B(t')A(t)$ if $t'>t$. An important property of the time-ordering operator is that its arguments commute. For instance, it can be checked from the definition that $T(A(t)B(t')) = T(B(t')A(t))$.

To complete the picture, we use the adiabatic hypothesis which states that

$$\lim_{t\to-\infty}|\Phi_n(t)\rangle \;=\; |\Phi^0_n\rangle,$$

so that

$$\lim_{t\to-\infty}V(t) \;=\; 1,$$

and $V(t) = U(t,-\infty)$. Thus, $V(t)$ is unitary. This has two important consequences: (i) the states $|\Phi_n(t)\rangle$ are complete at all times:

$$\sum_n |\Phi_n(t)\rangle\langle\Phi_n(t)| \;=\; V(t)\big(\sum_n |\Phi^0_n\rangle\langle\Phi^0_n|\big)V^\dagger(t) = V(t)V^\dagger(t) = 1,$$

and (ii) the scalar products are conserved: $\langle\Phi_m(t)|\Phi_n(t)\rangle = \langle\Phi^0_m|\Phi^0_n\rangle$.

To complete this section, we define the notion of anti-time-ordering operator, first considered by Dyson[40,41] (see also[42] p.94), which orders operators according to decreasing times. For any X which can be written as a product of field operators, the anti-time-ordering of X is defined as $T^*(X) = \big(T(X^\dagger)\big)^\dagger$ (see[36,43]). Notice that T^* is linear and its arguments commute. To understand the physical meaning of T^*, we take an example. If $t>t'$ we have $T^*(A(t)B(t')) = \big(T(B^\dagger(t')A^\dagger(t))\big)^\dagger = \big(A^\dagger(t)B^\dagger(t')\big)^\dagger = B(t')A(t)$. Analogously, $T^*(A(t)B(t')) = A(t)B(t')$ if $t<t'$. In other words, T^* orders its arguments so that the operators are on the right when they occur later. This is true for any number of arguments, and T^* orders its arguments in the reverse order with respect to T. This is why T^* is called the anti-time-ordering operator. The main example is

$$T^*\big(\psi(x)\bar\psi(y)\big) \;=\; \theta(y^0-x^0)\psi(x)\bar\psi(y) - \theta(x^0-y^0)\bar\psi(y)\psi(x) = T\big(\bar\psi(y)\psi(x)\big)^\dagger.$$

The most important application of the anti-time-ordering operator is the calculation of $U^\dagger(t,t')$.

$$\begin{aligned} U^\dagger(t,t') \;&=\; \Big(T\exp\big(-i\int_{t'}^{t} H^{\rm int}(\tau){\rm d}\tau\big)\Big)^\dagger \\ &=\; T^*\exp\big(i\int_{t'}^{t} H^{\rm int}(\tau){\rm d}\tau\big), \end{aligned} \tag{4}$$

because $H^{\rm int}(\tau)$ is Hermitian.

C. Evolution of density matrices

If $|\Phi^0_n(t)\rangle$ are solutions of the Schrödinger equation for H_0, a density matrix $\hat\rho^0_S(t)$ in the Schrödinger picture has the following general form

$$\hat\rho^0_S(t) \;=\; \sum_{mn}\rho_{nm}|\Phi^0_n(t)\rangle\langle\Phi^0_m(t)|,$$

where ρ_{nm} is a Hermitian matrix with non-negative eigenvalues such that $\sum_n \rho_{nn} = 1$. For later convenience, we do not require ρ_{nm} to be a diagonal matrix. From the Schrödinger equation, we see that the density matrix satisfies the equation

$$\frac{\partial \hat\rho^0_S(t)}{\partial t} = -i[H_0, \hat\rho^0_S(t)].$$

As for the wavefunctions, we define the density matrix in the Heisenberg picture $\hat\rho$ by $\hat\rho = \mathrm{e}^{iH_0 t}\hat\rho^0_S(t)\mathrm{e}^{-iH_0 t} = \sum_{mn}\rho_{nm}|\Phi^0_n\rangle\langle\Phi^0_m|$. Notice that $\hat\rho$ does not depend on time.

In the interacting case, we look for a density matrix $\hat\rho_S(t)$ in the Schrödinger picture that we write

$$\hat\rho_S(t) = \sum_{mn}\rho_{nm}|\Phi^S_n(t)\rangle\langle\Phi^S_m(t)|.$$

It satisfies the equation

$$\frac{\partial \hat\rho_S(t)}{\partial t} = -i[H, \hat\rho_S(t)].$$

We go to the interaction picture by defining $\hat\rho_I(t) = \mathrm{e}^{iH_0 t}\hat\rho_S(t)\mathrm{e}^{-iH_0 t}$, which satisfies the equation

$$\frac{\partial \hat\rho_I(t)}{\partial t} = -i[H^{\mathrm{int}}(t), \hat\rho_I(t)].$$

Now it is easy to see that the density matrix

$$\hat\rho_I(t) = \sum_{mn}\rho_{nm}V(t)|\Phi^0_n\rangle\langle\Phi^0_m|V^\dagger(t) = \sum_{mn}\rho_{nm}|\Phi_n(t)\rangle\langle\Phi_m(t)|,$$

satisfies the above equation. In other words, the density matrix $\hat\rho_I(t)$ describes the interacting system and it can be considered as the interacting density matrix that evolved from the non-interacting density matrix $\hat\rho$ because of the interactions.

D. Evolution of expectation values

The value of the observable $A(t)$ (in the interaction picture) for a system in a mixed state described by the density matrix $\hat\rho_I$ is (see[44] p.314)

$$\begin{aligned}\langle A(t)\rangle &= \mathrm{tr}\big(\hat\rho_I A(t)\big) = \sum_{mn}\rho_{nm}\langle\Phi_m(t)|A(t)|\Phi_n(t)\rangle \\ &= \sum_{mn}\rho_{nm}\langle\Phi^0_m|V^\dagger(t)A(t)V(t)|\Phi^0_n\rangle = \mathrm{tr}\big(\hat\rho V^\dagger(t)A(t)V(t)\big) \\ &= \mathrm{tr}\big(\hat\rho U(-\infty,t)A(t)U(t,-\infty)\big).\end{aligned} \tag{5}$$

The group property of $U(t,t')$ enables us to derive

$$\begin{aligned}\langle A(t)\rangle &= \mathrm{tr}\big(\hat\rho U(-\infty,t)U(t,+\infty)U(+\infty,t)A(t)U(t,-\infty)\big) \\ &= \mathrm{tr}\big(\hat\rho U(-\infty,+\infty)U(+\infty,t)A(t)U(t,-\infty)\big), \\ &= \mathrm{tr}\big(\hat\rho S^{-1}T(A(t)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big),\end{aligned} \tag{6}$$

where the interacting action is (up to a sign) $\mathcal{A}^{\mathrm{int}} = \int_{-\infty}^{\infty} H^{\mathrm{int}}(\tau)\mathrm{d}\tau$ and where the S-matrix is defined by $S = U(+\infty,-\infty) = T(\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})$. The last line of (6) was derived as follows. By equation (3)

$$\begin{aligned}U(+\infty,t)A(t)U(t,-\infty) = {}& T\big(\exp(-i\int_t^\infty H^{\mathrm{int}}(\tau)\mathrm{d}\tau)\big)A(t) \\ & T\big(\exp(-i\int_{-\infty}^t H^{\mathrm{int}}(\tau)\mathrm{d}\tau)\big).\end{aligned}$$

In that expression, the operators are on the left when their time arguments are larger. Thus, they are time ordered and we can rewrite this

$$
\begin{aligned}
U(+\infty,t)A(t)U(t,-\infty) &= T\Big(\exp(-i\int_t^\infty H^{\mathrm{int}}(\tau)\mathrm{d}\tau)A(t) \\
&\qquad \exp(-i\int_{-\infty}^t H^{\mathrm{int}}(\tau)\mathrm{d}\tau)\Big).
\end{aligned}
$$

The arguments of the time-ordering operator commute, thus

$$
\begin{aligned}
U(+\infty,t)A(t)U(t,-\infty) &= T\Big(A(t)\exp(-i\int_t^\infty H^{\mathrm{int}}(\tau)\mathrm{d}\tau) \\
&\qquad \exp(-i\int_{-\infty}^t H^{\mathrm{int}}(\tau)\mathrm{d}\tau)\Big) \\
&= T\Big(A(t)\exp(-i\int_{-\infty}^\infty H^{\mathrm{int}}(\tau)\mathrm{d}\tau)\Big) \\
&= T\big(A(t)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}}\big).
\end{aligned}
$$

To obtain equation (6), we inserted $1 = U(t,+\infty)U(+\infty,t)$ before $A(t)$ in equation (5). Of course, we can also insert $1 = U(t,+\infty)U(+\infty,t)$ after $A(t)$ in equation (5). This gives us the alternative formula

$$
\langle A(t)\rangle = \mathrm{tr}\big(\hat\rho T^*(A(t)\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})S\big). \tag{7}
$$

E. Correlation functions

Finally, we shall have to determine the correlation function between an observable $A(t)$ at time t and an observable $B(t')$ at time t'. To do this, we must determine which picture must be used to describe the observables at two different times. It turns out that the Heisenberg picture does the job. There are three reasons for this: (i) the equation for the observables in the Heisenberg picture are similar to the equations for the corresponding classical observables (see[44] p.316), (ii) the correlation functions of observables calculated in the Heisenberg picture agree with the experimental measurement of these observables (see[45], p. 655), (iii) the quantum description of photodetectors shows that they measure the correlation functions of the photon field in the Heisenberg picture (see[45], chapter 14).

The relation between the observables in the Schrödinger and Heisenberg pictures is given by $A_H(t) = V_S^\dagger(t)A_S(t)V_S(t)$ (see[38], p. 143), where V_S satisfies the Schrödinger equation for the full Hamiltonian $H_S(t)$:

$$
\frac{\partial V_S(t)}{\partial t} = -iH_S(t)V_S(t).
$$

The standard boundary condition is $V_S(0) = 1$ and the solution of this equation is $V_S(t) = \mathrm{e}^{-iH_0t}U(t,0)$. The boundary condition means that the Heisenberg and Schrödinger pictures coincide at $t = 0$. Therefore, the time-independent density matrix of the Heisenberg picture is equal to the Schrödinger density matrix at $t = 0$, i.e.

$$
\hat\rho_H = \hat\rho_S(0) = \sum_{mn}\rho_{nm}|\Phi_n^S(0)\rangle\langle\Phi_m^S(0)|.
$$

The correlation function for the two variables $A(t)$ and $B(t')$ is now

$$
\begin{aligned}
\langle A(t)B(t')\rangle &= \mathrm{tr}\big(\hat\rho_H A_H(t)B_H(t')\big) \\
&= \sum_{mn}\rho_{nm}\langle\Phi_m^S(0)|A_H(t)B_H(t')|\Phi_n^S(0)\rangle \\
&= \sum_{mn}\rho_{nm}\langle\Phi_m^0|U(-\infty,0)A_H(t)B_H(t')U(0,-\infty)|\Phi_n^0\rangle \\
&= \sum_{mn}\rho_{nm}\langle\Phi_m^0|U(-\infty,0)U(0,t)\mathrm{e}^{iH_0t}A_S(t)\mathrm{e}^{-iH_0t}U(t,0) \\
&\qquad U(0,t')\mathrm{e}^{iH_0t'}B_S(t')\mathrm{e}^{-iH_0t'}U(t',0)U(0,-\infty)|\Phi_n^0\rangle \\
&= \mathrm{tr}\big(\hat\rho U(-\infty,t)A(t)U(t,t')B(t')U(t',-\infty)\big).
\end{aligned}
$$

As in the previous subsection, the group property of the evolution operators $U(t,t')$ enables us to rewrite three kinds of correlation functions, for the operator product of fields, the time-ordered product of fields and the anti-time-ordered product of fields.

$$
\begin{aligned}
\langle A(t)B(t')\rangle &= \mathrm{tr}\big(\hat\rho T^*(A(t)\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})T(B(t')\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big),\\
\langle T(A(t)B(t'))\rangle &= \mathrm{tr}\big(\hat\rho S^{-1}T(A(t)B(t')\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big),\\
\langle T^*(A(t)B(t'))\rangle &= \mathrm{tr}\big(\hat\rho T^*(A(t)B(t')\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})S\big).
\end{aligned}
$$

More generally

$$
\langle T^*\big(A(t_1)\cdots A(t_m)\big)T\big(B(t'_1)\cdots B(t'_n)\big)\rangle = \mathrm{tr}\Big(\hat\rho T^*\big(A(t_1)\cdots A(t_m)\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}}\big)T\big(B(t'_1)\cdots B(t'_n)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}}\big)\Big). \tag{8}
$$

On the left hand side of this equation, the fields are written in the Heisenberg picture and on the left hand side in the interaction picture.

This enables us to define various Green functions. For example

$$
\begin{aligned}
G_{++}(x,y) &= -i\mathrm{tr}\big(\hat\rho T^*(\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})T(\psi(x)\bar\psi(y)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big),\\
G_{+-}(x,y) &= i\mathrm{tr}\big(\hat\rho T^*(\bar\psi(y)\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})T(\psi(x)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big),\\
G_{-+}(x,y) &= -i\mathrm{tr}\big(\hat\rho T^*(\psi(x)\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})T(\bar\psi(y)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big),\\
G_{--}(x,y) &= -i\mathrm{tr}\big(\hat\rho T^*(\psi(x)\bar\psi(y)\mathrm{e}^{i\mathcal{A}^{\mathrm{int}}})T(\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}})\big).
\end{aligned}
$$

III. FUNCTIONAL DERIVATIVE APPROACH

A. Functional derivatives of the S-matrix

The use of functional derivatives in quantum field theory was advocated by Schwinger[46]. The S-matrix for a nonrelativistic systems of electrons with Coulomb interaction is given by

$$
S = U(+\infty,-\infty) = T(\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}}).
$$

In solid-state physics, we usually consider the free and interaction Hamiltonians ([47] p.44)

$$
\begin{aligned}
H_0 &= \sum_{s=1}^{2}\int \bar\psi_s(t,\mathbf{r})(-\frac{\Delta}{2m}+U_N(\mathbf{r}))\psi_s(t,\mathbf{r})\mathrm{d}\mathbf{r},\\
H^{\mathrm{int}}(t) &= \frac{1}{2}\sum_{s,s'}\int \bar\psi_s(t,\mathbf{r})\bar\psi_{s'}(t,\mathbf{r}')V_e(\mathbf{r}-\mathbf{r}')\psi_{s'}(t,\mathbf{r}')\psi_s(t,\mathbf{r})\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',
\end{aligned}
$$

where $U_N(\mathbf{r})$ describes the interaction with the nuclei and $V_e(\mathbf{r}) = e^2/(4\pi\epsilon_0|\mathbf{r}|)$ the electron-electron interaction. We define now an S-matrix which depends on two external fermion sources $\eta(x)$ and $\bar\eta(x)$ as

$$
S(\bar\eta,\eta) = T\exp\big(-i\mathcal{A}^{\mathrm{int}} + i\int\bar\eta(x)\psi(x)\mathrm{d}x + i\int\bar\psi(x)\eta(x)\mathrm{d}x\big).
$$

For a nonrelativistic fermion, $\psi(x)$ and $\bar\psi(x)$ are two-component vectors. Thus, the sources are also two-component vectors and

$$
\bar\eta(x)\psi(x) = \sum_{s=1}^{2}\bar\eta_s(x)\psi_s(x), \qquad \bar\psi(x)\eta(x) = \sum_{s=1}^{2}\bar\psi_s(x)\eta_s(x).
$$

The functional derivative with respect to the fermion source $\eta(x)$ satisfies

$$
\begin{aligned}
\frac{\delta}{\delta\eta(x)}\eta(y) &= \delta(x-y), \quad \frac{\delta}{\delta\eta(x)}\bar\eta(y) = 0,\\
\frac{\delta}{\delta\eta(x)}(uv) &= \big(\frac{\delta u}{\delta\eta(x)}\big)v + (-1)^{|u|}u\big(\frac{\delta v}{\delta\eta(x)}\big).
\end{aligned} \tag{9}
$$

In this equation, we assumed that u is the product of a certain number of fermion fields or sources, and this number is denoted by $|u|$. Similar relations are satisfied by the functional derivative with respect to $\bar\eta(x)$. Equation (9) is known as Leibniz' rule.

The sources η and $\bar\eta$ anticommute, so the functional derivatives anticommute:

$$\frac{\delta^2}{\delta\eta(x)\delta\eta(y)} \;=\; -\frac{\delta^2}{\delta\eta(y)\delta\eta(x)}.$$

To see how functional derivatives act with respect to the time-ordering operator, we first notice that the sources can be taken out of the time-ordering operator. For example, if $x^0 > y^0$

$$\begin{aligned} T(\bar\eta(x)\psi(x)\bar\psi(y)\eta(y)) &= \bar\eta(x)\psi(x)\bar\psi(y)\eta(y) = \bar\eta(x)\eta(y)\psi(x)\bar\psi(y) \\ &= \bar\eta(x)\eta(y)T(\psi(x)\bar\psi(y)), \end{aligned}$$

if $x^0 < y^0$

$$\begin{aligned} T(\bar\eta(x)\psi(x)\bar\psi(y)\eta(y)) &= \bar\psi(y)\eta(y)\bar\eta(x)\psi(x) = -\bar\eta(x)\eta(y)\bar\psi(y)\psi(x) \\ &= \bar\eta(x)\eta(y)T(\psi(x)\bar\psi(y)). \end{aligned}$$

Thus, the functional derivative with respect to $\eta(x)$ or $\bar\eta(x)$ commutes with the time-ordering operator. In particular

$$\begin{aligned} \frac{\delta S(\bar\eta,\eta)}{\delta\bar\eta(x)}|_{\bar\eta=\eta=0} &= iT\big(\psi(x)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}}\big) = iU(+\infty,t)\psi(x)U(t,-\infty), \\ \frac{\delta S(\bar\eta,\eta)}{\delta\eta(x)}|_{\bar\eta=\eta=0} &= -iT\big(\bar\psi(x)\mathrm{e}^{-i\mathcal{A}^{\mathrm{int}}}\big) = -iU(+\infty,t)\bar\psi(x)U(t,-\infty), \end{aligned}$$

where $x=(t,\mathbf{r})$[48] and the minus sign in the last equation comes from the fact that the functional derivative must jump over $\bar\psi(x)$ to reach $\eta(x)$ in the definition of $S(\bar\eta,\eta)$. With this definition, we can write

$$\langle\psi_H(x)\rangle \;=\; i\frac{\delta}{\delta\bar\eta(x)}\sum_{mn}\rho_{nm}\langle\Phi^0_m|S(0,0)^{-1}S(\bar\eta,\eta)|\Phi^0_n\rangle|_{\bar\eta=\eta=0}. \tag{10}$$

In the vacuum, the density matrix is $|0\rangle\langle 0|$ and

$$\langle\psi_H(x)\rangle_0 \;=\; i\frac{\delta}{\delta\bar\eta(x)}\langle 0|S(0,0)^{-1}S(\bar\eta,\eta)|0\rangle|_{\bar\eta=\eta=0}.$$

One then invokes the "stability of the vacuum"[48] to derive

$$\begin{aligned} \langle\psi_H(x)\rangle_0 &= i\frac{\delta}{\delta\bar\eta(x)}\langle 0|S(0,0)^{-1}|0\rangle\langle 0|S(\bar\eta,\eta)|0\rangle|_{\bar\eta=\eta=0} \\ &= i\frac{\delta}{\delta\bar\eta(x)}\frac{\langle 0|S(\bar\eta,\eta)|0\rangle}{\langle 0|S(0,0)|0\rangle}|_{\bar\eta=\eta=0}, \end{aligned} \tag{11}$$

which is the Gell-Mann and Low formula[49]. The denominator is a pure phase, thus the main problem is to calculate the numerator of equation (11). A standard result of the functional derivative approach[48,50] is that the interacting S-matrix $S(\bar\eta,\eta)$ can be obtained from the non-interacting S-matrix $S^0(\bar\eta,\eta)$ with $S^0(\bar\eta,\eta) = T\exp\big(i\int\bar\eta(x)\psi(x)+\bar\psi(x)\eta(x)\mathrm{d}x\big)$ by the equation

$$S(\bar\eta,\eta) \;=\; \exp\big(-i\int_{-\infty}^{\infty}H^{\mathrm{int}}(\frac{-i\delta}{\delta\bar\eta(x)},\frac{i\delta}{\delta\eta(x)})\mathrm{d}t\big)S^0(\bar\eta,\eta),$$

where $x=(t,\mathbf{r})$. For a state described by a density matrix $\hat\rho = \rho_{nm}|\Phi^0_n\rangle\langle\Phi^0_m|$, the Gell-Mann and Low formula does not hold and we must deal with the term $S(0,0)^{-1}$ in equation (10). This is done by doubling the sources.

B. Source doubling

The idea of doubling the sources was proposed independently by Schwinger[29] and Symanzik[51,52]. It is a basic technique of nonequilibrium quantum field theory[37,53–58] where it is also known as the closed time-path Green function formalism. For equilibrium quantum field theory, Wagner showed that it can be useful to triple the sources[59]. In equation (10), we have the operator product of $S(0,0)^{-1}$ and $S(\bar\eta,\eta)$. In contrast with the case of a non-degenerate system, $S(0,0)^{-1}$ must now be calculated in detail. It is not possible to use $S(\bar\eta,\eta)^{-1}$ with the same sources as for $S(\bar\eta,\eta)$, because the functional derivative will then act on both $S(\bar\eta,\eta)^{-1}$ and $S(\bar\eta,\eta)$. To avoid this, we shall use sources to calculate $S(\bar\eta,\eta)^{-1}$ and sources to calculate $S(\bar\eta,\eta)$: we define

$$Z_\rho = \sum_{mn} \rho_{nm} \langle \Phi^0_m | S(\bar\eta_-,\eta_-)^{-1} S(\bar\eta_+,\eta_+) | \Phi^0_n \rangle. \tag{12}$$

Here Z_ρ is a function of the sources $\bar\eta_-,\eta_-,\bar\eta_+,\eta_+$. Notice that $Z_\rho = 1$ when $\bar\eta_- = \bar\eta_+$ and $\eta_- = \eta_+$, because $S(\bar\eta,\eta)^{-1}S(\bar\eta,\eta)=1$ and $\mathrm{tr}\hat\rho = 1$. To calculate $S(\bar\eta,\eta)^{-1}$, we recall that S is unitary, so that

$$\begin{aligned} S(\bar\eta_-,\eta_-)^{-1} &= S(\bar\eta_-,\eta_-)^\dagger \\ &= \Big(T \exp\big(-i\mathcal{A}^{\mathrm{int}} + i\int \bar\eta_-(x)\psi(x) + \bar\psi(x)\eta_-(x)\mathrm{d}x\big)\Big)^\dagger \\ &= T^* \exp\big(i\mathcal{A}^{\mathrm{int}} - i\int \bar\eta_-(x)\psi(x) + \bar\psi(x)\eta_-(x)\mathrm{d}x\big), \end{aligned}$$

where T^* is the anti-time-ordering operator defined in section II B.

At this point, there are two possibilities: either we leave the definition of $S(\bar\eta_-,\eta_-)^{-1}$ as it is (this is the convention used by Schwinger[29] for example), or we make the change $\eta_- \to -\eta_-$ and $\bar\eta_- \to -\bar\eta_-$. The first convention has some advantages (for instance $S(\bar\eta_-,\eta_-)^{-1}S(\bar\eta_+,\eta_+)=1$ when $\eta_+=\eta_-$ and $\bar\eta_+=\bar\eta_-$) but the second simplifies the calculation of average values and the Feynman rules. This is also the most common convention since Keldysh[31,55]. Therefore, we define now

$$S(\bar\eta_-,\eta_-)^{-1} = T^* \exp\big(i\mathcal{A}^{\mathrm{int}} + i\int \bar\eta_-(x)\psi(x) + \bar\psi(x)\eta_-(x)\mathrm{d}x\big). \tag{13}$$

But now of course $S(\bar\eta_-,\eta_-)^{-1}S(\bar\eta_+,\eta_+)=1$ when $\eta_+=-\eta_-$ and $\bar\eta_+=-\bar\eta_-$.

As for $S(\bar\eta_+,\eta_+)$, we can write

$$S(\bar\eta_-,\eta_-)^{-1} = \exp\big(i\int_{-\infty}^{\infty} H^{\mathrm{int}}(\frac{-i\delta}{\delta\bar\eta_-(x)},\frac{i\delta}{\delta\eta_-(x)})\mathrm{d}t\big) S^0(\bar\eta_-,\eta_-)^{-1},$$

where $x=(t,\mathbf{r})$ and

$$S^0(\bar\eta_-,\eta_-)^{-1} = T^* \exp\big(i\int \bar\eta_-(x)\psi(x) + \bar\psi(x)\eta_-(x)\mathrm{d}x\big).$$

If we put all this together, we obtain

$$Z_\rho = \mathrm{e}^{-iD} Z^0_\rho, \tag{14}$$

where

$$D = \int_{-\infty}^{\infty} H^{\mathrm{int}}(\frac{-i\delta}{\delta\bar\eta_+(x)},\frac{i\delta}{\delta\eta_+(x)}) - H^{\mathrm{int}}(\frac{-i\delta}{\delta\bar\eta_-(x)},\frac{i\delta}{\delta\eta_-(x)})\mathrm{d}t \tag{15}$$

and

$$Z^0_\rho = \sum_{mn} \rho_{nm} \langle \Phi^0_m | S^0(\bar\eta_-,\eta_-)^{-1} S^0(\bar\eta_+,\eta_+) | \Phi^0_n \rangle. \tag{16}$$

Notice that the functional derivatives with respect to $\eta_-(x)$ and $\bar\eta_-(x)$ correspond to anti-time-ordering. These are the basic equations for the calculation of Z_ρ. The next step is now the evaluation of Z^0_ρ.

IV. CALCULATION OF Z^0_ρ

In the calculation of Z^0_ρ, we first write $S^0(\bar\eta_-,\eta_-)^{-1}S^0(\bar\eta_+,\eta_+)$ in terms of normally ordered operators, then we calculate the trace of the normal ordered term. The use of normal order is very convenient to calculate matrix elements.

A. Normal ordering

If we call $A = i\int \bar\eta_-(x)\psi(x) + \bar\psi(x)\eta_-(x)\mathrm{d}x$ and $B = i\int \bar\eta_+(x)\psi(x) + \bar\psi(x)\eta_+(x)\mathrm{d}x$, we have $S^0(\bar\eta_-,\eta_-)^{-1}S^0(\bar\eta_+,\eta_+) = T^*(\mathrm{e}^A)T(\mathrm{e}^B)$. We want to write $T^*(\mathrm{e}^A)T(\mathrm{e}^B)$ as the product of scalar terms with the normally ordered exponential $:\mathrm{e}^{A+B}:$. To achieve this, we use the identity giving the time-ordered exponential in terms of the normally-ordered exponential: $T(\mathrm{e}^B) = \mathrm{e}^\beta:\mathrm{e}^B:$ (see eq.(4-73) p. 183 of ref.[48]), where

$$\beta = -\int \bar\eta_+(x)\langle 0|T\psi(x)\bar\psi(y)|0\rangle\eta_+(y)\mathrm{d}x\mathrm{d}y.$$

This identity is a generating function for Wick's theorem. The same proof leads to the corresponding identity for the anti-time-ordered products $T^*(\mathrm{e}^A) = \mathrm{e}^\alpha:\mathrm{e}^A:$, where

$$\alpha = -\int \bar\eta_-(x)\langle 0|T^*\psi(x)\bar\psi(y)|0\rangle\eta_-(y)\mathrm{d}x\mathrm{d}y.$$

Thus, $T^*(\mathrm{e}^A)T(\mathrm{e}^B) = \mathrm{e}^{\alpha+\beta}:\mathrm{e}^A::\mathrm{e}^B:$ and it remains to normally order the operator product of $:\mathrm{e}^A:$ and $:\mathrm{e}^B:$. To do so, we write the operator exponential in terms of a normally ordered exponential $\mathrm{e}^A = \mathrm{e}^{\alpha'}:\mathrm{e}^A:$ and $\mathrm{e}^B = \mathrm{e}^{\beta'}:\mathrm{e}^B:$, where

$$\begin{aligned}\alpha' &= -\frac{1}{2}\int \bar\eta_-(x)\langle 0|[\psi(x),\bar\psi(y)]|0\rangle\eta_-(y)\mathrm{d}x\mathrm{d}y,\\ \beta' &= -\frac{1}{2}\int \bar\eta_+(x)\langle 0|[\psi(x),\bar\psi(y)]|0\rangle\eta_+(y)\mathrm{d}x\mathrm{d}y.\end{aligned}$$

This identity is the generating function for Wick's theorem for operator products. To obtain this result we start from eq.(4-72) p. 183 of ref.[48] and we use the fact that $\{\psi^{(-)}(x),\bar\psi^{(+)}(y)\} = \langle 0|\bar\psi(y)\psi(x)|0\rangle$ and $\{\bar\psi^{(-)}(x),\psi^{(+)}(y)\} = \langle 0|\psi(y)\bar\psi(x)|0\rangle$. Thus, $:\mathrm{e}^A::\mathrm{e}^B: = \mathrm{e}^{-\alpha'-\beta'}\mathrm{e}^A\mathrm{e}^B$. To transform the product $\mathrm{e}^A\mathrm{e}^B$, we can employ the classical expression $\mathrm{e}^A\mathrm{e}^B = \mathrm{e}^{A+B+[A,B]/2}$, valid when $[A,B]$ commutes with A and B (eq. (4-15) p. 167 of ref.[48]). This is the case here because

$$\begin{aligned}[A,B] = -\int & \bar\eta_-(x)\{\psi(x),\bar\psi(y)\}\eta_+(y)\\ & +\eta_-(x)\{\bar\psi(x),\psi(y)\}\bar\eta_+(y)\mathrm{d}x\mathrm{d}y,\end{aligned}$$

is not an operator but a function (i.e. $\{\psi(x),\bar\psi(y)\} = \langle 0|\{\psi(x),\bar\psi(y)\}|0\rangle$. Now, we transform again the exponential e^{A+B} into a normally ordered exponential by $\mathrm{e}^{A+B} = \mathrm{e}^{\gamma'}:\mathrm{e}^{A+B}:$, where

$$\gamma' = -\frac{1}{2}\int \bar\eta_d(x)\langle 0|[\psi(x),\bar\psi(y)]|0\rangle\eta_d(y)\mathrm{d}x\mathrm{d}y,$$

with $\bar\eta_d = \bar\eta_+ + \bar\eta_-$ and $\eta_d = \eta_+ + \eta_-$. Putting all this together, we find $:\mathrm{e}^A::\mathrm{e}^B: = \mathrm{e}^\gamma:\mathrm{e}^{A+B}:$, with $\gamma = -\alpha' - \beta' + [A,B]/2 + \gamma'$, so that

$$\begin{aligned}\gamma = -\int & \eta_-(x)\langle 0|\bar\psi(x)\psi(y)|0\rangle\bar\eta_+(y)\\ & +\bar\eta_-(x)\langle 0|\psi(x)\bar\psi(y)|0\rangle\eta_+(y)\mathrm{d}x\mathrm{d}y.\end{aligned}$$

Thus, $T^*(\mathrm{e}^A)T(\mathrm{e}^B) = \mathrm{e}^{\alpha+\beta+\gamma}:\mathrm{e}^{A+B}:$. The calculation of $\alpha+\beta+\gamma$ gives us

$$T^*(\mathrm{e}^A)T(\mathrm{e}^B) = \exp[-i\int \bar\eta(x)G_0^0(x,y)\eta(y)\mathrm{d}x\mathrm{d}y]N^0(\bar\eta_d,\eta_d).$$

The two-dimensional vectors η and $\bar\eta$ are

$$\eta(x) = \begin{pmatrix}\eta_+(x)\\ \eta_-(x)\end{pmatrix} \qquad \bar\eta(x) = \begin{pmatrix}\bar\eta_+(x)\\ \bar\eta_-(x)\end{pmatrix},$$

the free Green function is

$$G_0^0(x,y) = \begin{pmatrix} -i\langle 0|T\big(\psi(x)\bar\psi(y)\big)|0\rangle & i\langle 0|\bar\psi(y)\psi(x)|0\rangle \\ -i\langle 0|\psi(x)\bar\psi(y)|0\rangle & -i\langle 0|T^*\big(\psi(x)\bar\psi(y)\big)|0\rangle\end{pmatrix}, \tag{17}$$

and the normally ordered exponential is

$$N^0(\bar\eta_d,\eta_d) \;=\; :\exp\big[i\int \bar\eta_d(x)\psi(x)+\bar\psi(x)\eta_d(x)\mathrm{d}x\big]:.$$

Two remarks will be useful in the sequel: the Green function is a solution of the equation

$$\big(i\partial_{x^0}-h_0(x)\big)G_0^0(x,y) \;=\; \big(-i\partial_{y^0}-h_0(y)\big)G_0^0(x,y)=\begin{pmatrix}\delta(x-y) & 0\\ 0 & -\delta(x-y)\end{pmatrix},$$

and it satisfies the relation

$$G^0_{0++}(x,y)+G^0_{0--}(x,y) \;=\; G^0_{0+-}(x,y)+G^0_{0-+}(x,y).$$

This last relation can be obtained for different times $x^0\neq y^0$ from the definition of the time-ordered and anti-time-ordered products. The unitarity of the S-matrix ensures that it is still true at $x^0=y^0$[60].

Finally, the generating function is

$$Z^0_\rho \;=\; \exp[-i\int \bar\eta(x)G_0^0(x,y)\eta(y)\mathrm{d}x\mathrm{d}y]\mathrm{tr}[\hat\rho N^0(\bar\eta_d,\eta_d)].$$

This is the standard expression of nonequilibrium quantum field theory[55].

Schwinger[29] showed that this expression can be rewritten in terms of advanced and retarded Green functions, using the sources $\bar\eta_m=(\bar\eta_+-\bar\eta_-)/2$ and $\eta_m=(\eta_+-\eta_-)/2$.

$$\begin{aligned}Z^0_\rho \;=\;& \exp[-i\int \bar\eta_d(x)G_r^0(x,y)\eta_m(y)+\bar\eta_m(x)G_a^0(x,y)\eta_d(y)\\ &+\frac{1}{2}\bar\eta_d(x)G_c^0(x,y)\eta_d(y)\mathrm{d}x\mathrm{d}y]\mathrm{tr}[\hat\rho N^0(\bar\eta_d,\eta_d)],\end{aligned}$$

with

$$\begin{aligned}G_r^0(x,y) &= G^0_{++}(x,y)-G^0_{+-}(x,y)=G^0_{-+}(x,y)-G^0_{--}(x,y)=-i\theta(x^0-y^0)\langle 0|\{\psi(x),\bar\psi(y)\}|0\rangle,\\ G_a^0(x,y) &= G^0_{++}(x,y)-G^0_{-+}(x,y)=G^0_{+-}(x,y)-G^0_{--}(x,y)=i\theta(y^0-x^0)\langle 0|\{\psi(x),\bar\psi(y)\}|0\rangle,\\ G_c^0(x,y) &= G^0_{++}(x,y)+G^0_{--}(x,y)=G^0_{+-}(x,y)+G^0_{-+}(x,y)=-i\langle 0|[\psi(x),\bar\psi(y)]|0\rangle.\end{aligned}$$

B. Calculation of $\mathrm{tr}[\hat\rho N^0(\bar\eta_d,\eta_d)]$

The calculation of $\mathrm{tr}[\hat\rho N^0(\bar\eta_d,\eta_d)]$ is relegated to appendix because it is rather technical. We give here the results. The unperturbed eigenstates of H_0 will now be called $|K\rangle$ and $|L\rangle$ instead of $|\Phi^0_m\rangle$ and $|\Phi^0_n\rangle$. They are defined from the vacuum $|0\rangle$ by application of creation operators $|K\rangle=b^\dagger_{i_N}\dots b^\dagger_{i_1}|0\rangle$ and $|L\rangle=b^\dagger_{j_N}\dots b^\dagger_{j_1}|0\rangle$. Here, N is the number of electrons and the indices i_k and j_k take their values in the set of indices of the M orbitals. We assume that the indices are ordered: $i_1<\dots<i_N$ and $j_1<\dots<j_N$. If we take the example of Cr^{3+}, the number of d electrons is $N=3$ and the number of d orbitals is $M=10$. We assume that the orbitals are ordered in such a way that the M orbitals that come into play are numbered from $n=1$ to $n=M$. We define integrals of the product of the wavefunctions with external sources by $\bar\alpha_n=\int\bar\eta_d(x)u_n(x)\mathrm{d}x$ and $\alpha_n=\int\bar u_n(x)\eta_d(x)\mathrm{d}x$, where $u_n(x)=\mathrm{e}^{-i\epsilon_n t}u_n(\mathbf{r})$ and $\bar u_n(x)=\mathrm{e}^{i\epsilon_n t}\bar u_n(\mathbf{r})$, with $x=(t,\mathbf{r})$. Recall that $\bar\eta_d=\bar\eta_++\bar\eta_-$ and $\eta_d=\eta_++\eta_-$. The result can now be stated in its simplest form as $\mathrm{tr}\big(\hat\rho N^0(\bar\eta_d,\eta_d)\big)=\sum_{KL}\rho_{LK}N^0_{KL}$ with

$$\begin{aligned}N^0_{KL} \;&=\; \langle K|N^0(\bar\eta_d,\eta_d)|L\rangle\\ &=\; \exp\Big(\sum_{n=1}^M\frac{\partial^2}{\partial\alpha_n\partial\bar\alpha_n}\Big)\bar\alpha_{j_1}\alpha_{i_1}\dots\bar\alpha_{j_N}\alpha_{i_N}.\end{aligned}\tag{18}$$

A more explicit but more cumbersome form of this result is given in the appendix.

It is interesting to consider the particular case of a closed shell (see equation (60) in the appendix). This happens when all orbitals are occupied, i.e. $N=M$. Then there is only one state $|K\rangle$, which is a Slater determinant, so we have $\hat\rho=|K\rangle\langle K|$ and

$$\mathrm{tr}\big(\hat\rho N^0\big) \;=\; \prod_{k=1}^N(1+\bar\alpha_{i_k}\alpha_{i_k}).$$

V. THE HOPF ALGEBRA OF DERIVATIONS

The term quantum group has a broad meaning[61], ranging from general Hopf algebras to q-deformed groups. In this section we use the more precise term of Hopf algebra.

We introduce now the Hopf algebra of functional derivations $\mathcal{D}$, which plays a vital role in this paper. In particular, the calculation of $\mathrm{tr}(\hat\rho N^0(\bar\eta_d, \eta_d))$ and the resummation leading to the hierarchy of Green functions for degenerate systems make essential use of the Hopf structure of $\mathcal{D}$. Writing this hierarchy without Hopf-algebraic tools would be quite cumbersome. Since the introduction of the Hopf algebra of renormalization by Kreimer[62], it has become clear that Hopf algebras are going to play a substantial role in quantum field theory[35,36].

Many textbooks on Hopf algebras are now available[61,63] but we shall use only a very limited amount of this theory. For the convenience of the reader, we give now a short survey of the Hopf algebra of derivations.

A. A familiar example of coproduct

The most unusual object of a Hopf algebra is the coproduct. To make the reader familiar with this concept, we present it in the case of the algebra $\mathcal{A}$ of differential operators with constant coefficients. We consider the coordinates $x_1, \dots, x_n$ of an n-dimensional space, and the differential operators $P = \sum_{\boldsymbol\alpha} a_{\boldsymbol\alpha} D^{\boldsymbol\alpha}$, where $\boldsymbol\alpha = (\alpha_1, \dots, \alpha_n)$ is a multi-index, $a_{\boldsymbol\alpha}$ is a complex number and $D^{\boldsymbol\alpha} = \partial_1^{\alpha_1} \dots \partial_n^{\alpha_n}$, where ∂_i denotes the partial derivative ∂/∂_{x_i}. It is clear that $\mathcal{A}$ is a vector space with basis $D^{\boldsymbol\alpha}$, where $\boldsymbol\alpha$ runs over all the possible multi-indices. $\mathcal{A}$ is also an associative algebra with the product induced by the product of the basis elements $D^{\boldsymbol\alpha} D^{\boldsymbol\beta} = D^{\boldsymbol\alpha+\boldsymbol\beta}$. To this algebra we add a unit $\mathbf{1}$ such that $D\mathbf{1} = \mathbf{1}D = D$ for any element D of $\mathcal{A}$.

In this context, the coproduct comes from the action of a differential operator on a product of two functions. The action of ∂_i on the product fg is given by the Leibniz rule $\partial_i(fg) = (\partial_i f)g + f(\partial_i g)$. For a product ot two partial derivatives we have

$$\partial_i\partial_j(fg) \;=\; (\partial_i\partial_j f)g + f(\partial_i\partial_j g) + (\partial_i f)(\partial_j g) + (\partial_j f)(\partial_i g). \tag{19}$$

More generally, for any differential operator $P \in \mathcal{A}$, we can write $P(fg)$ as a sum of terms that are the product of a differential operator acting on f and a differential operator acting on g. We write this using Sweedler's notation $P(fg) = \sum (P_{(1)} f)(P_{(2)} g)$. For example, if $P = \partial_i$ we have a sum of two terms, in the first term $P_{(1)} = \partial_i$ and $P_{(2)} = \mathbf{1}$ (with the convention that, for any function f, $\mathbf{1}f = f$) and in the second term $P_{(1)} = \mathbf{1}$ and $P_{(2)} = \partial_i$. The idea of the coproduct is now to remove the reference to the functions f and g and to keep only the sum of terms with $P_{(1)}$ on the left and $P_{(2)}$ on the right. This is done formally by defining the coproduct Δ from $\mathcal{A}$ to $\mathcal{A} \otimes \mathcal{A}$ as $\Delta P = \sum P_{(1)} \otimes P_{(2)}$. From the known properties of the action of a differential operator on a product of two functions we deduce the following properties of the coproduct: $\Delta\mathbf{1} = \mathbf{1} \otimes \mathbf{1}$, $\Delta\partial_i = \partial_i \otimes \mathbf{1} + \mathbf{1} \otimes \partial_i$ and the recursive relation

$$\Delta(PP') \;=\; \sum (PP')_{(1)} \otimes (PP')_{(2)} = \sum\sum P_{(1)}P'_{(1)} \otimes P_{(2)}P'_{(2)}.$$

From the last rule we obtain $\Delta(\partial_i\partial_j) = (\partial_i\partial_j) \otimes \mathbf{1} + \mathbf{1} \otimes (\partial_i\partial_j) + \partial_i \otimes \partial_j + \partial_j \otimes \partial_i$, and we recover equation (19). The main property of the coproduct is its coassociativity, which means that

$$\sum \Delta(P_{(1)}) \otimes P_{(2)} \;=\; \sum P_{(1)} \otimes \Delta(P_{(2)}) = \sum P_{(1)} \otimes P_{(2)} \otimes P_{(3)}.$$

For example, if $P = \partial_i$,

$$\begin{aligned}\sum P_{(1)} \otimes P_{(2)} \otimes P_{(3)} \;&=\; \sum (\Delta\partial_i) \otimes \mathbf{1} + (\Delta\mathbf{1}) \otimes \partial_i \\ &=\; \partial_i \otimes \mathbf{1} \otimes \mathbf{1} + \mathbf{1} \otimes \partial_i \otimes \mathbf{1} + \mathbf{1} \otimes \mathbf{1} \otimes \partial_i.\end{aligned}$$

With this definition we can obtain the action of P on a product of three functions as $P(fgh) = \sum (P_{(1)} f) \otimes (P_{(2)} g) \otimes (P_{(3)} h)$.

After this introduction, we can now define the algebra of functional derivations. The main changes are that the partial derivatives are replaced by functional derivatives with respect to external sources, and the fact that the anticommutativity of external sources generates signs in the formulas.

B. The algebra structure of $\mathcal{D}$

The symbol ∂ is used to denote the functional derivative with respect to the external souces $\eta(x)$ or $\bar\eta(x)$. More precisely, since the external sources are two-dimensional vectors, ∂ stands for the functional derivative with respect to $\eta_s(x)$ or $\bar\eta_s(x)$, where $s = 1$ or $s = 2$. Products of symbols stands for repeated derivations. For instance, if $\partial_1 = \delta/\delta\eta_1(x)$, $\partial_2 = \delta/\delta\bar\eta_2(y)$ and $\partial_3 = \delta/\delta\eta_2(x)$, then

$$\partial_1\partial_2\partial_3 \;=\; \frac{\delta^3}{\delta\eta_1(x)\delta\bar\eta_2(y)\delta\eta_2(x)}.$$

The functional derivatives anticommute, thus $\partial\partial' = -\partial'\partial$ for any functional derivatives ∂ and ∂'. Therefore, for any functional derivative ∂, we have $\partial\partial = 0$.

A basis of the vector space $\mathcal{D}$ of functional derivatives with respect to external sources is given by the products of derivations $\partial_1 \dots \partial_n$ for all $n \geq 1$ and the unit $\mathbf{1}$. Here, the unit is not the constant function 1, it is a symbol that satisfies $\mathbf{1}\partial = \partial\mathbf{1} = \partial$ for any functional derivative ∂. Thus, for instance,

$$4\mathbf{1} + 2\frac{\delta}{\delta\eta_1(x)} + \frac{1}{6}\frac{\delta^2}{\delta\bar\eta_2(y)\delta\eta_2(x)}$$

is an element of $\mathcal{D}$.

In $\mathcal{D}$, the terms of the form $\partial_1 \dots \partial_n$ generate a subspace of $\mathcal{D}$ denoted by $\mathcal{D}_n$ (for $n > 0$). The elements $\mathcal{D}_0$ have the form $\lambda\mathbf{1}$, where λ is a complex number. If $D \in \mathcal{D}$ belongs to $\mathcal{D}_n$ for some n, we say that D is homogeneous and its degree, written $\deg(D)$, is n. For instance $\deg(\mathbf{1}) = 0$, $\deg(\partial) = 1$, $\deg(\partial\partial') = 2$. The vector space $\mathcal{D}$ becomes an algebra if we define the product of two elements of $\mathcal{D}$ to be the composition of derivations. For instance, the product of ∂_1 and ∂_2 is $\partial_1\partial_2$. This product is anticommutative. It can be checked that $\mathcal{D}$ is an associative algebra with unit $\mathbf{1}$. Moreover, $\deg(DD') = \deg(D) + \deg(D')$ for any homogeneous elements D and D' of $\mathcal{D}$. From the degree $\deg(D)$ of a homogeneous element D we can define its parity $|D|$ by $|D| = 0$ if $\deg(D)$ is even and $|D| = 1$ if $\deg(D)$ is odd. If $|D|$=0 (resp. $|D| = 1$) we say that D is even (resp. odd).

Now we prove a useful property of the product in $\mathcal{D}$: if D and D' are elements with a specific parity $|D|$ and $|D'|$, then

$$DD' = (-1)^{|D||D'|}D'D. \tag{20}$$

An important consequence of this is the fact that an even element of $\mathcal{D}$ commutes with all elements of $\mathcal{D}$. To prove equation (20), we first show it for homogeneous elements. We start with $D = \partial$ and $D' = \partial'_1 \dots \partial'_n$, then $\partial\partial'_1 \dots \partial'_n = (-1)^n\partial'_1 \dots \partial'_n\partial$ because ∂ must jump n times over a ∂'. Now, if $D = \partial_1 \dots \partial_m$, ∂_m jumps over D', giving $(-1)^n$, then ∂_{m-1} jumps over D' giving another $(-1)^n$, and so on until ∂_1 and we obtain $DD' = (-1)^{mn}D'D = (-1)^{\deg(D)\deg(D')}$. Equation (20) is recovered because $(-1)^{\deg(D)\deg(D')} = (-1)^{|D||D'|}$. If D and D' are not homogeneous but have a definite parity, they can be written as sums of homogeneous elements, and the result follows by linearity.

C. The coalgebra structure of $\mathcal{D}$

We introduce now the coproduct Δ of $\mathcal{D}$. In concrete terms, the coproduct of an element D of $\mathcal{D}$ is the sum of the ways to split D into the product of two elements of $\mathcal{D}$. Formally, the coproduct is defined as a map from $\mathcal{D}$ to $\mathcal{D}\otimes\mathcal{D}$, where $\otimes$ stands for the tensor product. We recall the main property of the tensor product[64]: for any $D, D', E, E' \in \mathcal{D}$ and $\lambda, \lambda', \mu, \mu' \in \mathbb{C}$,

$$\begin{aligned}(\lambda D + \lambda' D') \otimes (\mu E + \mu' E') \;&=\; \lambda\mu D \otimes E + \lambda\mu' D \otimes E' \\ &\quad + \lambda'\mu D' \otimes E + \lambda'\mu' D' \otimes E'.\end{aligned}$$

The coproduct of the elements of smallest degrees is given by

$$\Delta\mathbf{1} \;=\; \mathbf{1}\otimes\mathbf{1}, \tag{21}$$

$$\Delta\partial \;=\; \partial\otimes\mathbf{1} + \mathbf{1}\otimes\partial. \tag{22}$$

To define the coproduct of elements of higher degree, we need a notation for the coproduct. Following Sweedler, we write $\Delta D = \sum D_{(1)} \otimes D_{(2)}$. For instance, if $D = \partial$, the sum has two terms. The first term is $D_{(1)} = \partial$, $D_{(2)} = \mathbf{1}$ the second term is $D_{(1)} = \mathbf{1}$, $D_{(1)} = \partial$. The coproduct can now be defined recursively by

$$\Delta(DD') \;=\; \sum(-1)^{|D_{(2)}||D'_{(1)}|}(D_{(1)}D'_{(1)}) \otimes (D_{(2)}D'_{(2)}). \tag{23}$$

As an exercise, we calculate $\Delta(\partial\partial')$, so that $D = \partial$ and $D' = \partial'$. Equation (22) gives us $\Delta\partial = \partial\otimes\mathbf{1} + \mathbf{1}\otimes\partial$ and $\Delta\partial' = \partial'\otimes\mathbf{1} + \mathbf{1}\otimes\partial'$. The first term of $\Delta(\partial\partial')$ is obtained from formula (23) with $D_{(1)} = \partial$, $D_{(2)} = \mathbf{1}$, $D'_{(1)} = \partial'$ and

$D'_{(2)} = \mathbf{1}$. The degrees are $|D_{(2)}| = 0$, $|D'_{(1)}| = 1$ and their product is $|D_{(2)}||D'_{(1)}| = 0$ so we obtain the term $\partial\partial' \otimes \mathbf{1}$. The other terms are calculated analogously and the result is

$$\Delta(\partial\partial') = \partial\partial' \otimes \mathbf{1} + \mathbf{1} \otimes \partial\partial' + \partial \otimes \partial' - \partial' \otimes \partial.$$

The minus sign is due to the fact that the corresponding term comes from $D_{(1)} = \mathbf{1}$, $D_{(2)} = \partial$, $D'_{(1)} = \partial'$ and $D'_{(2)} = \mathbf{1}$, so that $|D_{(2)}||D'_{(1)}| = 1$.

It can be checked[64] that the coproduct of a basis element $D = \partial_1 \dots \partial_n$ of $\mathcal{D}$ is

$$\begin{aligned}\Delta D &= D \otimes \mathbf{1} + \mathbf{1} \otimes D \\ &\quad + \sum_{p=1}^{n-1} \sum_{\sigma} (-1)^\sigma \partial_{\sigma(1)} \dots \partial_{\sigma(p)} \otimes \partial_{\sigma(p+1)} \dots \partial_{\sigma(n)},\end{aligned}$$

where σ runs over the $(p, n-p)$-shuffles and $(-1)^\sigma$ is the signature of the permutation σ. Recall that a $(p, n-p)$-shuffle is a permutation σ of $\{1, \dots, n\}$ such that $\sigma(1) < \sigma(2) < \dots < \sigma(p)$ and $\sigma(p+1) < \dots < \sigma(n)$. Notice that we always have $D = D_{(1)} D_{(2)}$.

With this definition, we know the coproduct for a basis of $\mathcal{D}$, the coproduct of a general term of $\mathcal{D}$ is obtained by linearity: $\Delta(\lambda D + \lambda' D') = \lambda(\Delta D) + \lambda'(\Delta D')$.

The most important property of the coproduct is its *coassociativity*. We saw that the coproduct of an element D gives the ways to split D into two elements $D_{(1)}$ and $D_{(2)}$. Now assume that we want to split D into three elements. We can achieve this either by splitting $D_{(1)}$ or by splitting $D_{(2)}$. Coassociativity means that the result does not depend on this choice. This is expressed more formally by $(\mathrm{Id} \otimes \Delta)\Delta = (\Delta \otimes \mathrm{Id})\Delta$. For example the reader can check that

$$\begin{aligned}(\mathrm{Id} \otimes \Delta)\Delta\mathbf{1} &= \mathbf{1} \otimes \mathbf{1} \otimes \mathbf{1} = (\Delta \otimes \mathrm{Id})\Delta\mathbf{1}, \\ (\mathrm{Id} \otimes \Delta)\Delta\partial &= \partial \otimes \mathbf{1} \otimes \mathbf{1} + \mathbf{1} \otimes \partial \otimes \mathbf{1} + \mathbf{1} \otimes \mathbf{1} \otimes \partial = (\Delta \otimes \mathrm{Id})\Delta\partial.\end{aligned}$$

The coproduct Δ is coassociative for all elements of $\mathcal{D}$[64]. It can also be shown that the coproduct satisfies $\Delta D = \sum D_{(1)} \otimes D_{(2)} = \sum (-1)^{|D_{(1)}||D_{(2)}|} D_{(2)} \otimes D_{(1)}$ (this property is called graded cocommutativity).

We can define recursively the splitting of D into n parts by $\Delta^{(0)} D = \mathbf{1}$, $\Delta^{(1)} D = D$, $\Delta^{(2)} D = \Delta D$ and $\Delta^{(n)} D = (\Delta \otimes \mathrm{Id}^{n-2})\Delta^{(n-1)} D$ for $n > 2$. The result of the action of $\Delta^{(n)}$ on D is denoted by

$$\Delta^{(n)} D = \sum D_{(1)} \otimes \dots \otimes D_{(n)}. \tag{24}$$

To make a Hopf algebra, we need also a counit and an antipode, but we shall not use these concepts in the present paper.

D. The derivative of a product

To show immediately the power of the Hopf algebraic concepts, we prove the following formula for the derivative of a product of two functions. If $D \in \mathcal{D}$ is a product of functional derivatives and u and v are functions of Dirac fields and sources we have

$$D(uv) = \sum (-1)^{|D_{(2)}||u|} (D_{(1)} u)(D_{(2)} v). \tag{25}$$

In this equation, $|u|$ is the parity of the function u. The parity of a function is defined as follows. We first define the degree of a function: for a Dirac field or a fermion source we have $\deg(\psi) = \deg(\bar\psi) = \deg(\eta) = \deg(\bar\eta) = 1$. The degree of a product of fields and sources is the sum of the degrees of the fields and sources: $\deg(uv) = \deg(u) + \deg(v)$, and the parity of a function of fields and sources is equal to the 0 or 1 when its degree is even or odd. Notice that, if $\deg(D) \le \deg(u)$ we have $|Du| = |u| + |D|$ modulo 2 because $\deg(Du) = \deg(u) - \deg(D)$. The proof of (25) is recursive. Equation (25) is true for $D = \mathbf{1}$ because $\mathbf{1}(uv) = uv$ and for $D = \partial$ because of Leibniz' rule (9). If this is true for all elements of degree up to n, take D an element of degree n and define $D' = \partial D$. On the one hand

$$\begin{aligned}D'(uv) &= \partial\big(D(uv)\big) = \sum (-1)^{|D_{(2)}||u|} \partial\big((D_{(1)} u)(D_{(2)} v)\big) \\ &= \sum (-1)^{|D_{(2)}||u|} (\partial D_{(1)} u)(D_{(2)} v) \\ &\quad + (-1)^{|D_{(2)}||u| + |D_{(1)}| + |u|} (D_{(1)} u)(\partial D_{(2)} v)\big).\end{aligned} \tag{26}$$

To obtain the last line, we used Leibniz' rule and the fact that $|D_{(1)}u| = |u| + |D_{(1)}|$ modulo 2. On the other hand, by equation (23)

$$\Delta(\partial D) \;=\; \sum (\partial D_{(1)}) \otimes D_{(2)} + (-1)^{|D_{(1)}|} D_{(1)} \otimes (\partial D_{(2)}).$$

So that, if equation (25) is true,

$$\begin{aligned} D'(uv) \;&=\; \sum (-1)^{|D_{(2)}||u|} (\partial D_{(1)}u)(D_{(2)}v) \\ &\qquad +(-1)^{|D_{(1)}|+(1+|D_{(2)}|)|u|} (D_{(1)}u)(\partial D_{(2)}v). \end{aligned}$$

But this is indeed equal to (26), so equation (25) is satisfied for D'. Since the elements ∂D generate $\mathcal{D}_{n+1}$, equation (25) is true for $\mathcal{D}$.

More generally

$$D(u_1 \dots u_n) \;=\; \sum (-1)^{\sum_{k=2}^{n} \sum_{l=1}^{k-1} |D_{(k)}||u_l|} (D_{(1)}u_1) \dots (D_{(n)}u_n). \tag{27}$$

The recursive proof is left to the reader.

E. Elimination of closed shells

As a second application, we calculate $\mathrm{tr}(\hat\rho N^0)$ when the system is composed of closed shells and open shells. A closed shell is an electron state i_k which is occupied in all states $|K\rangle$. The open shells are the electron states which are present in some but not all states $|K\rangle$. Thus, the closed and open shells have no electron state in common. We rewrite equation (18) as $\mathrm{tr}(\hat\rho N^0) = \mathrm{e}^d(uv)$ where $d = \sum_n \partial^2/\partial\alpha_n\partial\bar\alpha_n$, $u = \bar\alpha_{m_1}\alpha_{m_1} \dots \bar\alpha_{m_C}\alpha_{m_C}$ describes the closed shells containing C electrons and $v = \sum_{KL} \rho_{LK} \bar\alpha_{j_1}\alpha_{i_1} \dots \bar\alpha_{j_N}\alpha_{i_N}$ describes the open shells. Notice that in u the index of each $\bar\alpha$ is the same as the index of the following α. This is because the electron states are ordered so that the closed shell have an index smaller than the open shells, and the closed shells are occupied in all $|K\rangle$ and $|L\rangle$. To calculate $\mathrm{tr}(\hat\rho N^0)$ we first compute $d(uv)$. According to equation (25)

$$d(uv) \;=\; \sum (-1)^{|d_{(2)}||u|} (d_{(1)}u)(d_{(2)}v) = \sum (d_{(1)}u)(d_{(2)}v), \tag{28}$$

because $|u| = 2C = 0$ modulo 2. Now

$$\Delta d \;=\; \sum_n \frac{\partial^2}{\partial\alpha_n\partial\bar\alpha_n} \otimes \mathbf{1} + \frac{\partial}{\partial\alpha_n} \otimes \frac{\partial}{\partial\bar\alpha_n} - \frac{\partial}{\partial\bar\alpha_n} \otimes \frac{\partial}{\partial\alpha_n} + \mathbf{1} \otimes \frac{\partial^2}{\partial\alpha_n\partial\bar\alpha_n}.$$

The terms $\partial u/\partial\alpha_n \partial v/\partial\bar\alpha_n$ and $\partial u/\partial\bar\alpha_n \partial v/\partial\alpha_n$ in equation (28) are zero because the closed and open shells have no state in common. Therefore $d(uv) = (du)v + u(dv)$. Moreover,

$$du \;=\; \sum_{k=1}^{C} \frac{u}{\bar\alpha_{m_k}\alpha_{m_k}},$$

is a sum of closed shells, so we can apply the same argument again to show that

$$d^k(uv) \;=\; \sum_{l=0}^{k} \binom{k}{l} (d^l u)(d^{k-l}v).$$

Therefore

$$\begin{aligned} \mathrm{tr}(\hat\rho N^0) \;&=\; \mathrm{e}^d(uv) = \sum_{k=0}^{\infty} \frac{1}{k!} d^k(uv) = \sum_{k=0}^{\infty}\sum_{l=0}^{k} \frac{1}{l!(k-l)!} (d^l u)(d^{k-l}v), \\ &=\; \sum_{l=0}^{\infty} \frac{1}{l!} d^l u \sum_{m=0}^{\infty} \frac{1}{m!} d^m v = (\mathrm{e}^d u)(\mathrm{e}^d v) = \prod_{i=1}^{C} (1 + \bar\alpha_{m_i}\alpha_{m_i})(\mathrm{e}^d v). \end{aligned}$$

In other words, the closed shells factorize in $\mathrm{tr}(\hat\rho N^0)$. This result will be important to restrict the size of the problem.

Notice that, in the proof, we used only the fact that the closed and open shells have no electron state in common. So the same reasoning shows that, if the system is composed of two independent subsystems, then N^0_{KL} is the product of the N^0_{KL} of both systems. More precisely, if all states can be written as $|K\rangle = |K_1\rangle \wedge |K_2\rangle$, where $\wedge$ antisymmetrizes the electron states of $|K_1\rangle$ and $|K_2\rangle$, where $|K_1\rangle$ has the same number of electron states for all $|K\rangle$ and where no $|K_1\rangle$ and $|K_2'\rangle$ have any electron state in common for any $|K\rangle$ and $|K'\rangle$, then $N^0_{KL} = N^0_{K_1L_1} N^0_{K_2L_2}$.

VI. CALCULATION OF W_ρ^0

It will be very useful to define $W_\rho^0 = \log(Z_\rho^0)$. If the system has $N+C$ electrons with C electrons in closed shells, Z_ρ^0 can be written

$$Z_\rho^0 \;=\; \exp[-i\int \bar\eta(x)G_0^0(x,y)\eta(y)\mathrm{d}x\mathrm{d}y]\prod_{i=1}^{C}(1+\bar\alpha_{m_i}\alpha_{m_i})\rho(\bar\alpha,\alpha), \tag{29}$$

with

$$\rho(\bar\alpha,\alpha) \;=\; \sum_{k=0}^{N}\rho_k(\bar\alpha,\alpha), \tag{30}$$

where ρ_k contains products of k $\bar\alpha$ and k α. More explicitly

$$\rho_N(\bar\alpha,\alpha) \;=\; \sum \rho_{j_N\dots j_1,i_N\dots i_1}\bar\alpha_{j_1}\alpha_{i_1}\dots\bar\alpha_{j_N}\alpha_{i_N}, \tag{31}$$

$$\rho_k(\bar\alpha,\alpha) \;=\; \frac{1}{(N-k)!}\Big(\sum_n \frac{\partial^2}{\partial\alpha_n\partial\bar\alpha_n}\Big)^{N-k}\rho_N(\bar\alpha,\alpha). \tag{32}$$

According to equation (51) of the appendix, an alternative formula is

$$\rho_k(\bar\alpha,\alpha) \;=\; \frac{(-1)^k}{(k!)^2}\sum_{n_1\dots m_k}\alpha_{n_1}\dots\alpha_{n_k}\bar\alpha_{m_1}\dots\bar\alpha_{m_k}\sum_{KL}\rho_{LK}\langle K|b^\dagger_{n_1}\dots b^\dagger_{n_k}b_{m_1}\dots b_{m_k}|L\rangle.$$

In particular,

$$\begin{aligned}
\rho_0(\bar\alpha,\alpha) \;&=\; \mathrm{tr}(\hat\rho),\\
\rho_1(\bar\alpha,\alpha) \;&=\; \sum \rho_{j_N\dots j_1,i_N\dots i_1}\Big(\sum_{l=1}^{N}\bar\alpha_{j_l}\alpha_{i_l}\prod_{p\neq l}\delta_{j_p,i_p}\\
&\quad+\sum_{l=1}^{N-1}\sum_{m=l+1}^{N}(-1)^{l+m}\bar\alpha_{j_l}\alpha_{i_m}\prod_{p<l}\delta_{j_p,i_p}\prod_{l<p\le m}\delta_{j_p,i_{p-1}}\prod_{p>m}\delta_{j_p,i_p}\\
&\quad+\sum_{l=2}^{N}\sum_{m=1}^{l-1}(-1)^{l+m}\bar\alpha_{j_l}\alpha_{i_m}\prod_{p<m}\delta_{j_p,i_p}\prod_{m\le p<l}\delta_{j_p,i_{p+1}}\prod_{p>l}\delta_{j_p,i_p}\Big),
\end{aligned} \tag{33}$$

will be useful. It is important to isolate $\rho_1(\bar\alpha,\alpha)$, which depends linearly on $\bar\alpha$ and α, because it will become a part of the free propagator.

The closed shells are dealt with easily:

$$\begin{aligned}
\log\Big(\prod_{i=1}^{C}(1+\bar\alpha_{m_i}\alpha_{m_i})\Big) \;&=\; \sum_{i=1}^{C}\log(1+\bar\alpha_{m_i}\alpha_{m_i})\\
&=\; \sum_{i=1}^{C}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}(\bar\alpha_{m_i}\alpha_{m_i})^n.
\end{aligned}$$

However, $\bar\alpha_{m_i}$ and α_{m_i} are fermionic variables, thus $(\bar\alpha_{m_i}\alpha_{m_i})^2 = \bar\alpha_{m_i}\alpha_{m_i}\bar\alpha_{m_i}\alpha_{m_i} = -\bar\alpha_{m_i}\bar\alpha_{m_i}\alpha_{m_i}\alpha_{m_i} = 0$ because, as fermionic variables, $\bar\alpha_{m_i}^2 = \alpha_{m_i}^2 = 0$. Consequently, only the term $n=1$ remains in the sum and

$$\log\Big(\prod_{i=1}^{C}(1+\bar\alpha_{m_i}\alpha_{m_i})\Big) \;=\; \sum_{i=1}^{C}\bar\alpha_{m_i}\alpha_{m_i}.$$

This result is important because it justifies the fact that the propagator of the Green function in many-body theory is obtained by summing the contribution of all occupied shells. We see now that this procedure is justified when the vacuum $|\Phi_0\rangle$ can be written as a full shell. In all other cases, this procedure must be modified. The modification comes from the term $\rho(\bar\alpha,\alpha)$ that we write

$$\rho(\bar\alpha,\alpha) \;=\; \mathrm{tr}(\hat\rho)+\sum_{k=1}^N \rho_k(\bar\alpha,\alpha)=\mathrm{tr}(\hat\rho)\big(1+\sum_{k=1}^N \frac{\rho_k(\bar\alpha,\alpha)}{\mathrm{tr}(\hat\rho)}\big).$$

The usual convention is to impose $\mathrm{tr}(\hat\rho)=1$, but we want to relax this constraint for later convenience. Thus

$$\begin{aligned}\log(\rho(\bar\alpha,\alpha)) \;&=\; \log(\mathrm{tr}(\hat\rho))+\log\big(1+\sum_{k=1}^N \frac{\rho_k(\bar\alpha,\alpha)}{\mathrm{tr}(\hat\rho)}\big),\\ &=\; \log(\mathrm{tr}(\hat\rho))+\frac{\rho_1(\bar\alpha,\alpha)}{\mathrm{tr}(\hat\rho)}+\rho^c(\bar\alpha,\alpha),\end{aligned}$$

where $\rho^c(\bar\alpha,\alpha)$ is defined by the last equation. We can write $\rho^c(\bar\alpha,\alpha)$ as

$$\rho^c(\bar\alpha,\alpha) \;=\; \sum_{n=2}^\infty \rho^c_n(\bar\alpha,\alpha), \tag{34}$$

where ρ^c_n is the sum of the terms of ρ^c which have degree n in $\bar\alpha$ and degree n in α. Notice that the sum over n is finite. For instance, if the states $|K\rangle$ are built by choosing N electron orbitals among M (for instance, for Cr^{3+}, we have three d electrons so that $N=3$ and $M=10$). Therefore, $\rho_n(\bar\alpha,\alpha)^{1+M/n}=0$ because in each term of $\rho_n(\bar\alpha,\alpha)^{1+M/n}$ at least one α_{i_p} is found twice and $\alpha_{i_p}^2=0$. Therefore, $\rho^c_n(\bar\alpha,\alpha)=0$ for $n>M$.

If we gather all these results we obtain that

$$\begin{aligned}W^0_\rho \;&=\; \log(Z^0_\rho)=-i\int\bar\eta(x)G^0_0(x,y)\eta(y)\mathrm{d}x\mathrm{d}y+\sum_{i=1}^C\bar\alpha_{m_i}\alpha_{m_i}\\ &\quad+\log(\mathrm{tr}(\hat\rho))+\frac{\rho_1(\bar\alpha,\alpha)}{\mathrm{tr}(\hat\rho)}+\rho^c(\bar\alpha,\alpha),\end{aligned} \tag{35}$$

where we recall that $\bar\alpha_n=\int(\bar\eta_+(x)+\bar\eta_-(x))u_n(x)\mathrm{d}x$ and $\alpha_n=\int\bar u_n(x)(\eta_+(x)+\eta_-(x))\mathrm{d}x$. The term containing $G^0_0(x,y)$ is linear in $\bar\eta$ and η. Thus, we shall include the other linear terms by defining

$$G^0_\rho(x,y) \;=\; G^0_0(x,y)+i\big(\sum_{i=1}^C u_{m_i}(x)\bar u_{m_i}(y)+\frac{\rho_1(x,y)}{\mathrm{tr}(\hat\rho)}\big)\begin{pmatrix}1&1\\1&1\end{pmatrix}, \tag{36}$$

with $\rho_1(x,y)$ defined so that $\rho_1(\bar\alpha,\alpha)=\int\bar\eta_d(x)\rho_1(x,y)\eta_d(y)\mathrm{d}x\mathrm{d}y$, in other words, $\rho_1(x,y)$ is obtained by replacing all $\bar\alpha_{j_k}$ by $u_{j_k}(x)$ and all α_{i_k} by $\bar u_{i_k}(y)$ in equation (33). It is at this stage that, when the system has only closed shells, the effect of the closed shells is entirely taken into account by adding the occupied orbitals to the free Green function. This procedure, which is universally used in the quantum many-body approach, is usually deduced from the particle-hole transformation. This transformation is itself justified by showing that the Hamiltonian without interaction H_0 is left invariant (up to a pure number)[38]. However, this justification falls short of being a proof that this procedure is valid at all orders of the interacting theory. From the previous discussion, we see that the procedure is correct at all orders when the noninteracting system can be described by a single Slater determinant (i.e. a closed shell). However, the most interesting phenomenon occurs when open shells are present. We rewrite

$$W^0_\rho \;=\; -i\int\bar\eta(x)G^0_\rho(x,y)\eta(y)\mathrm{d}x\mathrm{d}y+\log(\mathrm{tr}(\hat\rho))+\rho^c(\bar\alpha,\alpha). \tag{37}$$

This is the final result of the section. Notice that the expression $Z^0_\rho=\exp W^0_\rho$ is a cluster expansion of Z^0_ρ which was used in this context by Hall[37] and Fauser and Wolter[58]. Hall has also shown that this cluster expansion was necessary to obtain consistent Feynman rules for the perturbative calculation of Green functions with initial correlation[37].

VII. THE GREEN FUNCTION HIERARCHY

In this section, the Green function hierarchy is established in the presence of open shells.

A. Definition of Green functions

According to the discussion of II A, the expectation value of the Heisenberg field $\psi_H(x)$ is given by

$$\langle\psi_H(x)\rangle = -i\frac{\delta Z_\rho}{\delta\bar\eta_+(x)}|_{\bar\eta=\eta=0}. \tag{38}$$

The density matrix is normalised by $\mathrm{tr}(\hat\rho)=1$, so that $Z_\rho|_{\bar\eta=\eta=0}=1$. Therefore, we can also define

$$\langle\psi_H(x)\rangle = \Big(\frac{1}{Z_\rho}\frac{-i\delta Z_\rho}{\delta\bar\eta_+(x)}\Big)|_{\bar\eta=\eta=0}. \tag{39}$$

Although these definitions are equivalent, equation (39) has some advantages over equation (38): (i) If we multiply ρ by λ, equation (39) is not changed because the factor λ is cancelled between the numerator and the denominator. Thus, it is possible to relax the constraint $\mathrm{tr}(\hat\rho)=1$ and we can consider unconstrained density matrices. In particular, we can use $\hat\rho=\exp[-\beta H]$ for equilibrium quantum field theory. (ii) If equations (38) and (39) are written as a sum of Feynman diagrams, equation (38) has vacuum diagrams which are cancelled by the denominator of equation (39), in other words, only equation (39) is a sum of connected diagrams. (iii) When the density matrix $\hat\rho$ is that of the vacuum (i.e. $\hat\rho=|0\rangle\langle 0|$), equation (39) is the Gell-Mann and Low equation[49] which is known to be correct.

It turns out that a complete set of equations cannot be obtained by functional derivatives with respect to η_+ and $\bar\eta_+$ alone. So we define the following expectations values:

$$\begin{aligned}\langle\psi_H(x)\rangle &= \Big(\frac{1}{Z_\rho}\frac{-i\delta Z_\rho}{\delta\bar\eta_+(x)}\Big)|_{\bar\eta=\eta=0} = \Big(\frac{1}{Z_\rho}\frac{-i\delta Z_\rho}{\delta\bar\eta_-(x)}\Big)|_{\bar\eta=\eta=0},\\ \langle\bar\psi_H(x)\rangle &= \Big(\frac{1}{Z_\rho}\frac{i\delta Z_\rho}{\delta\eta_+(x)}\Big)|_{\bar\eta=\eta=0} = \Big(\frac{1}{Z_\rho}\frac{i\delta Z_\rho}{\delta\eta_-(x)}\Big)|_{\bar\eta=\eta=0}.\end{aligned}$$

B. Hierarchy of disconnected Green functions

We rewrite equation(14) as $Z_\rho = \mathrm{e}^{-iD}Z^0_\rho$ where

$$D = \int H^{\mathrm{int}}\big(\frac{-i\delta}{\delta\bar\eta_+(x)},\frac{i\delta}{\delta\eta_+(x)}\big) - H^{\mathrm{int}}\big(\frac{-i\delta}{\delta\bar\eta_-(x)},\frac{i\delta}{\delta\eta_-(x)}\big)\mathrm{d}x. \tag{40}$$

The operator D contains products of 2 or 4 functional derivatives, thus D is even and D commutes with the elements of $\mathcal{D}$. Thus, if $\beta=\eta_\pm(x)$ or $\beta=\bar\eta_\pm(x)$

$$\frac{\delta Z_\rho}{\delta\beta} = \mathrm{e}^{-iD}\frac{\delta Z^0_\rho}{\delta\beta}.$$

We use the fact that $Z^0_\rho=\mathrm{e}^{W^0_\rho}$ with $|W^0_\rho|=0$ to get

$$\begin{aligned}\frac{\delta Z_\rho}{\delta\beta} &= \mathrm{e}^{-iD}\Big(\frac{\delta W^0_\rho}{\delta\beta}\mathrm{e}^{W^0_\rho}\Big) = \mathrm{e}^{-iD}\Big(\frac{\delta W^0_\rho}{\delta\beta}Z^0_\rho\Big)\\ &= \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}D^n\big(\frac{\delta W^0_\rho}{\delta\beta}Z^0_\rho\big).\end{aligned} \tag{41}$$

The action of the operator D^n is expanded with equation (25), using $|\delta W^0_\rho/\delta\beta|=1$:

$$\frac{\delta Z_\rho}{\delta\beta} = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\sum(-1)^{|D^n_{(2)}|}\big(D^n_{(1)}\frac{\delta W^0_\rho}{\delta\beta}\big)\big(D^n_{(2)}Z^0_\rho\big).$$

We transform this infinite sum into a finite sum by using reduced coproducts. The reduced coproduct with respect to D is denoted by $\Delta' D$. It is defined as follows, the reduced coproduct with respect to D of D itself is defined by $\Delta' D = \Delta D - 1\otimes D - D\otimes 1$. The Sweedler notation for it is $\Delta' D = \sum D_{(1')}\otimes D_{(2')}$. The reduced coproduct of D^n is defined recursively by

$$\Delta'(D^{n+1}) = \sum(-1)^{|D_{(1')}||D^n_{(2')}|}D^n_{(1')}D_{(1')}\otimes D^n_{(2')}D_{(2')}. \tag{42}$$

This is extended to $n = 0$ by $\Delta'(D^0) = 1 \otimes 1$. An equivalent definition is that $\Delta'(D^n)$ is the sum of all terms of $\Delta(D^n)$ which do not contain any D. The relation between $\Delta(D^n)$ and $\Delta'(D^n)$ is given by

$$\Delta(D^n) \;=\; \sum_{k=0}^{n}\sum_{l=0}^{n-k} \frac{n!}{k!l!(n-k-l)!} D_{(1')}^{n-k-l} D^k \otimes D_{(2')}^{n-k-l} D^l. \tag{43}$$

This can be shown by a recursive proof. The definition of $\Delta' D$ gives us

$$\Delta D \;=\; D \otimes 1 + 1 \otimes D + \sum D_{(1')} \otimes D_{(2')}, \tag{44}$$

so equation (43) is true for $n = 1$. Assume that it is true for all D^k up to $k = n$. From equations (23), (43) and (44) we obtain (using $|D| = 0$),

$$\begin{aligned}\Delta(D^n D) \;=\; \sum_{k+l+m=n} \frac{n!}{k!l!m!}\Big(& D_{(1')}^{m} D^{k+1} \otimes D_{(2')}^{m} D^l \\ & + D_{(1')}^{m} D^{k} \otimes D_{(2')}^{m} D^{l+1} \\ & + (-1)^{|D_{(1')}||D_{(2')}^m|} D_{(1')}^{m} D_{(1')} D^{k} \otimes D_{(2')}^{m} D_{(2')} D^{l}\Big).\end{aligned}$$

Using the recursive definition (42) we get

$$\begin{aligned}\Delta(D^n D) \;=\; \sum_{k+l+m=n} \frac{n!}{k!l!m!}\Big(& D_{(1')}^{m} D^{k+1} \otimes D_{(2')}^{m} D^l \\ & + D_{(1')}^{m} D^{k} \otimes D_{(2')}^{m} D^{l+1} + D_{(1')}^{m+1} D^{k} \otimes D_{(2')}^{m+1} D^{l}\Big).\end{aligned}$$

This can be rewritten

$$\begin{aligned}\Delta(D^n D) \;=\; \sum_{k+l+m=n+1} & \Big(\frac{n!}{(k-1)!l!m!} + \frac{n!}{k!(l-1)!m!} + \frac{n!}{k!l!(m-1)!}\Big) \\ & D_{(1')}^{m} D^{k} \otimes D_{(2')}^{m} D^{l}.\end{aligned}$$

The first three integers can be summed to

$$\Delta(D^n D) \;=\; \sum_{k+l+m=n+1} \frac{n!(k+l+m)}{k!l!m!} D_{(1')}^{m} D^{k} \otimes D_{(2')}^{m} D^{l},$$

and equation (43) is proved for D^{n+1}.

By summing equation (43) over n we obtain the important identity

$$\Delta \mathrm{e}^D \;=\; \sum_{n=0}^{\infty} \frac{1}{n!} D_{(1')}^{n} \mathrm{e}^D \otimes D_{(2')}^{n} \mathrm{e}^D = (\Delta' \mathrm{e}^D)(\mathrm{e}^D \otimes \mathrm{e}^D). \tag{45}$$

Note that this identity is true for any graded commutative Hopf algebra and any D of degree > 0.

Using identity (45), the equation (41) for $\delta Z_\rho / \delta\beta$ becomes

$$\begin{aligned}\frac{\delta Z_\rho}{\delta\beta} \;&=\; \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \sum (-1)^{|D_{(2')}^n|} \big(D_{(1')}^{n} \mathrm{e}^{-iD} \frac{\delta W_\rho^0}{\delta\beta}\big)\big(D_{(2')}^{n} \mathrm{e}^{-iD} Z_\rho^0\big), \\ &=\; \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \sum (-1)^{|D_{(2')}^n|} \big(D_{(1')}^{n} \frac{\delta W_\rho^1}{\delta\beta}\big)\big(D_{(2')}^{n} Z_\rho\big),\end{aligned}$$

where $W_\rho^1 = \mathrm{e}^{-iD} W_\rho^0$ adds the electron-electron interactions to the cumulant W_ρ^0 of the moment generating function Z_ρ^0. Since the cumulant W_ρ^0 is a finite polynomial in $\bar\alpha$ and α, the interacting cumulant W_ρ^1 is also a finite polynomial in $\bar\alpha$ and α. Now each $D_{(1')}^{m}$ (for $m \neq 0$) contains at least m functional derivatives with respect to $\bar\eta_\pm$ or $\eta_\pm$ (this is why the reduced coproduct was defined), thus $D^m_{(1')}$ is zero for m large enough. In fact, $m = 2M-1$ is a possible bound and we obtain our final formula, isolating the contribution of $n=0$

$$\frac{\delta Z_\rho}{\delta\beta} = \frac{\delta W^1_\rho}{\delta\beta} Z_\rho + \sum_{n=1}^{2M-1} \frac{(-i)^n}{n!} \sum (-1)^{|D^n_{(2')}|} \big(D^n_{(1')} \frac{\delta W^1_\rho}{\delta\beta}\big)\big(D^n_{(2')} Z_\rho\big). \tag{46}$$

We have transformed the infinite sum (41) into the finite sum (46). To be complete, we still have to replace the disconnected Green functions defined by functional derivatives with respect to Z_ρ by connected Green functions defined by functional derivatives with respect to $W_\rho = \log Z_\rho$.

C. Calculation of W^1_ρ

Apparently, $W^1_\rho = \mathrm{e}^{-iD} W^0_\rho$ includes some interaction in W^0_ρ, but in the interaction Hamiltonian H^{int} that we consider, we have $W^1_\rho = W^0_\rho$. Indeed, D contains integrals over $d = \delta^2/\delta\eta_\pm(x)\delta\bar\eta_\pm(x)$. The action of d on the term of W^0_ρ containing the Green function $G^0_\rho(x,y)$ is irrelevant because it gives a term independent of α and $\bar\alpha$ (the term W^1_ρ always appears with an additional functional derivative, such as $\delta/\delta\beta$ in equation (46), which cancels any term independent of α and $\bar\alpha$). For the action on $\rho^c(\bar\alpha,\alpha)$ we have

$$\frac{\delta\rho^c}{\delta\bar\eta_\pm(x)} = \sum_n \frac{\partial\rho^c}{\partial\bar\alpha_n}\frac{\delta\bar\alpha_n}{\delta\bar\eta_\pm(x)} = \sum_n \frac{\partial\rho^c}{\partial\bar\alpha_n} u_n(x),$$

$$\frac{\delta^2\rho^c}{\delta\eta_\pm(x)\delta\bar\eta_\pm(x)} = \sum_{mn} \frac{\partial^2\rho^c}{\partial\alpha_m\partial\bar\alpha_n}\bar u_m(x) u_n(x).$$

Remark that the right hand side of these equations does not depend on the sign $\pm$ of the source. The diffential operator D can be written as $D = D_+ - D_-$, where D_+ and D_- are the same operators, but the first one involves derivatives with respect to the $+$ sources and the second one with respect to the $-$ sources. According to our remark, $D_+\rho^c = D_-\rho^c$. Thus, $D\rho^c = 0$ and $W^1_\rho = W^0_\rho$. This result corresponds to the correlation dentate structure theorem derived by Hall[37]. A much more general cancellation theorem was given by Tikhodeev[65].

D. Hierarchy of connected Green functions

In formula (46), the differential operator $D^n_{(2')}$ acts on $Z_\rho = \mathrm{e}^{W_\rho} = \sum_{n=0}^\infty W^n_\rho/n!$. Thus, we must determine the action of a differential operator on W^n_ρ. Notice that $|Z_\rho| = 0$, thus $|W_\rho| = 0$.

So we take an even element u (even means that $|u| = 0$) and a differential operator d such that $\deg(d) > 0$ and we want to calculate du^n. We shall use now the standard reduced coproduct $\underline{\Delta}$ defined, for any element $d \in \mathcal{D}$ by $\underline{\Delta} d = \Delta d - d\otimes 1 - 1\otimes d$, and we write $\underline{\Delta} d = \sum d_{(\underline{1})}\otimes d_{(\underline{2})}$. This reduced coproduct is coassociative. The basic identity that we need is

$$d(u^n) = \sum_{k=1}^n \binom{n}{k} u^{n-k} \sum d_{(\underline{1})}u \dots d_{(\underline{k})}u, \tag{47}$$

where $d_{(\underline{1})}u = du$ if $k=1$ and $\underline{\Delta}^{(k)} d = \sum d_{(\underline{1})}\otimes\cdots\otimes d_{(\underline{k})}$ is defined recursively from $\underline{\Delta}$ as in equation (24). For example, using equation (25) and $|u| = 0$

$$\begin{aligned} d(u^2) &= \sum (d_{(1)}u)(d_{(2)}u) = (du)u + u(du) + \sum (d_{(\underline{1})}u)(d_{(\underline{2})}u), \\ &= 2u\,du + \sum (d_{(\underline{1})}u)(d_{(\underline{2})}u), \end{aligned}$$

and equation (47) is valid for $n=2$ (it is also obviously valid for $n=1$). The general case is proved recursively.

Assume that it is true up to n, then

$$
\begin{aligned}
d(u^{n+1}) &= \sum (d_{(1)}u^n)(d_{(2)}u) = u^n du + d(u^n)u + \sum (d_{\underline{(1)}}u^n)(d_{\underline{(2)}}u),\\
&= u^n du + \sum_{k=1}^{n} \binom{n}{k} u^{n-k+1} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u\\
&\quad + \sum_{k=1}^{n} \binom{n}{k} u^{n-k} \sum (d_{\underline{(1)}\,\underline{(1)}}u \dots d_{\underline{(1)}\,\underline{(k)}}u)(d_{\underline{(2)}}u)\\
&= u^n du + \sum_{k=1}^{n} \binom{n}{k} u^{n-k+1} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u\\
&\quad + \sum_{k=1}^{n} \binom{n}{k} u^{n-k} \sum d_{\underline{(1)}}u \dots d_{\underline{(k+1)}}u\\
&= u^n du + \sum_{k=1}^{n} \binom{n}{k} u^{n-k+1} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u\\
&\quad + \sum_{k=2}^{n+1} \binom{n}{k-1} u^{n-k+1} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u\\
&= \sum_{k=1}^{n+1} \binom{n+1}{k} u^{n+1-k} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u.
\end{aligned}
$$

We used the coassociativity of the reduced coproduct. From equation (47) we can calculate

$$
\begin{aligned}
d(\mathrm{e}^u) &= \sum_{n=0}^{\infty} \frac{1}{n!} d(u^n) = \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{k=1}^{n} \binom{n}{k} u^{n-k} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u,\\
&= \sum_{m=0}^{\infty} \frac{u^m}{m!} \sum_{k=1}^{\infty} \frac{1}{k!} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u,\\
&= \mathrm{e}^u \sum_{k=1}^{\infty} \frac{1}{k!} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u.
\end{aligned} \tag{48}
$$

The sum over k is not infinite because $\underline{\Delta}^{(k)} d = 0$ if $k > \deg(d)$ and the sum stops at $k = \deg(d)$. More generally, for an analytic function $f(z)$,

$$
d\big(f(u)\big) = \sum_{k=1}^{\infty} \frac{f^{(k)}(u)}{k!} \sum d_{\underline{(1)}}u \dots d_{\underline{(k)}}u,
$$

where $f^{(k)}(u)$ is the k-th derivative of f at u. The cocommutativity of the coproduct ensures that the factor $1/k!$ disappears from the expanded formulas.

If equation (48) is applied to $u = W_\rho$, we obtain a relation between unconnected Green functions $(1/Z_\rho)dZ_\rho$ and connected Green functions dW_ρ. For instance, if $d = \partial\partial'$, then $\underline{\Delta} d = \partial \otimes \partial' - \partial' \otimes \partial$ and $(1/Z_\rho)dZ_\rho = dW_\rho + (1/2)(\partial W_\rho)(\partial' W_\rho) - (1/2)(\partial' W_\rho)(\partial W_\rho)$. At $\bar\eta_\pm = \eta_\pm = 0$ we obtain $dZ_\rho = dW_\rho$. Similarly, if $d = \overline{\partial}\,\overline{\partial}'\partial\partial'$, where ∂ and ∂' are derivative with respect to η and $\overline{\partial}$ and $\overline{\partial}'$ with respect to $\bar\eta$, we find at $\bar\eta_\pm = \eta_\pm = 0$, $dZ_\rho = dW_\rho - (\overline{\partial}\partial W_\rho)(\overline{\partial}'\partial' W_\rho) + (\overline{\partial}\partial' W_\rho)(\overline{\partial}'\partial W_\rho)$.

Equation (48) is now introduced into (46), where we use the fact that $0 = |D^n| = |D^n_{(1')}| + |D^n_{(2')}|$, so that $|D^n_{(2')}| = |D^n_{(1')}|$:

$$
\begin{aligned}
\frac{\delta Z_\rho}{\delta\beta} &= \sum_{n=0}^{2M-1} \frac{(-i)^n}{n!} \sum (-1)^{|D^n_{(1')}|} \big(D^n_{(1')} \frac{\delta W^1_\rho}{\delta\beta}\big)\\
&\quad \times Z_\rho \sum_{k=1}^{\infty} \frac{1}{k!} \sum \big(D^n_{(2')\underline{(1)}} W_\rho \dots\big)\big(D^n_{(2')\underline{(k)}} W_\rho\big).
\end{aligned}
$$

Using again the definition of W_ρ in terms of Z_ρ, we obtain an equation involving only the connected Green functions:

$$\begin{aligned} \frac{\delta W_\rho}{\delta\beta} &= \frac{1}{Z_\rho}\frac{\delta Z_\rho}{\delta\beta} \\ &= \sum_{n=0}^{2M-1}\frac{(-i)^n}{n!}\sum_{k=1}^{\infty}\sum\frac{(-1)^{|D^n_{(1')}|}}{k!}\big(D^n_{(1')}\frac{\delta W^1_\rho}{\delta\beta}\big) \\ &\qquad (D^n_{(2')(\underline{1})}W_\rho)\dots(D^n_{(2')(\underline{k})}W_\rho). \end{aligned} \tag{49}$$

This sum is finite because, for each n, the sum over k stops at $k=\deg(D^n_{(2')})$.

VIII. CONCLUSION

This paper had two purposes: (i) to determine the hierarchy of Green functions for degenerate systems, and more generally for systems whose initial state cannot be written as a Slater determinant; (ii) to show the power of quantum groups and Hopf algebras to solve problems of quantum field theory. A detailed application of the formulas obtained in this paper can be found in reference[66].

In this paper we dealt with a nonrelativistic electronic system with Coulomb interaction. A generalization to quantum electrodyamics is possible, which would provide an alternative to the new methods recently developed to carry out quantum electrodynamical calculations of many-electron systems[67–71]. Again, the present method has the advantage of being self-consistent and of preserving the symmetry of the system.

Moreover, a functional derivation of the energy with respect to the density matrix provides equations that enable us to unify the Green-function formalism and the diagonalization method of many-body theory[72].

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X. APPENDIX : CALCULATION OF THE TRACE

The calculation of $\mathrm{tr}[\hat\rho N^0(\bar\eta_d,\eta_d)]$ is an essential ingredient of this work. We rewrite the density matrix as $\hat\rho = \sum_{KL}\rho_{LK}|L\rangle\langle K|$, where $|K\rangle$ and $|L\rangle$ are Slater determinants defined by $|K\rangle = b^\dagger_{i_N}\dots b^\dagger_{i_1}|0\rangle$ and $|L\rangle = b^\dagger_{j_N}\dots b^\dagger_{j_1}|0\rangle$. Here $b^\dagger_{i_k}$ and $b^\dagger_{j_l}$ are creation operators of the one-electron orbitals indexed by i_k and j_l. The indices are ordered ($i_1<\dots<i_N$, $j_1<\dots<j_N$). The total number of electrons in the system is N. Moreover, $|0\rangle$ is the true vacuum of the system (i.e. containing no electron). We must calculate $\mathrm{tr}[\hat\rho N^0(\bar\eta_d,\eta_d)] = \sum_{KL}\rho_{LK}N^0_{KL}$ with

$$N^0_{KL} = \langle K|\!:\exp\big(i\int\bar\eta_d(x)\psi(x)+\bar\psi(x)\eta_d(x)\mathrm{d}x\big)\!:\!|L\rangle. \tag{50}$$

The fields are expanded over time-dependent eigenstates of the one-body Hamiltonian

$$\psi(x) = \sum_n b_n u_n(x),\quad \bar\psi(x)=\sum_n b^\dagger_n u^\dagger_n,$$

where $u_n(x)$ are the time-dependent solutions defined in section IV B and n is the index of the electron orbital, $b_n, b^\dagger_n$ are the annihilation and creation operators of an electron in orbital n[34].

We can rewrite N^0_{KL} as

$$
\begin{aligned}
N^0_{KL} &= \sum_{l=0}^{\infty} \frac{i^l}{l!} \langle K| {:}\Big(\sum_n \int \bar\eta_d(x) u_n(x) \mathrm{d}x\, b_n + b_n^\dagger \int \bar u(x) \eta_d(x) \mathrm{d}x \Big)^l {:} |L\rangle \\
&= \sum_{l=0}^{\infty} \frac{i^l}{l!} \langle K| {:}\Big(\sum_n \bar\alpha_n b_n + b_n^\dagger \alpha_n \Big)^l {:} |L\rangle,
\end{aligned}
$$

where $\bar\alpha_n = \int \bar\eta_d(x) u_n(x)\mathrm{d}x$ and $\alpha_n = \int \bar u_n(x)\eta_d(x)\mathrm{d}x$ are anticommuting variables. To calculate N^0_{KL}, we first notice that the anticommutativity of $b_n, b_n^\dagger, \alpha_n$ and $\bar\alpha_n$ for the normal product gives us the commutation rules ${:}\bar\alpha_i b_i \bar\alpha_j b_j{:} = {:}\bar\alpha_j b_j \bar\alpha_i b_i{:}$, ${:}\bar\alpha_i b_i b_j^\dagger \alpha_j{:} = {:}b_j^\dagger \alpha_j \bar\alpha_i b_i{:}$ and ${:}b_i^\dagger \alpha_i b_j^\dagger \alpha_j{:} = {:}b_j^\dagger \alpha_j b_i^\dagger \alpha_i{:}$. Thus, we can expand the power with the binomial formula

$$
\begin{aligned}
N^0_{KL} &= \sum_{l=0}^{\infty} \frac{i^l}{l!} \sum_{k=0}^{l} \binom{l}{k} \\
&\quad \sum_{n_1\cdots n_l} \langle K| b_{n_1}^\dagger \alpha_{n_1} \dots b_{n_k}^\dagger \alpha_{n_k} \bar\alpha_{n_{k+1}} b_{n_{k+1}} \dots \bar\alpha_{n_l} b_{n_l} |L\rangle \\
&= \sum_{l=0}^{\infty} \frac{i^l}{l!} \sum_{k=0}^{l} \binom{l}{k} (-1)^{k+l(l-1)/2} \sum_{n_1\cdots n_l} \alpha_{n_1} \dots \alpha_{n_k} \bar\alpha_{n_{k+1}} \dots \bar\alpha_{n_l} \\
&\quad \langle K| b_{n_1}^\dagger \dots b_{n_k}^\dagger b_{n_{k+1}} \dots b_{n_l} |L\rangle.
\end{aligned}
$$

The transition between $|K\rangle$ and $|L\rangle$ is zero if $l \neq 2k$ or if $l > 2N$ because $|K\rangle$ and $|L\rangle$ contain N electrons. Thus we obtain the finite sum

$$
\begin{aligned}
N^0_{KL} &= \sum_{k=0}^{N} \frac{(-1)^k}{(k!)^2} \sum_{n_1\cdots m_k} \alpha_{n_1} \dots \alpha_{n_k} \bar\alpha_{m_1} \dots \bar\alpha_{m_k} \\
&\quad \langle K| b_{n_1}^\dagger \dots b_{n_k}^\dagger b_{m_1} \dots b_{m_k} |L\rangle.
\end{aligned}
\tag{51}
$$

A. Hopf calculation

The Hopf algebraic techniques developed in ref.[36] will be used to obtain an explicit expression for N^0_{KL}. We first denote

$$
A_{KL} = \langle K| b_{n_1}^\dagger \dots b_{n_k}^\dagger b_{m_1} \dots b_{m_k} |L\rangle,
$$

and we write $u = b_{i_1} \dots b_{i_N}$, $v = b_{j_N}^\dagger \dots b_{j_1}^\dagger$, $s = b_{n_1}^\dagger \dots b_{n_k}^\dagger$ and $t = b_{m_1} \dots b_{m_k}$. Thus $A_{KL} = \langle 0| u ({:}st{:}) v |0\rangle$ and we use the Hopf version of Wick's theorem[36]

$$
\begin{aligned}
({:}st{:})v &= \sum (-1)^{|v_{(1)}|(|s_{(2)}|+|t_{(2)}|)} ({:}st{:}_{(1)}|v_{(1)}){:}({:}st{:}_{(2)} v_{(2)}){:}, \\
&= \sum (-1)^{|v_{(1)}||s_{(2)}|+|v_{(1)}||t_{(2)}|+|t_{(1)}||s_{(2)}|} ({:}s_{(1)} t_{(1)}{:}|v_{(1)}){:}s_{(2)} t_{(2)} v_{(2)}{:}.
\end{aligned}
$$

Therefore

$$
\begin{aligned}
A_{KL} &= \big(u|({:}st{:})v\big), \\
&= \sum (-1)^{|v_{(1)}||s_{(2)}|+|v_{(1)}||t_{(2)}|+|t_{(1)}||s_{(2)}|} ({:}s_{(1)} t_{(1)}{:}|v_{(1)}) (u|{:}s_{(2)} t_{(2)} v_{(2)}{:}).
\end{aligned}
$$

In general

$$
({:}c_1 \dots c_m{:}|{:}d_1 \dots d_n{:}) = \delta_{m,n} (-1)^{n(n-1)/2} \det(M), \tag{52}
$$

where c_i and d_j are creation or annihilation operators and M is the $n \times n$ matrix with elements $M_{ij} = (c_i|d_j)$[73]. The Laplace pairing $(c_i|d_j)$ is obtained from $(b_i|b_j^\dagger) = \delta_{i,j}$, $(b_i|b_j) = 0$, $(b_i^\dagger|b_j) = 0$ and $(b_i^\dagger|b_j^\dagger) = 0$. Because of the value of

$(b_i|d_j)$, $(:c_1 \dots c_n:|:d_1 \dots d_n:)$ is zero if any c_i is a creation operator or any d_j an annihilation operator (because one row or one column of M is zero). Therefore, we need $s_{(1)} = 1$ and $t_{(2)} = 1$, so that $s_{(2)} = s$ and $t_{(1)} = t$:

$$A_{KL} = \sum (-1)^{|v_{(1)}||s|+|t||s|} (t|v_{(1)})(u|{:}sv_{(2)}{:}), \tag{53}$$

$$= \sum (-1)^{|v_{(1)}||s|+|t||s|+|u_{(2)}||s|} (t|v_{(1)})(u_{(1)}|s)(u_{(2)}|v_{(2)}). \tag{54}$$

We rewrite $v = (-1)^{N(N-1)/2} b^\dagger_{j_1} \dots b^\dagger_{j_N}$ so that

$$\Delta u = \sum_{p=0}^{N} \sum_{\sigma} (-1)^\sigma b_{i_{\sigma(1)}} \dots b_{i_{\sigma(p)}} \otimes b_{i_{\sigma(p+1)}} \dots b_{i_{\sigma(N)}},$$

$$\Delta v = (-1)^{N(N-1)/2} \sum_{q=0}^{N} \sum_{\tau} (-1)^\tau b^\dagger_{j_{\tau(1)}} \dots b^\dagger_{j_{\tau(q)}} \otimes b^\dagger_{j_{\tau(q+1)}} \dots b^\dagger_{j_{\tau(N)}},$$

where σ runs over the $(p, N-p)$-shuffles and τ over the $(q, N-q)$-shuffles. A $(p, N-p)$-shuffle is a permutation σ of $(1, \dots, N)$ such that $\sigma(1) < \sigma(2) < \dots < \sigma(p)$ and $\sigma(p+1) < \dots < \sigma(N)$. If $p = 0$ or $p = N$, σ is the identity permutation. Equation (52) applied to (54), gives us $p = k$ and $q = k$ so that $|v_{(1)}| = |s| = |t| = k$, $|u_{(2)}| = N - k$ and

$$A_{KL} = \sum (-1)^{N(N-1)/2+(N-k)k+k(k-1)+(N-k)(N-k-1)/2} \sum_{\sigma\tau} (-1)^{\sigma+\tau} \det(\delta_{m_p, j_{\tau(q)}}) \det(\delta_{i_{\sigma(p)}, n_q}) \det(\delta_{i_{\sigma(p)}, j_{\tau(q)}}), \tag{55}$$

where p and q run from 1 to k in the first two matrices and from $k+1$ to N in the last one. The determinant of a $n \times n$ matrix a_{ij} is $\det(a) = \sum_\lambda (-1)^\lambda \prod_{i=1}^n a_{i\lambda(i)} = \sum_\lambda (-1)^\lambda \prod_{i=1}^n a_{\lambda(i)i}$, where λ runs over the permutations of n elements. Therefore, to calculate the last determinant in equation (55), we must sum over all permutations of $\tau(k+1), \dots, \tau(N)$, but the indices satisfy $i_1 < \dots < i_N$ and $j_1 < \dots < j_N$. By definition of the $(k, N-k)$-shuffle, we have $i_{\sigma(k+1)} < \dots < i_{\sigma(N)}$ and $j_{\tau(k+1)} < \dots < j_{\tau(N)}$ so any permutation of $\tau(k+1), \dots, \tau(N)$ would break this ordering (for example, $\delta_{j_1, i_2} \delta_{j_2, i_1} = 0$ because $j_1 < j_2$ and $i_1 < i_2$). Thus the only nonzero term of $\det(\delta_{i_{\sigma(p)}, j_{\tau(q)}})$ is $\delta_{i_{\sigma(k+1)}, j_{\tau(k+1)}} \dots \delta_{i_{\sigma(N)}, j_{\tau(N)}}$. This gives us the following expression for A_{KL}:

$$A_{KL} = \sum (-1)^{k(k-1)/2} \sum_{\sigma\tau} (-1)^{\sigma+\tau} \det(\delta_{m_p, j_{\tau(q)}}) \det(\delta_{i_{\sigma(p)}, n_q}) \prod_{p=k+1}^{N} \delta_{i_{\sigma(p)}, j_{\tau(p)}},$$

where σ and τ run over the $(k, N-k)$ shuffles.

To calculate $\det(\delta_{m_p, j_{\tau(q)}})$ we write

$$\det(\delta_{m_p, j_{\tau(q)}}) = \sum_\lambda (-1)^\lambda \delta_{m_{\lambda(1)}, j_{\tau(1)}} \dots \delta_{m_{\lambda(k)}, j_{\tau(k)}},$$

where λ runs over the permutations of $\{1, \dots, k\}$ and we obtain

$$\sum_{m_1, \dots, m_k} \bar{\alpha}_{m_1} \dots \bar{\alpha}_{m_k} \det(\delta_{m_p, j_{\tau(q)}}) = k! \bar{\alpha}_{j_{\tau(1)}} \dots \bar{\alpha}_{j_{\tau(k)}}.$$

Hence

$$N^0_{KL} = \sum_{k=0}^{N} (-1)^{k(k+1)/2} \sum_{\sigma\tau} (-1)^{\sigma+\tau} \alpha_{i_{\sigma(1)}} \dots \alpha_{i_{\sigma(k)}} \bar{\alpha}_{j_{\tau(1)}} \dots \bar{\alpha}_{j_{\tau(k)}} \prod_{p=k+1}^{N} \delta_{i_{\sigma(p)}, j_{\tau(p)}}.$$

Therefore, our final result is

$$N^0_{KL} = \sum_{k=0}^{N} (-1)^{k(k-1)/2} \sum_{\sigma\tau} (-1)^{\sigma+\tau} \prod_{p=1}^{k} \bar{\alpha}_{j_{\tau(p)}} \prod_{p=1}^{k} \alpha_{i_{\sigma(p)}} \prod_{p=k+1}^{N} \delta_{i_{\sigma(p)}, j_{\tau(p)}},$$

$$= \sum_{k=0}^{N} \sum_{\sigma\tau} (-1)^{\sigma+\tau} \prod_{p=1}^{k} (\bar{\alpha}_{j_{\tau(p)}} \alpha_{i_{\sigma(p)}}) \prod_{p=k+1}^{N} \delta_{i_{\sigma(p)}, j_{\tau(p)}}, \tag{56}$$

where we recall that σ and τ run over the $(k, N-k)$ shuffles.

We calculated N^0_{KL} for a system where all the states have the same number of electrons, but the same methods can be used when $|K\rangle$ and $|L\rangle$ have a different number of electrons.

B. Alternative formula for N^0_{KL}

Now we are going to derive the alternative formula (18) for N^0_{KL}. This result can be obtained directly from equation (56) but we shall provide an independent proof.

We first rewrite the expression (51) for N^0_{KL} as

$$N^0_{KL} \;=\; \sum_{k=0}^{N} \frac{(-1)^k}{(k!)^2}\langle 0|b_{i_1}\dots b_{i_N} B_+^k B^k b^\dagger_{j_N}\dots b^\dagger_{j_1}|0\rangle,$$

where $B=\sum_n \bar\alpha_n b_n$ and $B_+=\sum_n b^\dagger_n\alpha_n$. It is easy to prove recursively that $[b_{i_N}, B_+^k] = k\alpha_{i_N}B_+^{k-1}$ and $[B^k, b^\dagger_{j_N}] = kB^{k-1}\bar\alpha_{j_N}$. If we write $|K^-\rangle = b^\dagger_{i_{N-1}}\dots b^\dagger_{i_1}$, so that $\langle K| = \langle K^-|b_{i_N}$, we obtain the recursion

$$\langle K|B_+^k B^k|L\rangle \;=\; \langle K^-|B_+^k b_{i_N} B^k|L\rangle + k\langle K^-|\alpha_{i_N}B_+^{k-1}B^k|L\rangle.$$

If we use $|L^-\rangle = b^\dagger_{j_{N-1}}\dots b^\dagger_{j_1}$, we obtain the following recursive equation between the matrix elements of $B_+^k B^k$ for N particles and $N-1$ particles:

$$\begin{aligned}\langle K|B_+^k B^k|L\rangle \;=\;& \langle K^-|B_+^k B^k|L^-\rangle\delta_{j_N,i_N}\\ &-k^2\langle K^-|B_+^{k-1}B^{k-1}|L^-\rangle\bar\alpha_{j_N}\alpha_{i_N}\\ &-k(-1)^{N-1}\langle K^-|B_+^{k-1}b^\dagger_{j_N}B^k|L^-\rangle\alpha_{i_N}\\ &+k(-1)^{N-1}\langle K^-|B_+^k b_{i_N}B^{k-1}|L^-\rangle\bar\alpha_{j_N}\\ &-\langle K^-|B_+^k b^\dagger_{j_N}b_{i_N}B^{k-1}|L^-\rangle. \end{aligned}\tag{57}$$

Now we are going to show that the expression (18) satisfies the same recursive equation. We write $d=\sum_n \partial^2/\partial\alpha_n\partial\bar\alpha_n$, $u=(\bar\alpha_{i_1}\alpha_{j_1}\dots\bar\alpha_{i_{N-1}}\alpha_{j_{N-1}})$ and $v=\bar\alpha_{i_N}\alpha_{j_N}$, so that $N^0_{KL}=\mathrm{e}^d(uv)$. Equations (25) and (45) yield

$$\mathrm{e}^d(uv) \;=\; \sum_{p=0}^{\infty}\frac{1}{p!}d^p_{(1')}(\mathrm{e}^d u)d^p_{(2')}(\mathrm{e}^d v).$$

The sum is not infinite because $\mathrm{e}^d v=\delta_{j_N,i_N}+\bar\alpha_{j_N}\alpha_{i_N}$ so the sum stops at $p=2$. Using

$$\begin{aligned}\Delta' d \;=\;& \sum_n \frac{\partial}{\partial\alpha_n}\otimes\frac{\partial}{\partial\bar\alpha_n} - \frac{\partial}{\partial\bar\alpha_n}\otimes\frac{\partial}{\partial\alpha_n},\\ \Delta' d^2 \;=\;& \sum_{mn} -\frac{\partial^2}{\partial\alpha_m\partial\alpha_n}\otimes\frac{\partial^2}{\partial\bar\alpha_m\partial\bar\alpha_n} - \frac{\partial^2}{\partial\bar\alpha_m\partial\bar\alpha_n}\otimes\frac{\partial^2}{\partial\alpha_m\partial\alpha_n}\\ &+\frac{\partial^2}{\partial\alpha_m\partial\bar\alpha_n}\otimes\frac{\partial^2}{\partial\bar\alpha_m\partial\alpha_n} + \frac{\partial^2}{\partial\bar\alpha_m\partial\alpha_n}\otimes\frac{\partial^2}{\partial\alpha_m\partial\bar\alpha_n},\end{aligned}$$

we obtain the recursive equation

$$\begin{aligned}\mathrm{e}^d(uv) \;=\;& (\mathrm{e}^d u)\delta_{j_N,i_N} + (\mathrm{e}^d u)\bar\alpha_{j_N}\alpha_{i_N} + \frac{\partial(\mathrm{e}^d u)}{\partial\alpha_{j_N}}\alpha_{i_N} + \frac{\partial(\mathrm{e}^d u)}{\partial\bar\alpha_{i_N}}\bar\alpha_{j_N}\\ &+\frac{\partial^2\mathrm{e}^d u}{\partial\bar\alpha_{i_N}\partial\alpha_{j_N}}\end{aligned}\tag{58}$$

We use the derivatives

$$\frac{\partial B_+}{\partial\alpha_{j_N}} \;=\; -b^\dagger_{j_N},\quad \frac{\partial B_+^k}{\partial\alpha_{j_N}} = -kB_+^{k-1}b^\dagger_{j_N},$$

to obtain

$$\frac{\partial\langle K^-|B_+^k B^k|L^-\rangle}{\partial\alpha_{j_N}} \;=\; -(-1)^{N-1}k\langle K^-|B_+^{k-1}b_{j_N}^\dagger B^k|L^-\rangle.$$

Similarly

$$\frac{\partial\langle K^-|B_+^k B^k|L^-\rangle}{\partial\bar\alpha_{i_N}} \;=\; (-1)^{N-1}k\langle K^-|B_+^k b_{i_N} B^{k-1}|L^-\rangle,$$

$$\frac{\partial^2\langle K^-|B_+^{k+1} B^{k+1}|L^-\rangle}{\partial\bar\alpha_{i_N}\partial\alpha_{j_N}} \;=\; (k+1)^2\langle K^-|B_+^k b_{j_N}^\dagger b_{i_N} B^k|L^-\rangle.$$

With these identities, it is easy to show that $N^0_{K^-L^-}$ and N^0_{KL} satisfy the same recursion as $\mathrm{e}^d(u)$ and $\mathrm{e}^d(uv)$. When there is only one electron ($N=1$) we have indeed

$$N^0_{KL} \;=\; \delta_{j_1,i_1} + \bar\alpha_{j_1}\alpha_{i_1} = \mathrm{e}^d(\bar\alpha_{j_1}\alpha_{i_1}). \tag{59}$$

Thus we have $N^0_{KL} = \mathrm{e}^d(\bar\alpha_{j_1}\alpha_{i_1}\dots\bar\alpha_{j_N}\alpha_{i_N})$ for all N.

Notice that equation (58) enables us to calculate N^0_{KL} for a closed shell, i.e. when $N=M$. For closed shells we shall prove that

$$N^0_{KL} \;=\; \prod_{k=1}^{N}(1+\bar\alpha_{i_k}\alpha_{i_k}). \tag{60}$$

In closed shells, there is only one state $|K\rangle$, where all orbitals are filled, and we have $i_k = j_k$ for all $k=1,\dots,N$. For $N=1$, we have indeed equation (60) because it is a particular case of equation (59) with $i_1 = j_1$. Assume now that equation (60) is true for closed shells containing up to $N-1$ electrons. Take $u = \bar\alpha_{i_1}\alpha_{i_1}\dots\bar\alpha_{i_{N-1}}\alpha_{i_{N-1}}$ and $v = \bar\alpha_{i_N}\alpha_{i_N}$. By the recursion hypothesis we have

$$\mathrm{e}^d u \;=\; \prod_{k=1}^{N-1}(1+\bar\alpha_{i_k}\alpha_{i_k}).$$

By Pauli's principle, the orbital i_N is different from the orbitals i_k for $1\le k<N$. Therefore, the functional derivative of $\mathrm{e}^d u$ with respect to $\bar\alpha_{j_N}$ or α_{i_N} is zero and only the first two terms in the right hand side of equation (58) remain. Thus, equation (58) becomes $\mathrm{e}^d(uv) = \mathrm{e}^d u + (\mathrm{e}^d u)\bar\alpha_{i_N}\alpha_{i_N}$ and equation (60) is proved for N electrons.

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